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Master in Glass and Ceramic Art and Science / BSc in Applied
Chemistry

OPTIMIZATION OF SILVER LUMINESCENT COATINGS FOR ARTISTIC PURPOSES

SCIENCE FOR THE ARTS

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Aos meus avós, que sempre quiseram estudar.

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“The object isn’t to make art, it’s to be in that wonderful state which makes art inevitable.”

— **Robert Henri**

ABSTRACT

This work explores the development of a silver luminescent coating designed for artists. The coating was prepared from two separate solutions, silver nitrate and sodium nitrate in water MilliQ. The solutions were deposited on commercial float glass samples by drop casting, followed by heat treatment at 360°C and 450°C, which allowed the formation of silver clusters through ion exchange, giving rise to luminescence layers on the glass. During this process, silver nanoparticles also formed due to the presence of tin on the glass, which reduced silver. Silver nanoparticles visually result in brown stains on the glass surface, on the tin side, that quench luminescence intensity. The silver nanoparticles formation was confirmed by an absorption band near 430 nm. For a process optimization, a kaolin layer was introduced beneath the samples, avoiding solution dripping on the tin side, which resulted in transparent glass with preserved luminescence and minimized stains. Silver nitrate solution alone was deposited by drop casting on the glass, aiming to understand the role of its concentration on luminescence intensity. There was no evident correlation between silver nitrate concentration and luminescence intensity, but it revealed the ability to give rise to luminescence layers, despite the very heterogeneous results, which underlined the important role of sodium nitrate on the homogeneity of the coating. Emission spectra suggested contributions from silver clusters, including $\text{Ag}^+ - \text{Ag}^+$ pairs (480–550 nm), Ag_2 dimers (440–450 nm), and Ag_3 trimers (580–590 nm), with overall intensity reflecting the combined contributions of all species. For scale up, alternative deposition methods were explored. Screen printing showed low surface coverage, whereas spray deposition combined with pre-cleaning using nitric acid and potassium hydroxide achieved uniform coatings. Frosted glass enhanced solution adhesion, producing optimized samples fired at 500°C with strong luminescence and surface homogeneity. This work culminated in a step by step manual for artists. This manual was used by VICARTE glass artists on mouth blown glass pieces, demonstrating its simple use, efficiency, and potential to create luminescent effects for contemporary glass art.

Keywords: Glass, Luminescence, Silver clusters, Ion Exchange, Art

RESUMO

Este trabalho explora o desenvolvimento de um revestimento luminescente à base de prata, concebido para artistas. O revestimento foi obtido a partir de duas soluções separadas, uma de nitrato de prata e outra de nitrato de sódio, ambas em água MilliQ. Estas soluções foram depositadas com micropipeta sobre vidro comercial, utilizado como substrato, e submetidas a temperaturas de 360°C e 450°C, formando clusters de prata através de troca iônica, originando camadas luminescentes. Paralelamente, devido à presença de estanho no substrato, ocorreu a formação de nanopartículas de prata, identificadas por manchas acastanhadas no lado do estanho do vidro e pela banda característica a 430 nm no espectro de absorção, que interferem na luminescência. Para minimizar este efeito, aplicou-se uma camada de caulino sob as amostras, evitando o derrame das soluções para o lado do estanho do vidro, preservando a transparência e melhorando a luminescência. Para avaliar a influência da concentração de nitrato de prata na luminescência, a solução foi depositada isoladamente. Esta deposição evidenciou luminescência com grande heterogeneidade, confirmando o papel essencial do nitrato de sódio na homogeneidade do revestimento. Os espectros de emissão sugeriram a presença de diferentes espécies de clusters de prata, $\text{Ag}^+ - \text{Ag}^+$ (480–550 nm), dímeros Ag_2 (440–450 nm) e trímeros Ag_3 (580–590 nm), cuja combinação contribui para a intensidade de luminescência observada. Para aplicações em larga escala, deposição como serigrafia e spray foram feitas. A serigrafia mostrou baixa cobertura do vidro, enquanto o spray revelou-se mais eficaz, exigindo, contudo, pré-limpeza com ácido nítrico e hidróxido de potássio. O uso de vidro fosco favoreceu a adesão ao revestimento, resultando numa amostra otimizada a 500°C, com luminescência intensa e homogênea. O estudo culminou com a elaboração de um manual artístico, pensado para orientar artistas no uso deste revestimento. O manual foi posteriormente utilizado por artistas do VICARTE, que aplicaram o revestimento em peças de vidro soprado. Os resultados demonstraram a simplicidade de aplicação, a eficiência do revestimento e o potencial de criar efeitos luminescentes em vidro, reforçando o potencial deste material na produção artística contemporânea em vidro.

Palavras-chave: Vidro, Luminescência, Clusters de prata, Troca Iônica, Arte

CONTENTS

List of Figures	x
1 Introduction	1
1.1 Glass	1
1.1.1 Glass structure and composition	2
1.1.2 Glass transformation range	3
1.2 Light and matter interaction	3
1.2.1 Understanding luminescence	4
1.2.2 Luminescent glass in the arts	5
1.2.3 Approaches to producing luminescent glass	6
1.2.4 Ion exchange as a process to obtain luminescent glass	7
2 Development of the luminescent coating on glass	11
2.1 Deposition processes for small scale pieces	11
2.1.1 Deposition by ion exchange bath	11
2.1.2 Deposition by drop casting	16
2.1.3 Silver concentration influence	25
2.1.4 Anion influence	27
2.2 Deposition processes for scale up pieces	29
2.2.1 Deposition by screen printing	29
2.2.2 Deposition by spray	31
3 A manual for artistic implementation of a silver luminescent coating on glass	36
4 Application of the luminescent coating by artists at VICARTE	43
4.0.1 Interview with artist Wai In Chan	43
4.0.2 Interview with artist Mayank Sahni	45
4.0.3 Artists feedback	47
5 Exhibition - Shall we meet by the fire	48

6 Conclusion	50
Bibliography	52
Appendices	
Annexes	
I Annex	57

LIST OF FIGURES

1.1	Diagram of Enthalpy (or volume) change of glass as it is cooled through the transition region (T_g).[6]	3
1.2	Perrin–Jablonski diagram illustrating radiative and non-radiative transitions [15].	4
1.3	Rui Sasaki, <i>Liquid Sunshine</i> (2019), phosphorescent glass installation commissioned by the Corning Museum of Glass. The work charges under ambient light and emits a controlled afterglow in darkness [17].	5
1.4	Yhonnie Scarce, mouth-blown uranium-infused glass (2024). Under UV illumination, the works exhibit vivid green fluorescence, foregrounding the political and material histories of uranium glass [18].	6
1.5	Glass sculptures with europium and cerium under UV-light lamp at $\lambda = 366$ nm [19]	6
1.6	Yellow silver-stained panel depicting St. Michael slaying Lucifer [17].	8
1.7	Schematic representation of ion exchange in a glass network.	8
1.8	Representative figure of silver clusters and nanoparticles formation in glass and its influence in glass coloration [26].	10
2.1	Representative figure of ion exchange bath deposition process in glass, on a petri dish. The petri dish is represented by the blue area, the glass is represented by the yellow square and the salts are represented by the grey dots.	11
2.2	Soda lime luminescent glass samples produced by ion exchange bath with AgNO_3 and NaNO_3 , on a weight (%wt/%wt) proportion of 1 AgNO_3 : 2 NaNO_3 , and fired at 360°C/450°C/500°C and 550°C. On top the samples are shown under natural sunlight, below the samples are shown under UV-light lamp at $\lambda = 366$ nm.	12
2.3	Absorption spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.	13
2.4	Emission (excitation wavelength of 360 nm) spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.	14

2.5	Excitation spectra (emission wavelength of 600 nm) of ion bath soda lime glass samples, 360°C, 450°C, 500°C, 550°C.	15
2.6	Emission (excitation wavelength of 360 nm) and Excitation (Emission wavelength of 600 nm) spectra of ion bath soda lime glass samples fired at 360°C, 450°C.	16
2.7	Representative Figure of drop casting deposition on glass, in a petri dish. The blue area represents the petri diish, the yellow square represents the glass and the drop illustrates the solution being deposited.	17
2.8	Solution tests AgNO ₃ and NaNO ₃ in a) distilled water; b) ethanol; c) 25 mL water MilliQ/25 mL glycerol, f) triethylene glycol monomethyl ether, e) polyethylene glycol 400; Ag ₂ SO ₄ and Na ₂ SO ₄ in d) decoflux	17
2.9	Test T1 (same deposition volume of [AgNO ₃] and [NaNO ₃]) at 360°C (above) and 450°C (below) with volumes of 56µL,112µL,168µL and 224µL, [AgNO ₃] = 0,18M and [NaNO ₃]=0,73M. Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366$ nm.	19
2.10	Test T2 (increasing deposition volume of [AgNO ₃], 56µL,112µL,168µL and 224µL, and constant deposition volume of [NaNO ₃], 112µL) at 360°C (above) and 450°C (below). Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366$ nm. [AgNO ₃] = 0,18M and [NaNO ₃]=0,73M.	19
2.11	Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of [AgNO ₃] and [NaNO ₃] with volumes of 56µL,112µL,168µL and 224µL) and T2 (increasing deposition volume of [AgNO ₃], 56µL,112µL,168µL and 224µL, and constant deposition volume of [NaNO ₃], 112µL) fired at 360°C. [AgNO ₃] = 0,18M and [NaNO ₃]=0,73M. . .	20
2.12	Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of [AgNO ₃] and [NaNO ₃] with volumes of 56µL,112µL,168µL and 224µL) and T2 (increasing deposition volume of [AgNO ₃], 56µL,112µL,168µL and 224µL, and constant deposition volume of [NaNO ₃], 112µL) fired at 450°C. [AgNO ₃] = 0,18M and [NaNO ₃]=0,73M. . .	21
2.13	Soda lime glass samples on a petri dish a layer of kaolin below. Samples under natural sunlight and before firing	21
2.14	Test T1 with kaolin (same deposition volume of [AgNO ₃] and [NaNO ₃]) at 360°C (above) and 450°C (below) with volumes of 56µL,112µL,168µL and 224µL, [AgNO ₃] = 0,18M and [NaNO ₃]=0,73M. Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366$ nm.	22

2.15	Test T2 with kaolin (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) at 360°C (above) and 450°C (below). Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366\text{ nm}$. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$	22
2.16	Absorption spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C without kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$	23
2.17	Absorption spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C with kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$	23
2.18	Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C , without kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$	24
2.19	Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C , with kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$	25
2.20	Test T1 (increasing deposition volume of $[\text{AgNO}_3]$ at 360°C (above) and 450°C (below) with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, $[\text{AgNO}_3] = 0,18\text{M}$. Above the samples are shown under natural sunlight and, below, the soda lime glass samples are shown under a UV-light lamp at $\lambda = 366\text{ nm}$	26
2.21	Absorption spectra of Test T1 on soda lime glass samples (with increasing deposition volume of AgNO_3 , with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) at 360°C and 450°C , $[\text{AgNO}_3] = 0,18\text{M}$	26
2.22	Emission (excitation wavelength of 360 nm) spectra of Test T1 soda lime glass samples (increasing deposition volume of $[\text{AgNO}_3]$ at 360°C and 450°C with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, $[\text{AgNO}_3] = 0,18\text{M}$	27

2.23	Sample of soda lime glass fired at 360°C and 500°C with $[\text{Ag}_2\text{SO}_4]=0,02 \text{ M}$ and $[\text{Na}_2\text{SO}_4]=0,08 \text{ M}$ in PEG. The first image on the left corresponds to the sample fired at 360°C under natural sunlight, the sample on the middle corresponds to the sample fired at 360°C under UV-light lamp at $\lambda = 366 \text{ nm}$, and the sample on the right corresponds to the sample fired at 500°C under a UV-light lamp at $\lambda = 366 \text{ nm}$	28
2.24	Emission spectra (excitation wavelength at 360 nm) of soda lime glass sample of $[\text{Ag}_2\text{SO}_4]=0,02 \text{ M}$ and $[\text{Na}_2\text{SO}_4]=0,08 \text{ M}$ in PEG fired at 500°C	28
2.25	Representative Figure of Screen Printing deposition of the solutions in glass	29
2.26	Screen Printing tests with Degussa Portuguesa with $[\text{AgNO}_3] = 0,18 \text{ M}$ and $[\text{NaNO}_3] = 0,73 \text{ M}$ at 450°C under natural sunlighth.	30
2.27	Screen Printing tests on soda lime glass fired at 450°C, with water MilliQ with $[\text{AgNO}_3] = 0,18 \text{ M}$ and $[\text{NaNO}_3] = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$	30
2.28	Screen Printing tests of soda lime glass samples fired at 360°C, 450°C and 500°C, with $[\text{Ag}_2\text{SO}_4] = 0,02 \text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0,08 \text{ M}$ in PEG. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$	31
2.29	Representative figure of deposition by spray on glass inside a hotte.	32
2.30	Spray test on normal (left) and frosted (right) soda lime glass at 360°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$	32
2.31	Spray test on normal (left) and frosted (right) soda lime glass at 450°C and 500°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$	33
2.32	Spray test on soda lime glass at 360°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$	33
2.33	Spray test on soda lime glass at 450°C and 500°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$	34
2.34	Spray test on frosted soda lime glass at 360°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$	34
2.35	Spray test on frosted soda lime glass at 450°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$	35
2.36	Spray test on frosted soda lime glass at 500°C. $\text{AgNO}_3 = 0,18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$	35

3.1	Soda-lime glass pieces after deposition of the luminescent coating by spray, from artist Mayank Sahni, under natural sunlight. non-conservation of transparency (left) and conservation of transparency (right).	36
3.2	Soda-lime glass sample under UV light at a wavelength of 254 nm with tin (left) and without tin (right).	37
3.3	Steps for solution preparation 1- Weigh silver nitrate, 2/3- grind sodium nitrate, 4- weigh sodium nitrate, 5- add water milliQ to each precipitation cup, ensuring it does not surpass the total volume desired, 6/7 - use an ultrasound bath to help with the dissolution of the salts at 25°C, 8 - transport the solutions from the precipitation cups to volumetric balloons until the calibration line	39
3.4	Sample cleaning with Potassium Hydroxide [KOH] = 0,8 M and Nitric Acid, (HNO ₃), small scale deposition by drop casting using a plastic pippette, kiln transport and firing.	40
3.5	Large scale deposition by spray, kiln transport and firing	41
3.6	Soda lime luminescent glass samples produced by ion exchange bath with AgNO ₃ and NaNO ₃ , on a weight (%wt/%wt) proportion of 1 AgNO ₃ : 2 NaNO ₃ , and fired at 360°C/450°C/500°C and 550°C. On top the samples are shown under natural sunlight, below the samples are shown under UV-light lamp at $\lambda = 366$ nm.	42
4.1	Soda-lime glass luminescence piece by Wai in Chan. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.	44
4.2	Soda-lime glass luminescence piece by Wai in Chan. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.	44
4.3	Soda-lime glass luminescence piece by Mayank Sahni. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.	46
4.4	Soda-lime glass luminescence piece by Mayank Sahni. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under a UV-light lamp at $\lambda = 366$ nm.	46
5.1	Metaphorical fire installation with 2D and 3D glass pieces under natural light.	48
5.2	Metaphorical fire installation with 2D and 3D glass pieces under UV light. .	49
I.1	Emission (excitation wavelength of 360 nm) spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.	57

INTRODUCTION

1.1 Glass

Before we dive into luminescent glass and its use in arts, first we need to understand better what glass is, its properties, and what makes it such a versatile material that can serve as a matrix for luminescent coating.

The glass making origin remains uncertain, but it is believed that the Mesopotamians in the 5th century BC accidentally discovered an ash that could produce a glaze when ceramics were fired. Additionally, glass beads dating to the 4th century have been excavated from burial sites in Egypt, suggesting that the intentional manufacture of glass was already a practice [2].

The word "glass" has a mysterious history, it is derived from the Teutonic term *Glaza*, meaning amber. Another possible origin is the Late Latin word *glaesum*, used to describe a lustrous and transparent material. A commonly used synonym for glassy substances is vitreous, originating from the Latin term *vitrum*, which denotes a transparent or clear substance. Additionally, the Greek word *amorphe*, meaning shapeless, has historically been used to describe glass[2, 3]. All the historic terms referring to glass gather some truth, reminding scientists and artists that glass does not have a unique and global definition or truth. Glass is a mysterious material, and that is what makes it fascinating.

But what really is glass? This transparent, ancient, and ubiquitous material.

There is no single, universally accepted definition of glass. Today, the term generally refers to a transparent material that combines the properties of hardness, rigidity, and brittleness. Glass exhibits characteristics of both solids and liquids. According to McMillan, glass may be described as a liquid with extremely high viscosity [4]. This ambiguity exists because glass draws features from solid and liquid materials, yet does not fit into either category.

Unlike crystalline materials, glass does not have a sharply defined melting point or defined structure. It softens gradually when heated, which is inconsistent with the melting behavior of crystals [5].

Numerous other definitions have been proposed over time. For example, J. E. Shelby

defined glass as “an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behaviour” [6]. Similarly, A. K. Varshneya described glass as “a solid having a non-crystalline structure, which continuously converts to a liquid upon heating” [3]. A more recent definition of glass was proposed in 2017 “Glass is a non-equilibrium, non-crystalline state of matter that appears solid on a short time scale but continuously relaxes toward the liquid state” [7].

While this work does not attempt to cover every definition, these perspectives help illustrate the unique structural nature of glass.

1.1.1 Glass structure and composition

The structure of glass is composed of elemental units of silicon-oxygen tetrahedron. In glasses, these units are linked to other tetrahedron at their corners, forming a three-dimensional network. As mentioned above, glass lacks long range order, so it's only possible to find order on a short range.

As Mozzi and Warren suggested, glass structure can be described as a random network [8], therefore, there is no particular chemical or physical condition for a substance to form glass. It is shown that almost any substance, if cooled sufficiently fast, could be obtained in the glassy state [5].

From a more practical perspective, glasses are generally produced either from high purity, high quality raw materials or from mixtures of lower purity compounds. Regardless of the purity level, the materials used in glass making can be grouped into five main categories, based on their specific roles in the process:[6, 9, 5]

1. **Network former or Glass former** – The network former is one of the main compounds in glass, giving rise to the backbone of the structure. In commercial oxide glasses, SiO_2 , B_2O_3 , PbO , and P_2O_5 are part of these compounds. The most well-known and used glass former is silica (SiO_2).
2. **Network modifier or Flux** – Silica by itself can form glass, but it has an extremely high synthesis temperature (1730°C) [10], making the process very expensive. To decrease this temperature, compounds such as Na_2O , K_2O , Li_2O , and PbO can be added. These oxides form non-bridging oxygens that bond ionically with the cations from the modifiers. While these small structural openings reduce the melting temperature, they also reduce stability, increasing vulnerability to corrosion and other external factors.
3. **Stabilizers or intermediates** – These compounds, such as CaO , Al_2O_3 , and ZnO , act as intermediates between the network former and the modifier, partially substituting the former.

4. **Secondary compounds** – These include colorants like Fe, Co, Cu, Ag and Au; decolorants such as As; fining agents like Sb_2O_3 , NaNO_3 , and NaCl ; and opacifiers such as F^- .

1.1.2 Glass transformation range

The glass transformation range refers to the thermodynamic range in which the material transitions from a supercooled liquid state to a rigid, glassy state. This behaviour can be observed in a Volume/Temperature diagram, as shown below in Figure 1.1, where the glass transition temperature (T_g) is represented. Nevertheless, it's needed to keep in mind that there is no single and sharp temperature value where the transition to the glassy state occurs. More correctly, it's a range of temperatures. The T_g can be found by intersecting the extrapolated liquid line with the glass state line [6, 3].

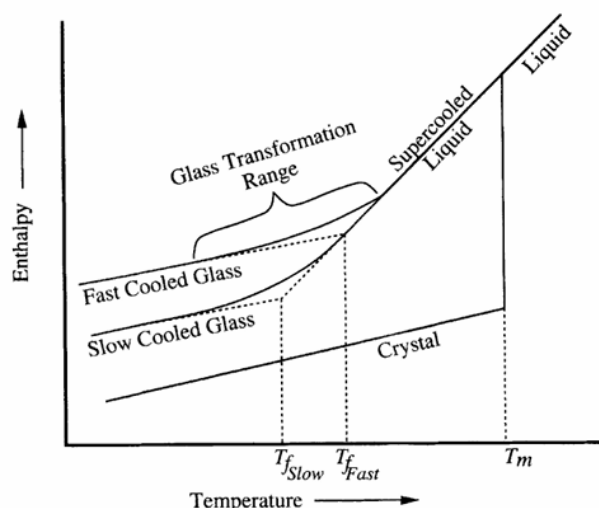


Figure 1.1: Diagram of Enthalpy (or volume) change of glass as it is cooled through the transition region (T_g). [6]

Having established the fundamentals of glass, its properties, and its transformation range, it is now essential to explore the phenomenon of luminescence. A clear comprehension of luminescence is crucial to contextualize how this property can be intentionally incorporated into glass, ultimately enabling its use in artistic practices.

1.2 Light and matter interaction

The interaction of light with matter is governed by fundamental optical processes such as reflection, refraction, absorption, and scattering, which together determine how a material responds to incident electromagnetic radiation [11]. When light is absorbed by a material, its energy can be converted into other forms, such as heat, charge carrier generation, or re-emitted as light. This re-emission of absorbed energy is the principle of luminescence.

Glass is a material that can host this phenomenon. The absorbed energy can excite electrons to higher energy levels, and their subsequent relaxation can occur through fluorescence or phosphorescence. The study of these processes is essential for understanding luminescence in glass. By controlling composition, dopant concentration, and thermal treatment, it becomes possible to engineer glasses that exhibit desirable luminescent properties for both technological and artistic applications [12, 13].

1.2.1 Understanding luminescence

The term *luminescence* was first introduced by German physicist Wiedemann in 1888, using the German word *luminescentz*, although the phenomenon had been observed long before. As early as the 17th century, the Italian shoemaker Vincenzo Cascariolo reported a stone, later identified as baryte, that continued to glow in the dark after exposure to sunlight [14].

Luminescence is defined as the spontaneous emission of electromagnetic radiation from a material, in this case, glass, following the absorption of external energy. In other words, the material absorbs energy from a stimulus and subsequently re-emits part of that energy as visible light. When a molecule absorbs a photon, the excitation energy can be dissipated by several mechanisms, most notably fluorescence and phosphorescence [9, 15]. These processes are often illustrated using a Perrin–Jablonski diagram (Figure 1.2), which shows the main different transitions.

Non-radiative transitions include internal conversion, which describes transitions between two excited states of the same spin multiplicity, and intersystem crossing, which occurs between excited states of different spin multiplicity.

Fluorescence and phosphorescence are distinguished primarily by their spin multiplicity and emission timescales. Fluorescence results from a radiative transition between states of the same spin multiplicity (typically $S_1 \rightarrow S_0$) and decays rapidly after excitation

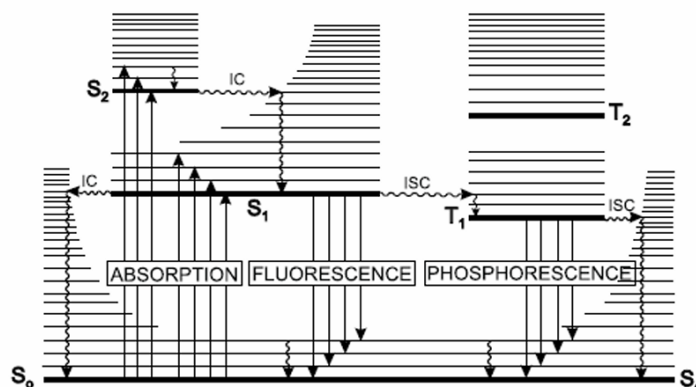


Figure 1.2: Perrin–Jablonski diagram illustrating radiative and non-radiative transitions [15].

($10^{-9} - 10^{-6}$ s), often too fast to be perceived once the excitation source is removed. Phosphorescence, on the other hand, involves a spin-forbidden transition from a triplet state (T_1) to the ground state (S_0), resulting in a much slower decay. This prolonged afterglow makes phosphorescence particularly relevant for artistic and design applications where visible persistence of light is desired [15].

Although luminescence has long been observed in minerals, its use in glass materials dates back to the early 19th century. Uranium glass, one of the earliest examples, was first produced around 1817 and owes its vivid green fluorescence to uranium oxide within the glass matrix. Since then, luminescent glasses have been developed using a variety of dopants, including transition metals, Ag, Cu and lanthanide oxides, Ce, Eu, Tb. [9].

1.2.2 Luminescent glass in the arts

The use of luminescent glass has expanded significantly in contemporary art, moving beyond historical silver stain techniques to embrace innovative luminescent materials. Current practices use rare earth, actinides and transition metal approaches (e.g., silver cluster formation by ion exchange) [16], enabling artists to choreograph works that shift appearance across natural, artificial, and ultraviolet illumination. These strategies transform glass from a passive transmitter of light into an active one. Several artists have explored the different possibilities of luminescent glass. Rui Sasaki's *Liquid Sunshine* (2019), Figure 1.3, commissioned by the Corning Museum of Glass, uses phosphorescent glass that charges under ambient light and emits a controlled afterglow in darkness, using the temporal dimension of light emission to evoke memory and climate [17].

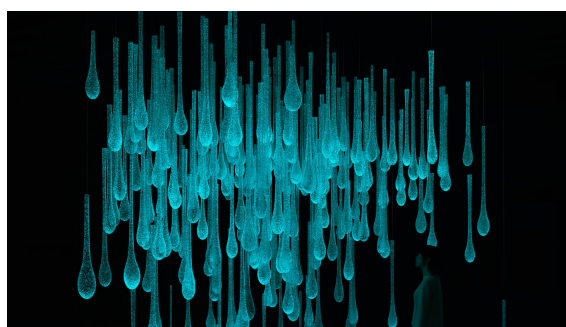


Figure 1.3: Rui Sasaki, *Liquid Sunshine* (2019), phosphorescent glass installation commissioned by the Corning Museum of Glass. The work charges under ambient light and emits a controlled afterglow in darkness [17].

Yhonnie Scarce's uranium mouth blown glass installations (2024) react vividly under UV light, recontextualizing the material's scientific and cultural histories within contemporary discourse [18].

In parallel, research by Teresa Almeida demonstrated work with rare earths, including europium, cerium, and terbium coatings applied in glass sculptures [19, 20].

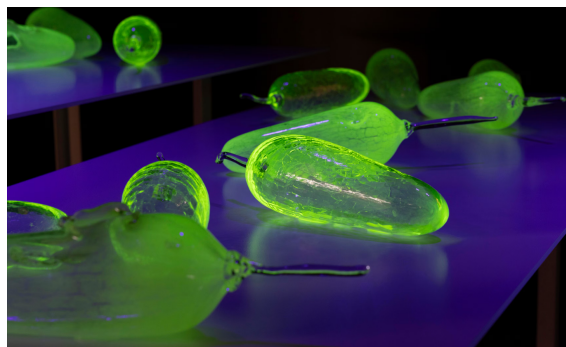


Figure 1.4: Yhonnie Scarce, mouth-blown uranium-infused glass (2024). Under UV illumination, the works exhibit vivid green fluorescence, foregrounding the political and material histories of uranium glass [18].



Figure 1.5: Glass sculptures with europium and cerium under UV-light lamp at $\lambda = 366$ nm [19]

Together, these examples demonstrate how artists can carefully control the final visual effect of luminescent glass. By choosing dopants, their concentration, and adjusting firing, artists are able to influence characteristics such as color, brightness, afterglow duration, and the uniformity of the luminescent layer. These factors are essential for achieving both the desired luminescence and the artistic expression.

1.2.3 Approaches to producing luminescent glass

Several strategies have been developed for producing luminescent glass, from traditional glassmaking approaches to modern nanotechnology methods.

One of the most established routes is in batch production, where oxides or ions are incorporated directly into the glass melt originating luminescent glass. This approach

allows large scale fabrication but requires precise control of melting temperature, atmosphere, and redox conditions[3]. A well known historical example is uranium glass, whose characteristic green fluorescence under UV light made it a popular decorative material in the 19th and early 20th centuries. Today, in batch doping often uses rare earth ions such as Eu^{3+} and Tb^{3+} , or transition metals such as copper and manganese. [21].

Beyond in batch doping, ion exchange is an effective way to introduce luminescent centers on the surface of a glass piece. In this process, glass pieces are submerged in a molten salt bath containing metal ions (e.g., Ag^+ , Au^+) that diffuse into the glass network, replacing alkali ions such as Na^+ . The subsequent thermal treatment promotes the formation of metal clusters (e.g., Ag_2 , Ag_3), which are responsible for strong emission bands [22, 23]. Ion exchange is particularly attractive for artistic applications because it allows selective patterning, localized treatment, and adaptation to complex shapes.

Another important route is the sol-gel method, which enables low temperature fabrication of glassy coatings doped with luminescent species. In this technique, a liquid containing dopants undergoes gelation and heat treatment, forming a dense, glassy layer. Sol-gel methods offer precise control over composition, porosity, and thickness, and it is appropriate for hybrid systems incorporating semiconductor quantum dots (e.g., Cd, Se, ZnS) or organic dyes, which can provide tailored photoluminescent responses for specific wavelengths or color effects [24, 25].

Recent research has also explored laser ion implantation as an alternative route to create luminescent centers in localized regions of glass, enabling three dimensional patterning of photonic devices and decorative elements with high resolution.

In the context of this work, particular focus is given to ion exchange process, as it offers a scalable, low cost, and artist friendly method for creating luminescent layers in glass [26]. Suitable for both small scale pieces and larger scale.

1.2.4 Ion exchange as a process to obtain luminescent glass

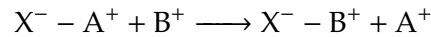
The application of luminescent effects in glass art can be traced back to the silver stain techniques of medieval stained glass windows (Figure1.6). Beginning in the 14th century, artisans applied silver compounds, silver nitrate or silver sulphide, to clear glass surfaces. Upon firing, these compounds produced vibrant yellow hues caused by the diffusion of Ag^+ ions into the glass network and their partial reduction to metallic nanoparticles. Although medieval artisans were unaware of the nanoscale mechanisms, modern analysis has shown that these silver stains represent one of the earliest uses of nanotechnology in art [27].

Apart from yellow tones derived from silver nanoparticles, this same method can also produce silver clusters that are responsible for the luminescence effects. Ion exchange using silver nitrate and sodium nitrate, as well as enameling processes, are now widely used to achieve controlled luminescence effects. Sodium nitrate serves as a flux, enabling controlled ion diffusion and preventing defects such as surface cracking [6]. In artistic

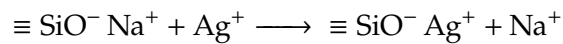


Figure 1.6: Yellow silver-stained panel depicting St. Michael slaying Lucifer [17].

practice, these coatings are often applied as glass enamels, finely powdered glass mixed with metal oxides or salts, and fired in a kiln. This allows artists to create glowing patterns, color gradients, and UV reactive surfaces. The process of ion exchange involves replacing ions (e.g., Na^+) in the glass network with other ions (e.g., Ag^+) from a molten or aqueous salt source. The general exchange reaction can be written as:



For silver ion exchange in silicate glass:



This process introduces silver ions into the glass matrix, as demonstrated below in Figure 1.7, which can subsequently form metallic clusters or nanoparticles depending on thermal treatment and reduction conditions.

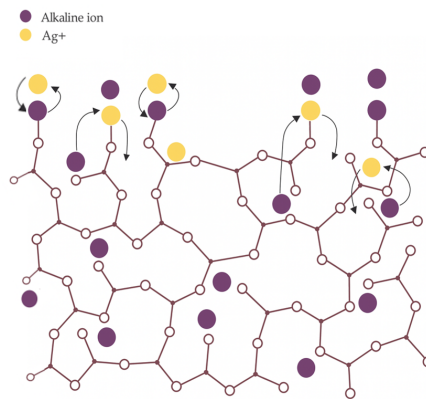


Figure 1.7: Schematic representation of ion exchange in a glass network.

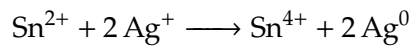
Ion exchange offers several advantages over other techniques, it allows the introduction of high concentrations of metal ions without damaging the glass matrix, it is compatible with large scale production, and it can be carried out at relatively low firing temperatures. However, achieving homogeneity in upscaled processes remains a significant challenge [26].

A key aspect of ion exchange is that it can lead to the formation of both silver clusters and nanoparticles, each with distinct optical contributions. Clusters are atomically small species, typically smaller than 2 nm, that exhibit quantum size effects, leading to size dependent fluorescence, large Stokes shifts, and long emission lifetimes. They are primarily responsible for the luminescent properties of the glass. Nanoparticles, on the other hand, are larger, typically bigger than 2 nm, and give rise to visible coloration through surface plasmon resonance (SPR), producing yellow or brown hues. These colors become especially evident at annealing temperatures around 450 °C and 500 °C, where SPR absorption bands near 430 nm appear in the spectra [28, 29, 30]. The summary of this differences will be shown below on table 1.1.

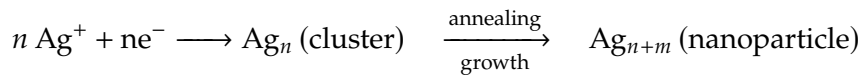
Table 1.1: Comparison of optical properties between silver clusters and silver nanoparticles in glass [31, 32, 33, 34, 28, 35]

Silver Clusters (size: < 2 nm)	Silver Nanoparticles (size: > clusters)
• Size dependent fluorescence (quantum size effect) • Strong luminescence • Large Stokes shift • Long emission lifetimes	• Metal based colloidal systems (e.g., Ag dispersions) • Bright yellow/brown coloration (due to SPR) • Distinct SPR absorption peak near 430 nm

The formation of either species depends strongly on the glass composition and processing conditions. For example, in commercial float glass, more specifically soda lime glass, which will be the glass used in this work, the presence of a tin rich surface promotes the reduction of silver ions, favoring nanoparticle formation. This is a desirable effect when color development is intended as shown in Figure 1.8, but less so when luminescence is the primary objective. The reduction of silver ions by tin can be expressed by the equation below [36]:



A simplified representation of silver cluster and nanoparticle formation is:



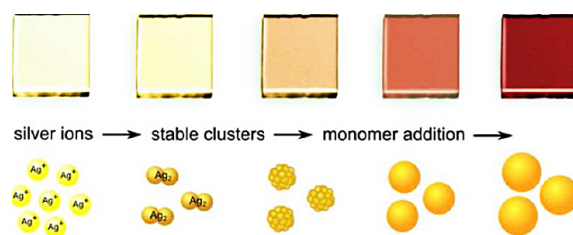


Figure 1.8: Representative figure of silver clusters and nanoparticles formation in glass and its influence in glass coloration [26].

The goal of this work is to develop a silver luminescent coating using an ion exchange process to induce cluster formation while minimizing nanoparticle growth. Unlike the conventional ion bath method, this study employs a reproducible approach that is easily upscaled and accessible to artists, enabling them to prepare and apply their own coatings and achieve controlled luminescent effects with low cost and low temperature firings.

DEVELOPMENT OF THE LUMINESCENT COATING ON GLASS

2.1 Deposition processes for small scale pieces

The development of the luminescent coating on glass began with tests on small scale pieces (dimensions minor or equal to 2 cm x 2 cm) that later enabled scaling up and application on artistic pieces.

2.1.1 Deposition by ion exchange bath

Before testing innovative deposition methods, such as drop casting, which involves a micropipette, a reference test was performed. This test is previously established in the literature, and it is inspired in the work of Anne Simo [26]. It consists on a deposition by ion exchange bath represented by the figure below 2.1.



Figure 2.1: Representative figure of ion exchange bath deposition process in glass, on a petri dish. The petri dish is represented by the blue area, the glass is represented by the yellow square and the salts are represented by the grey dots.

The procedure involved a mixture of silver nitrate and sodium nitrate in a weight ratio of 1:2, respectively. This ratio enables an eutetic mixture that lowers the melting point of the salts, allowing the ion exchange process to occur at lower temperatures.

Before the deposition, the glass samples were previously cleaned with nitric acid followed by potassium hydroxide. This step was present in every deposition method.

Both salts were thoroughly mixed in a petri dish, and small soda lime glass squares (1.5 cm × 1.5 cm) were placed over the salt mixture, ensuring that the non tin side of the glass was in contact with the salts, as tin facilitates silver reduction, which negatively affects luminescence intensity. The silver reduction by tin forms silver nanoparticles, which results in yellow and brown stains that affect luminescence. The presence of tin in glass can be detected under UV light at a wavelength of 254 nm, where tin exhibits a characteristic luminescent response.

After identifying tin side on the soda lime glass samples, the process began. Ion exchange bath samples were subjected to an initial firing at 360°C for 1 hour, during which the ion exchange process occurs. Following this, the samples went to a second firing, annealing, where nanoparticle and cluster formation were promoted at different temperatures for 1 hour: 450°C, 500°C, and 550°C. The results of these tests were washed and are shown below in Figure 2.2.

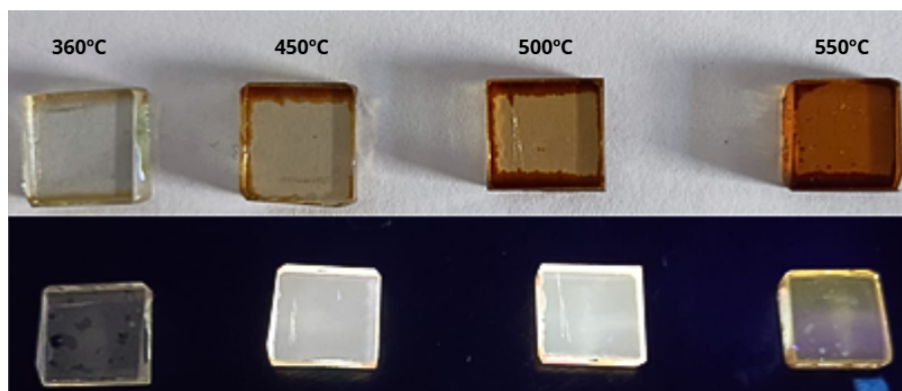


Figure 2.2: Soda lime luminescent glass samples produced by ion exchange bath with AgNO_3 and NaNO_3 , on a weight (%wt/%wt) proportion of 1 AgNO_3 : 2 NaNO_3 , and fired at 360°C/450°C/500°C and 550°C. On top the samples are shown under natural sunlight, below the samples are shown under UV-light lamp at $\lambda = 366$ nm.

The first noticeable aspect is that as the temperature increases, the color of the samples gradually shifts to darker tones. At 360°C, the sample remains almost uncolored. At 450°C, a slight pale yellow begins to form, at 500°C, a strong yellow is observed, and at 550°C, the color shifts to a brown tone.

Regarding luminescence, the layers are homogeneous, and the intensity increases with temperature. It seems that it increases until 500°C. At 550°C, it appears to be a slight decrease in intensity. While on the samples of 450°C and 500°C there is the presence of white light, the sample at 550°C appears to emit luminescence in yellow tones.

The yellow, 500°C, and brown, 550°C, tones under natural sunlight at different temperatures suggest the formation of silver nanoparticles (np's), while the observed luminescent properties, observed under UV-light lamp, indicate the development of silver clusters

during the process, which is present in every sample. For a better understanding, the absorption and emission spectra will be shown, this data was acquired using the equipment described on table I.2.

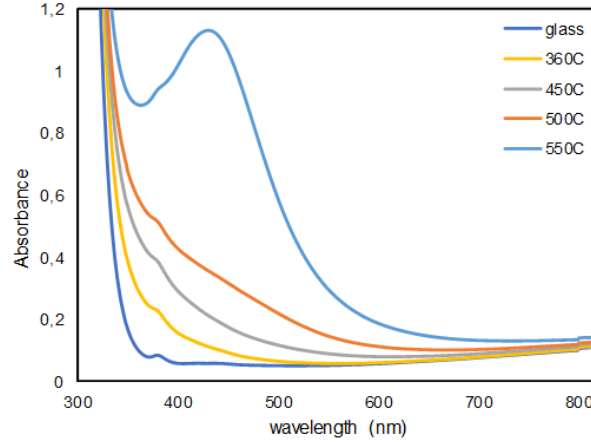


Figure 2.3: Absorption spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.

Figure 2.3 presents the absorption spectra of the samples fired at 360°C, 450°C, 500°C and 550°C. In the absorption spectra, a distinct peak appears at 430 nm at the sample at 550°C, this peaks refers to the presence of silver np's [30]. It is a surface plasmon resonance peak (SPR), a phenomenon where conduction electrons oscillate collectively and propagate along the metal surface. At the same wavelength, 430 nm, in other samples, it is possible to observe a rise in absorbance values with increasing temperature, which reflects the formation of silver np's, more evident in the sample at 500°C. The higher concentration of silver np's is visually confirmed by the darker tones presented at higher temperatures, observed in the glass in Figure 2.2. There is also a band observed around 390 nm that refers to the introduction of Ag^+ into the glass.

It is also possible to observe the absorption of glass below 360 nm and traces of iron species represented by a very low intensity broad band around 600 - 800 nm [37, 38, 39]. A table with summarized information about absorption wavelengths will be shown in table 2.1.

Table 2.1: Absorption elements wavelengths present in ion bath soda lime glass samples: glass, iron species, silver np's [37, 38, 39, 30].

Elements	Absorption λ (nm)
Glass	below 360
Iron Species	800
Silver np's	430 SPR band

Additionally, a red shift in the absorption wavelength values was observed as the annealing temperature increased. This shift is generally attributed to changes in the

characteristics of silver np's, such as particle size or geometry modifications, which directly influence their (SPR) response [22, 23, 29]. Since the detailed study of np's geometry and size effects does not fit the main scope of this work, this aspect will not be discussed further.

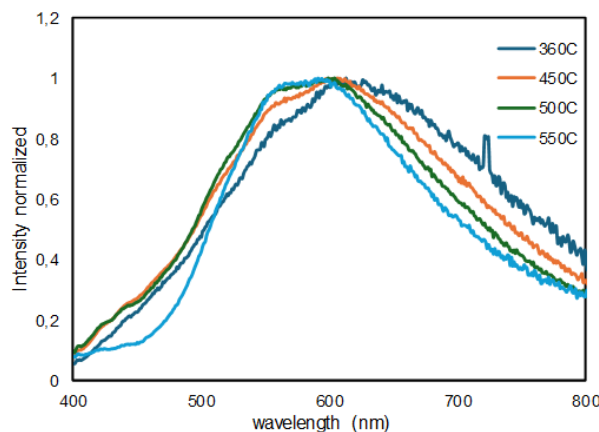


Figure 2.4: Emission (excitation wavelength of 360 nm) spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.

Turning to the emission spectra that is possible to consult in the annex, on Figure I.1, there is a significant difference in the emission intensity of the samples fired at 360°C, 450°C, 500°C, and 550°C. The results suggest that the increase continues until 500°C, but when it reaches 550°C, it decreases. This observation is accurate with Figure 2.2, where the luminescence seems to diminish at 550°C, accompanied by a yellow emission. This intensity decrease in emission is likely caused by self absorbing phenomena, as confirmed by the emission spectra. If observed carefully, the emission spectra of the 550°C sample only start to emit at 480 nm, which is after the other samples. And on the absorption spectra, this same sample has high absorbance values at the same wavelength of 480 nm, which confirms that this decrease of luminescent intensity might be due to a self-absorption effect that is caused by the absorption of silver np's. This phenomena also causes the luminescence to be yellow due to the brown surface present on the sample, which acts like a filter.

The species that are responsible for the luminescent features on the glass are clusters, which are possible to observe on the emission spectra in Figure 2.4. The clusters possibly responsible for the emission properties are mainly silver dimers (Ag_2) and trimers (Ag_3). Dimers emit light around 440 nm – 450 nm [40]. Trimers, in contrast, display an emission band near 590 nm [41, 42]. The most intense peak is consistently observed at 580–590 nm suggest the presence of Ag_3 trimers, suggesting that trimers contribute more strongly to the overall emission than dimers. Furthermore, luminescence can also be attributed to $\text{Ag}^+ - \text{Ag}^+$ pairs, which typically emit in the 480–550 nm range, giving rise to a band in this region of the spectrum [29]. The total luminescence intensity of the samples is a reflection

of the combined contribution of all these silver cluster species present within the glass. A table with summarized information about emissions wavelengths will be shown below:

Table 2.2: Attribution of the emissive elements wavelengths present in ion bath soda lime glass samples: Ag_2 clusters, Ag_3 clusters, $\text{Ag}^+ - \text{Ag}^+$ pairs [40, 41, 42, 29]

Clusters	Emission λ (nm)
$\text{Ag}^+ - \text{Ag}^+$ pairs	480-550
Ag_2	440-450
Ag_3	590

In addition, a shift in the emission peak position is observed depending on the annealing temperature. Samples fired at 500°C and 550°C exhibit a slight blue shift, which may be associated with a greater contribution from fluorescence. By contrast, samples treated at 360°C and 450°C show a red shift, suggesting that phosphorescence plays a significant role in their emission characteristics.

It is also visible a weak peak near 720 nm in the sample fired at 360°C, this is a “second harmonic” peak from the monochromator, which appears at twice the wavelength of a shorter wavelength emission feature. Such $2 \times \lambda$ peaks are well known in fluorescence emission spectra. This peak will appear further in this work on emission spectra [43]. For a better understanding of the presence of different silver cluster species on the glass samples the excitation spectra will be shown.

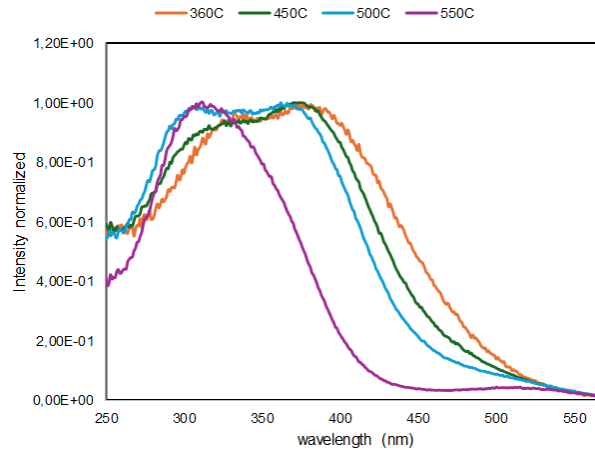


Figure 2.5: Excitation spectra (emission wavelength of 600 nm) of ion bath soda lime glass samples, 360°C, 450°C, 500°C, 550°C.

In Figure 2.5 is possible to observe the excitation spectra of the ion bath samples fired at 360°C, 450°C, 500°C, and 550°C.

What was to be expected was that the excitation spectra would be similar to the absorption spectra shown in Figure 2.3, but it is not, and this reveals something. The intensity values of samples at 450°C, 500°C, and 550°C should not be below the sample at

360°C because they have higher emission intensity as verified in Figure I.1 in the annex. This suggests that this data is deformed due to the presence of silver np's. The silver np's act like an internal filter that is interfering with the readings of excitation values.

It can also be observed that in the samples treated at 450°C, 500°C, and 550°C, a peak appears around 300 nm that is absent in the 360°C sample. This feature may be associated with the formation of additional silver clusters, suggesting that clusters of different sizes are produced at different treatment temperatures. The first peak, near 340 nm, is associated with silver dimers (Ag_2) [40], while the second peak, around 365 nm, is attributed to silver trimers (Ag_3) [42]. Furthermore, at lower temperatures, only Ag_2 dimers are formed, whereas at higher temperatures (450°C, 500°C), Ag_3 trimers also appear. Interestingly, at 550°C, the 355 nm band vanishes, indicating that only dimers remain under these conditions.

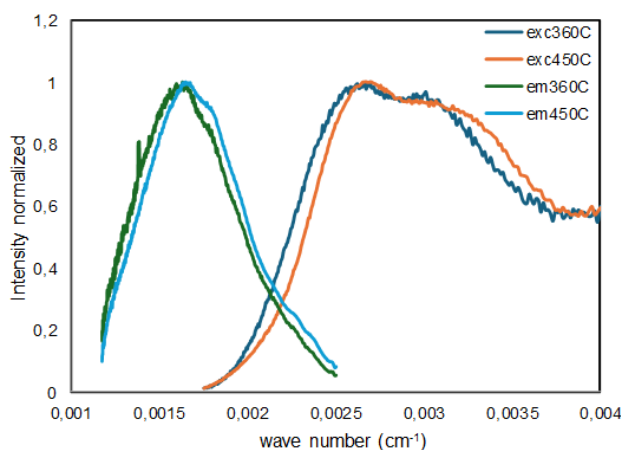


Figure 2.6: Emission (excitation wavelength of 360 nm) and Excitation (Emission wavelength of 600 nm) spectra of ion bath soda lime glass samples fired at 360°C, 450°C.

Regarding Figure 2.6, it illustrates the Stokes shift, which is the energy (or wavenumber) difference between the positions of the excitation and emission maxima. For the 360°C samples, the difference in wavenumber of excitation maxima and emission maxima is 0.001064 cm^{-1} , whereas for the 450°C samples it is 0.001024 cm^{-1} . A larger Stokes shift helps reduce self-absorption phenomena, since the emission spectrum becomes more separated from the absorption spectrum, minimizing their overlap. In contrast, smaller Stokes shifts lead to stronger overlap between absorption and emission bands, which increases the probability of re-absorption and may result in distorted or inaccurate luminescence measurements, as discussed earlier on the sample fired at 550°C.

2.1.2 Deposition by drop casting

After completing the ion bath deposition experiments, the next objective was to develop an alternative deposition process capable of producing a luminescent coating. The aim

was to formulate a solution that could function as a “paint,” allowing direct application onto glass surfaces, including artistic glass pieces. The tests began on laboratory scale pieces with a deposition by drop casting as illustrated in figure 2.7.



Figure 2.7: Representative Figure of drop casting deposition on glass, in a petri dish. The blue area represents the petri dish, the yellow square represents the glass and the drop illustrates the solution being deposited.

For this purpose, it was necessary to prepare a solution containing the two salts used in the ion bath deposition, namely silver nitrate and sodium nitrate.

After an extensive series of solution tests, several important observations were made. silver nitrate was found to be highly sensitive, and in the presence of sodium nitrate, it reduced, leading to the need for preparing the two salts in separate solutions. One solution containing silver nitrate and another solution containing sodium nitrate.



Figure 2.8: Solution tests AgNO_3 and NaNO_3 in a) distilled water; b) ethanol; c) 25 mL water MilliQ/25 mL glycerol, f) triethylene glycol monomethyl ether, e) polyethylene glycol 400; Ag_2SO_4 and Na_2SO_4 in d) decoflux .

Silver nitrate was dissolved in solvents such as ethanol, glycerol, polyethylene glycol 400, decoflux, triethylene glycol monomethyl ether, and distilled water. In all solvents silver nitrate was reduced, forming a grey precipitate, as illustrated in Figure 2.8. The

only solvent that demonstrated stable interaction with silver nitrate, avoiding reduction, was Milli-Q water, which is ultra pure water, being able to produce two solutions, one of silver nitrate, $[\text{AgNO}_3] = 0,18 \text{ M}$ and other of sodium nitrate $[\text{NaNO}_3] = 0,73 \text{ M}$.

These concentrations were chosen due to the solubility of silver nitrate in water and sodium nitrate in water ($s(\text{AgNO}_3) = 256 \text{ g}/100\text{mL}$ in water at 25°C and $s(\text{NaNO}_3) = 91,2 \text{ g}/100\text{mL}$ in water at 25°C , [44] [45]), maintaining the weight ratio of the salts that was used in the ion exchange bath test, $1(\text{AgNO}_3):2(\text{NaNO}_3)$. This weight ratio allows an eutectic mixture to be formed, which lowers the fusion point of the salts. The aim was to choose a concentration with the minimum salt possible that still allowed ion exchange to occur, maintaining the eutectic mixture and to be a sustainable and low cost process.

Having prepared the solutions, the tests with drop cast deposition started. These tests were separate in T1 and T2, in T1 it was made the deposition of the same volume ($56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) of both $[\text{AgNO}_3] = 0,18 \text{ M}$ / $[\text{NaNO}_3] = 0,73 \text{ M}$ (in water MilliQ). While on T2 it was deposited a constant volume of $[\text{NaNO}_3] = 0,73 \text{ M}$, $112\mu\text{L}$, and the volume of $[\text{AgNO}_3] = 0,18 \text{ M}$ increased ($112\mu\text{L}$, $168\mu\text{L}$, $224\mu\text{L}$, and $280\mu\text{L}$), as shown below in table 2.3.

Table 2.3: Test T1 and T2 volume description.

T1 $V(\text{AgNO}_3)/V(\text{NaNO}_3) \text{ mL}$	T2 $V(\text{AgNO}_3)/V(\text{NaNO}_3) \text{ mL}$
$56\mu\text{L}/56\mu\text{L}$	$112\mu\text{L}/112\mu\text{L}$
$112\mu\text{L}/112\mu\text{L}$	$168\mu\text{L}/112\mu\text{L}$
$168\mu\text{L}/168\mu\text{L}$	$224\mu\text{L}/112\mu\text{L}$
$224\mu\text{L}/224\mu\text{L}$	$280\mu\text{L}/112\mu\text{L}$

This test aimed to understand the behaviour of the solutions on the glass, their ability to form homogeneous luminescent coatings, and the influence of silver nitrate on the coating. The temperature of 450°C was chosen because, in previous tests 2.1.1, this temperature resulted in intense luminescent layers with minimal silver nanoparticle formation. Below in Figures 2.9, 2.10 the results of test T1 and T2 at 360°C and 450°C are shown.

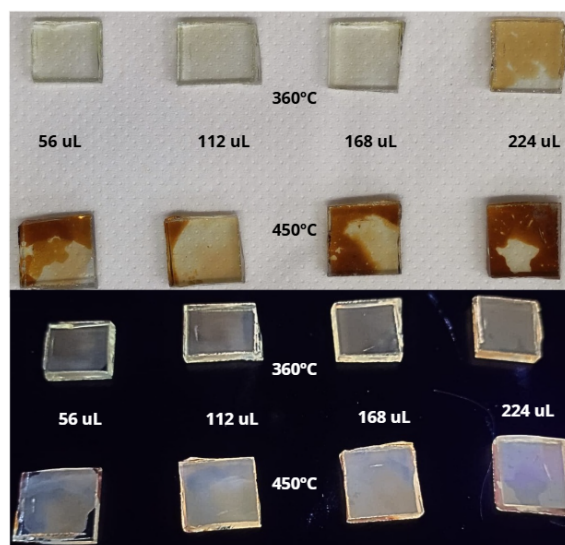


Figure 2.9: Test T1 (same deposition volume of [AgNO₃] and [NaNO₃]) at 360°C (above) and 450°C (below) with volumes of 56 μ L, 112 μ L, 168 μ L and 224 μ L, [AgNO₃] = 0,18M and [NaNO₃] = 0,73M. Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366$ nm.

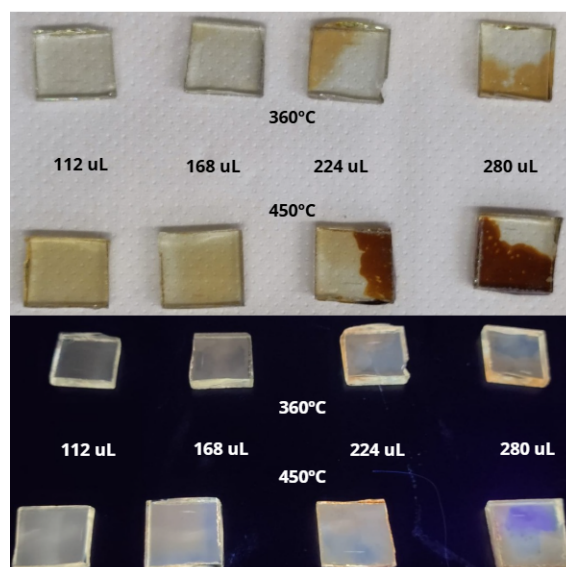


Figure 2.10: Test T2 (increasing deposition volume of [AgNO₃], 56 μ L, 112 μ L, 168 μ L and 224 μ L, and constant deposition volume of [NaNO₃], 112 μ L) at 360°C (above) and 450°C (below). Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366$ nm. [AgNO₃] = 0,18M and [NaNO₃] = 0,73M.

The main question was answered by the results shown in Figures 2.9 and 2.10. It was also possible to achieve homogeneous luminescent coatings on glass using these solutions. From these tests, it was also understood that controlling the deposition process

with aqueous solutions presents challenges, since water is not a viscous solvent, making it difficult to maintain the solution uniformly on the glass surface.

Visually, no major differences are observed between the samples of test T1 and T2. At 360°C, both T1 and T2 exhibit transparent, yellowish tones, while at 450°C, yellow to brown tones are present in both cases. The brown stains present on some of the samples fired at 450°C indicate the presence of silver np's. The luminescence appears homogeneous and becomes more intense at 450°C, as it was also verified on subchapter 2.1.1. But there is still one question that remains unanswered: whether the deposited volume of silver has a direct influence on luminescence intensity.

In Figures 2.11 and 2.12, the emission spectra of the samples presented in Figures 2.9 and 2.10 are shown.

The most evident distinction lies between the spectra of the samples treated at 360°C and those at 450°C. For the 450°C samples, the emission curves largely overlap, suggesting the dominance of the same cluster species regardless of the deposited volume. In contrast, at 360°C, some samples exhibit a noticeable shift toward lower wavelengths, particularly for the T2 samples with higher deposited volumes (224 μ L and 280 μ L). This shift may indicate the formation of different silver clusters. Specifically, these two samples could contain a higher concentration of Ag dimers (Ag_2), which emit in the 440–450 nm range, whereas the other samples show a stronger contribution from Ag trimers (Ag_3), with emission centered at 590 nm.

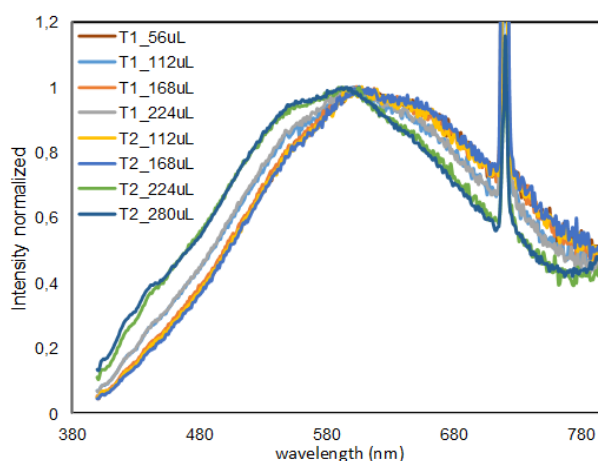


Figure 2.11: Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of 56 μ L, 112 μ L, 168 μ L and 224 μ L) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, 56 μ L, 112 μ L, 168 μ L and 224 μ L, and constant deposition volume of $[\text{NaNO}_3]$, 112 μ L) fired at 360°C. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

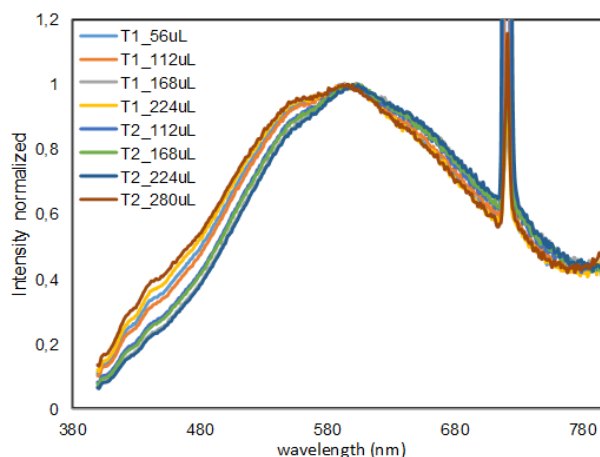


Figure 2.12: Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C . $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

In the 450°C spectra, Figure 2.12, the dominance of Ag trimers is clear (Ag_3), with a pronounced peak at 590 nm [41, 42], although Ag dimers (Ag_2) are still present, as suggested by the emission around 440–450 nm [40].

To address the undesirable formation of brown stains, which act as optical filters and interfere with the luminescent properties, an additional test was performed. In this case, a thin layer of kaolin was placed at the base of the Petri dish. The purpose of this was to prevent the solution from dripping onto the tin side of the glass, thereby avoiding silver nanoparticle formation, allowing any excess solution to be absorbed by the kaolin, as shown in Figure 2.13.



Figure 2.13: Soda lime glass samples on a petri dish a layer of kaolin below. Samples under natural sunlight and before firing

The T1 and T2 tests, as described in Table 2.3, were repeated with the addition of

a kaolin layer at the base of the Petri dish. This modification aimed to minimize the formation of silver nanoparticles, thereby reducing the appearance of brown stains that negatively affect the luminescent response of the samples. The results of these tests are presented below.

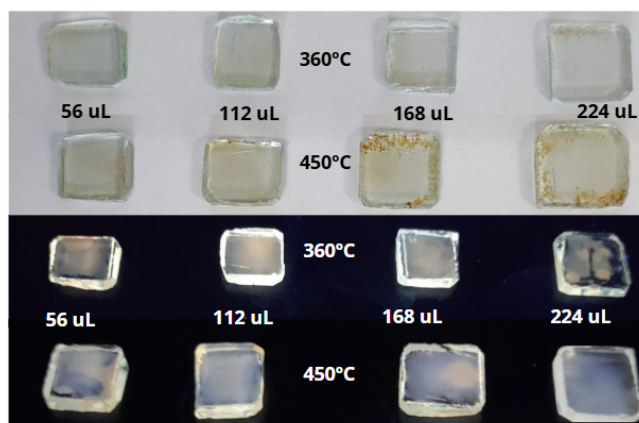


Figure 2.14: Test T1 with kaolin (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$) at 360°C (above) and 450°C (below) with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$. Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366\text{ nm}$.

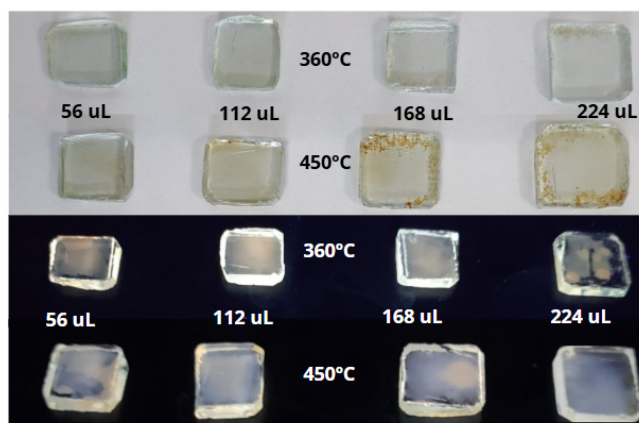


Figure 2.15: Test T2 with kaolin (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) at 360°C (above) and 450°C (below). Above, the soda lime glass samples are shown under natural sunlight, below, the samples are shown under UV-light lamp at $\lambda = 366\text{ nm}$. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

In Figures 2.14 and 2.15, clear improvements in staining can be observed. The use of kaolin minimized the formation of silver np's, with most samples appearing more transparent and only showing small yellow spots. To better understand these improvements and analyse the presence of silver np's, the absorbance spectra of the samples fired at 450°C corresponding to Figures 2.14, 2.15, 2.9, 2.10 will be shown.

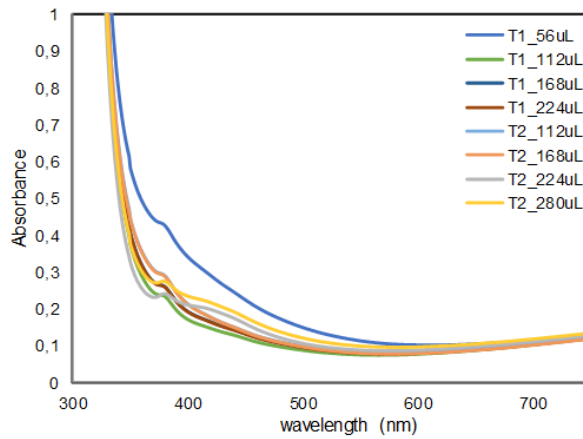


Figure 2.16: Absorption spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C without kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

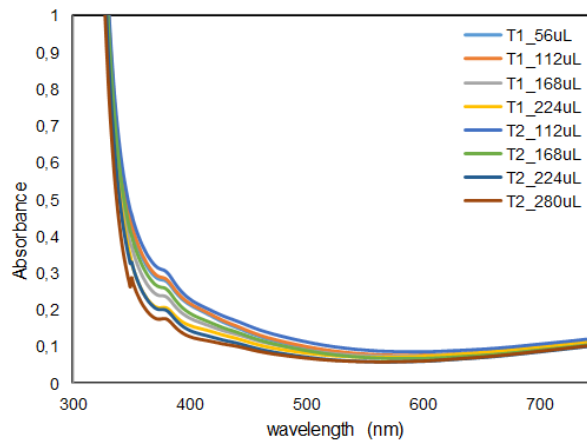


Figure 2.17: Absorption spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C with kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

From Figures 2.16 and 2.17, it can be observed that the samples without kaolin below the samples, Figure 2.16, exhibit increasing absorbance values around 430 nm, characteristic of silver np's, particularly in samples T1 with 56 μ L, T2 with 224 μ L, and T2 with 280 μ L. This explains the yellow and brown coloration observed in these samples. Sample T1 with 56 μ L stands out from other samples in absorbance values on Figure 2.16. This might be due to the reading having been performed on a more stained area of the glass.

In contrast, the spectra of the samples with kaolin, Figure 2.17, show a more condensed distribution of absorbance curves. Although the absorbance values differ among the samples, the band at 430nm is absent, indicating that silver np's were not formed. This result is consistent with the higher transparency of the kaolin samples, as seen in Figures 2.14 and 2.15.

Regarding luminescence, the emission spectra of these samples will be presented in order to evaluate whether the use of kaolin influenced the luminescent properties. The analysis focuses on the samples annealed at 450°C, as these exhibited the strongest luminescence.

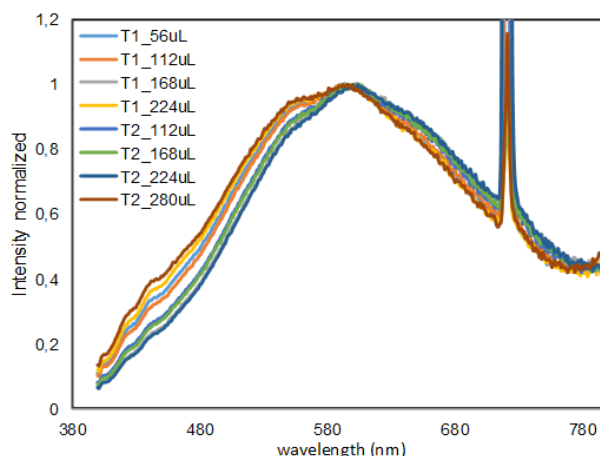


Figure 2.18: Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of 56 μ L, 112 μ L, 168 μ L and 224 μ L) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, 56 μ L, 112 μ L, 168 μ L and 224 μ L, and constant deposition volume of $[\text{NaNO}_3]$, 112 μ L) fired at 450°C, without kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

The most evident difference between the samples fired at 450°C without kaolin, Figure 2.18, and with kaolin, Figure 2.19, is the appearance of a pronounced band around 450-490 nm in the kaolin samples, which is absent in the samples without kaolin. This band is attributed to the presence of both Ag dimers (Ag_2) [40], and $\text{Ag}^+ - \text{Ag}^+$ pairs [29].

The results suggest that samples with higher transparency and the absence of silver nanoparticles make the contribution of these clusters, (Ag_2 and $\text{Ag}^+ - \text{Ag}^+$), more visible in the emission spectra, whereas in the samples displaying brown and yellow coloration, the presence of silver nanoparticles masks their signatures.

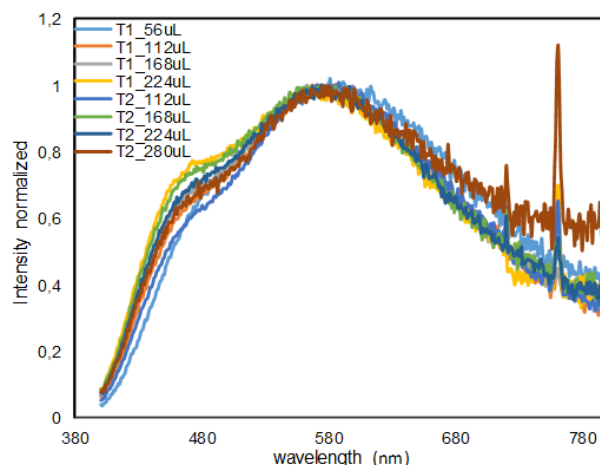


Figure 2.19: Emission (excitation wavelength at 360 nm) spectra of soda lime glass samples of test T1 (same deposition volume of $[\text{AgNO}_3]$ and $[\text{NaNO}_3]$ with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) and T2 (increasing deposition volume of $[\text{AgNO}_3]$, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and constant deposition volume of $[\text{NaNO}_3]$, $112\mu\text{L}$) fired at 450°C , with kaolin. $[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3] = 0,73\text{M}$.

In both conditions, with and without kaolin, a peak at 590nm is consistently observed, indicating the presence of Ag trimers (Ag_3) [41, 42]. Regarding to the different deposition volumes tested in T1 and T2, no clear influence on luminescence properties was identified, and no optimal deposition volume enhancing luminescence could be determined. Having this in mind, further tests were made but only with silver nitrate, AgNO_3 . These tests aimed to evaluate the ability of silver nitrate alone to form silver clusters within the glass matrix, without the contribution of sodium nitrate, and to investigate how variations in silver nitrate volume affect the luminescent properties of the coatings.

2.1.3 Silver concentration influence

To understand the ability of silver nitrate alone to form silver clusters and therefore create luminescent layers, a deposition by drop casting using a micropipette was performed. This test also aimed to understand if the deposited volume of silver nitrate had any influence on luminescence intensity.

For this purpose, it was deposited an increasing volume of AgNO_3 , corresponding to T1 test volumes, $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, and the samples were fired at both 360°C and 450°C . The results of these tests will be shown below.

From Figure 2.20, one of the most noticeable features is the presence of stains on the glass surface. In addition to the stains observed in previous tests, metallic silver deposits were also detected in this case, which were difficult to remove.

Despite this, luminescent properties can still be achieved in glass using only silver nitrate, with the emission being more intense at 450°C than at 360°C .

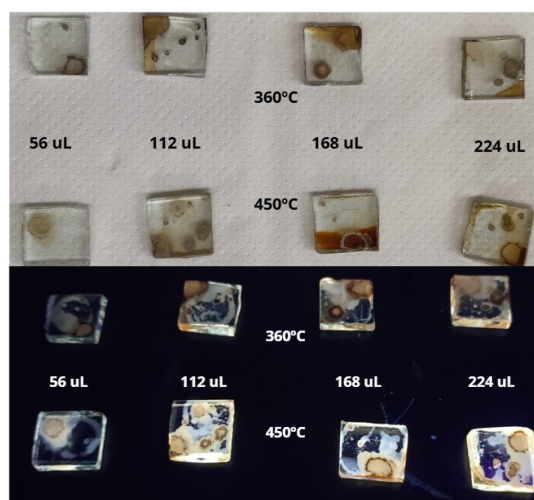


Figure 2.20: Test T1 (increasing deposition volume of $[\text{AgNO}_3]$ at 360°C (above) and 450°C (below) with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$, $[\text{AgNO}_3] = 0,18\text{M}$. Above the samples are shown under natural sunlight and, below, the soda lime glass samples are shown under a UV-light lamp at $\lambda = 366\text{ nm}$.

The variation in deposition volume does not appear to significantly affect luminescence intensity, although higher volumes tend to cover the entire glass surface. This study also reveals that to achieve homogeneous luminescent intensity, the role of sodium nitrate is indispensable.

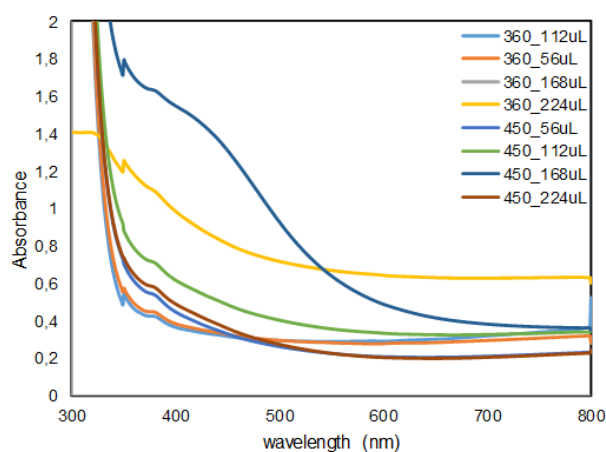


Figure 2.21: Absorption spectra of Test T1 on soda lime glass samples (with increasing deposition volume of AgNO_3 , with volumes of $56\mu\text{L}$, $112\mu\text{L}$, $168\mu\text{L}$ and $224\mu\text{L}$) at 360°C and 450°C , $[\text{AgNO}_3] = 0,18\text{M}$.

The absorption spectra in Figure 2.21 reveal a peak around 430 nm in the samples with $168\mu\text{L}$ fired at 450°C , $224\mu\text{L}$ at 360°C , and $112\mu\text{L}$ fired at 450°C , indicating the presence of silver nanoparticles. In the other samples, no clear nanoparticle signatures are observed.

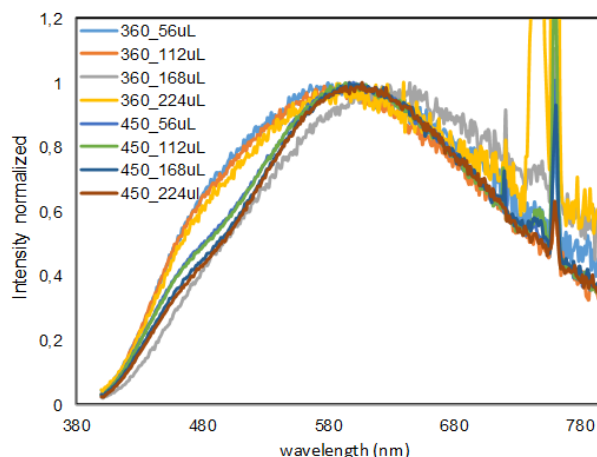


Figure 2.22: Emission (excitation wavelength of 360 nm) spectra of Test T1 soda lime glass samples (increasing deposition volume of $[\text{AgNO}_3]$ at 360°C and 450°C with volumes of 56 μL , 112 μL , 168 μL and 224 μL , $[\text{AgNO}_3] = 0,18\text{M}$).

In the emission spectra, the samples fired at 360°C exhibit a noticeable shift toward lower wavelengths, suggesting the formation of different cluster sizes at 360°C and 450°C. Specifically, the 360°C samples show emission around 440–450 nm, consistent with Ag dimers, Ag_2 [40], while the 450°C samples exhibit a strong emission band near 590 nm, characteristic of Ag trimers, Ag_3 [42, 41]. Aiming for a scale up and being water a difficult medium for deposition stability on glass surface, further tests were performed with a more viscous solvent, such as polyethylene glycol, PEG.

2.1.4 Anion influence

In order to test a more viscous solvent that could improve coating uniformity, adhesion on the glass surface, and also allow scale up, polyethylene glycol (PEG) was evaluated with silver nitrate (AgNO_3). However, silver nitrate was reduced almost immediately, making this approach unsuitable, as shown in Figure 2.8. To overcome this limitation, silver sulfate (Ag_2SO_4) was instead dissolved in PEG to study its behavior. In this case, reduction still occurred, but only after approximately 20 minutes, providing a practical time window for performing the deposition and initiating the firing program in the kiln.

Solutions of polyethylene glycol (PEG) containing silver sulfate and sodium sulfate were successfully prepared with concentrations of $[\text{Ag}_2\text{SO}_4] = 0.02\text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0.08\text{ M}$ and then deposited by drop casting.

To evaluate the luminescent properties of silver sulfate, individual drops of the prepared solutions were deposited onto the glass surface, using a plastic pipette, and their luminescence properties were subsequently analysed.

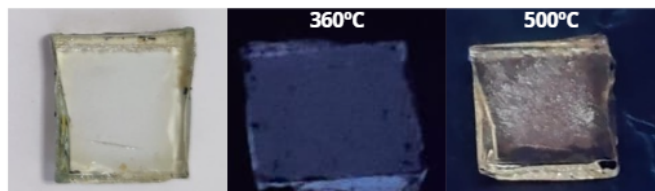


Figure 2.23: Sample of soda lime glass fired at 360°C and 500°C with $[\text{Ag}_2\text{SO}_4]=0,02$ M and $[\text{Na}_2\text{SO}_4]=0,08$ M in PEG. The first image on the left corresponds to the sample fired at 360°C under natural sunlight, the sample on the middle corresponds to the sample fired at 360°C under UV-light lamp at $\lambda = 366$ nm, and the sample on the right corresponds to the sample fired at 500°C under a UV-light lamp at $\lambda = 366$ nm.

As shown in Figure 2.23, the sample fired at 360°C displayed weak luminescent properties and low surface homogeneity, with a noticeable increase in emission intensity observed at 500°C. Based on these results, the emission spectra of this sample were collected to evaluate its luminescence intensity and to identify the presence of silver clusters.

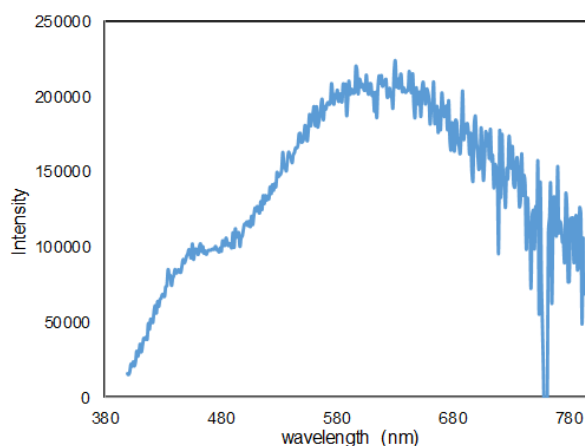


Figure 2.24: Emission spectra (excitation wavelength at 360 nm) of soda lime glass sample of $[\text{Ag}_2\text{SO}_4]=0,02$ M and $[\text{Na}_2\text{SO}_4]=0,08$ M in PEG fired at 500°C

In Figure 2.24, the emission spectra of the sample shown in Figure 2.23 is presented. Luminescent features appear on the sample fired at 500°C. A distinct band can be observed around 440–450 nm, which, despite its low intensity, corresponds to Ag dimers, (Ag_2) [40]. There is also an increase of intensity around 480–550 nm, which suggests the presence of cluster species Ag^+-Ag^+ [29].

Additionally, an emission peak appears at approximately 590 nm, corresponding to the presence of Ag trimers, (Ag_3) [41, 42]. These results indicate that silver clusters can still form when silver sulfate and sodium sulfate are dissolved in PEG. However, the method presents certain challenges due to the low stability of these salts in PEG.

This result highlighted that, despite the chemical instability of silver salts in PEG, silver sulfate presented better stability in this solvent than silver nitrate. The viscosity of PEG remains advantageous for achieving more controlled and homogeneous coatings. For this reason, PEG solutions were later revisited during the screen printing experiments, where the higher viscosity of the medium proved essential for spreading the solution evenly and achieving improved coating quality on glass substrates.

2.2 Deposition processes for scale up pieces

2.2.1 Deposition by screen printing

Aiming to scale up the already reached homogeneous luminescent layers on glass on subchapter 2.1.2, deposition by screen printing was performed as illustrated below Figure 2.25.

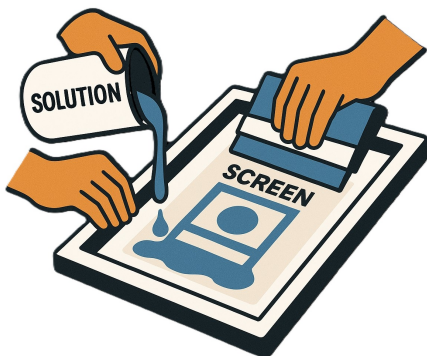


Figure 2.25: Representative Figure of Screen Printing deposition of the solutions in glass

Due to screen printing characteristics, it was tested to dissolve silver nitrate and sodium nitrate ($[\text{AgNO}_3] = 0,18\text{M}$ and $[\text{NaNO}_3]=0,73\text{M}$) in solvents like Degussa Portuguesa, ZusoPlast, which are typically used mediums for screen printing purposes. Water MilliQ was also tested despite low viscosity.

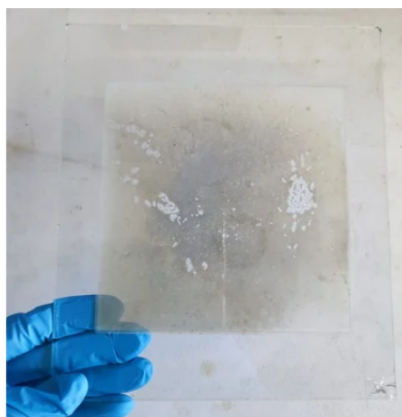


Figure 2.26: Screen Printing tests with Degussa Portuguesa with $[\text{AgNO}_3] = 0,18 \text{ M}$ and $[\text{NaNO}_3] = 0,73 \text{ M}$ at 450°C under natural sunlight.

The tests with Zusoplast and Degussa Portuguesa, shown in Figure 2.26, produced similar results, a grey coverage on the glass surface, and did not produce any luminescence, both at 360°C and 450°C .

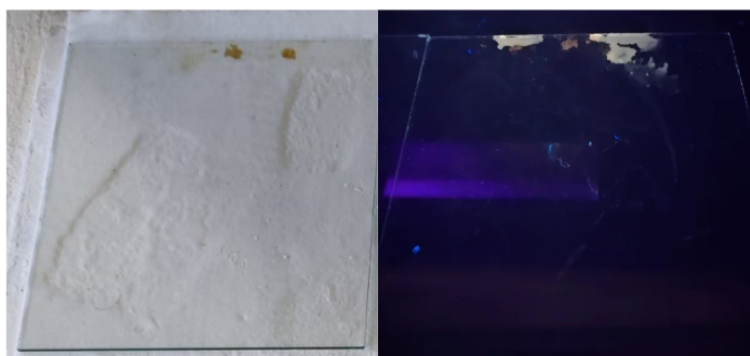


Figure 2.27: Screen Printing tests on soda lime glass fired at 450°C , with water MilliQ with $[\text{AgNO}_3] = 0,18 \text{ M}$ and $[\text{NaNO}_3] = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$.

The screen printing experiments using water MilliQ as a medium, Figure 2.27, resulted in the formation of two yellowish stains on the glass surface, indicative of the presence of silver nanoparticles. Although luminescence was detected, it exhibited very limited surface coverage and poor homogeneity, highlighting the unsuitability of water as a medium for this application. Since the trials with water did not show the desired results, alternative solutions containing silver sulfate and sodium sulfate in PEG, as described in subsection 2.1.4, were tested.

In this case, luminescence became detectable only after firing at 500°C , Figure 2.28, consistent with earlier observations.

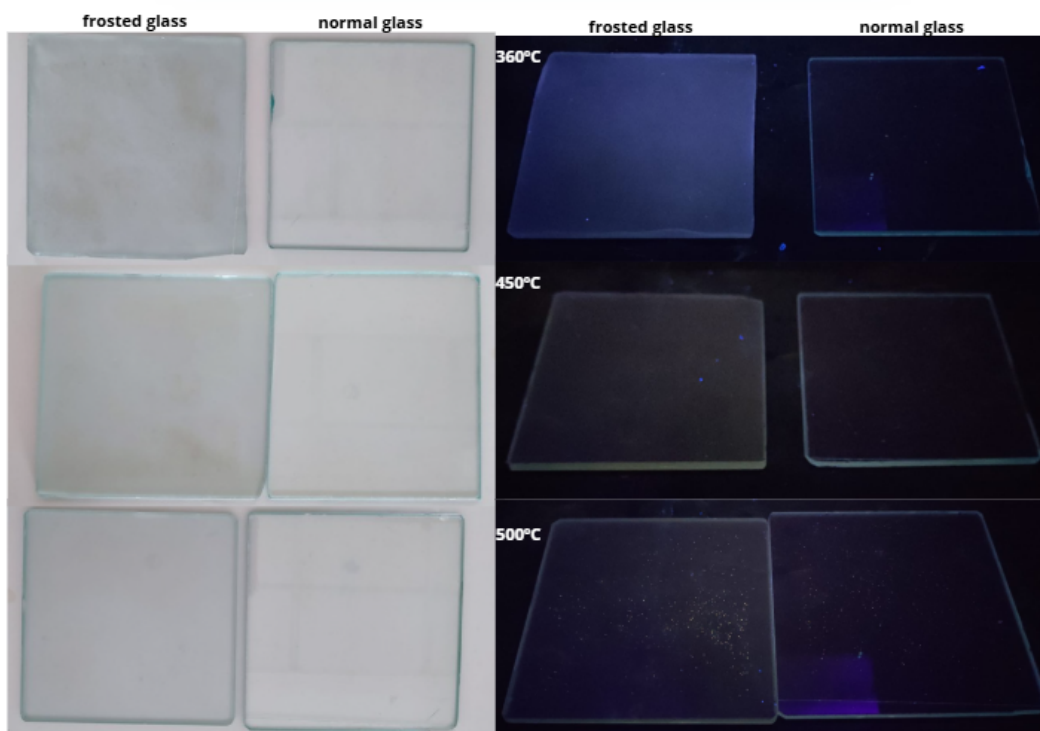


Figure 2.28: Screen Printing tests of soda lime glass samples fired at 360°C, 450°C and 500°C, with $[\text{Ag}_2\text{SO}_4] = 0,02 \text{ M}$ and $[\text{Na}_2\text{SO}_4] = 0,08 \text{ M}$ in PEG. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$

Despite being able to detect luminescence, the emission appeared only as isolated luminescent spots, suggesting that the salt concentration in the PEG solutions was too low to promote uniform cluster formation. The screen printing tests reveal two important limitations, water lacks the viscosity for coating required for controlled screen printing deposition, and the tested PEG solutions require optimization of salt concentration to ensure homogeneous coverage and consistent luminescence.

As the screen printing tests did not achieve the desired outcome, an alternative method was required to promote scale up while ensuring a more homogeneous luminescent coating. The method chosen for this purpose was spray.

2.2.2 Deposition by spray

As screen printing did not provide adequate coverage for larger pieces, spray deposition was explored as an alternative method to apply the coating to larger surfaces, such as artworks. Spray deposition experiments were carried out on 10 cm x 10 cm samples of both clear and frosted glass. The frosted substrates were included to evaluate whether their textured surface would enhance the coating adhesion. The deposited solutions consisted of two separate solutions, as described earlier, of silver nitrate and sodium

nitrate, ($\text{AgNO}_3 = 0.18 \text{ M}$) and $\text{NaNO}_3 = 0.73 \text{ M}$). Figure 2.29 shows a representative image of spray deposition on glass.



Figure 2.29: Representative figure of deposition by spray on glass inside a hotte.

Figure 2.30 presents the results of the spray tests performed on normal glass (left) and frosted glass (right). On normal glass, the coverage achieved was greater than with the screen printing method, however, the coating still exhibited low homogeneity. In contrast, the frosted glass samples exhibited improved performance, as the roughened surface interacted more effectively with the solution, resulting in more homogeneous coverage.

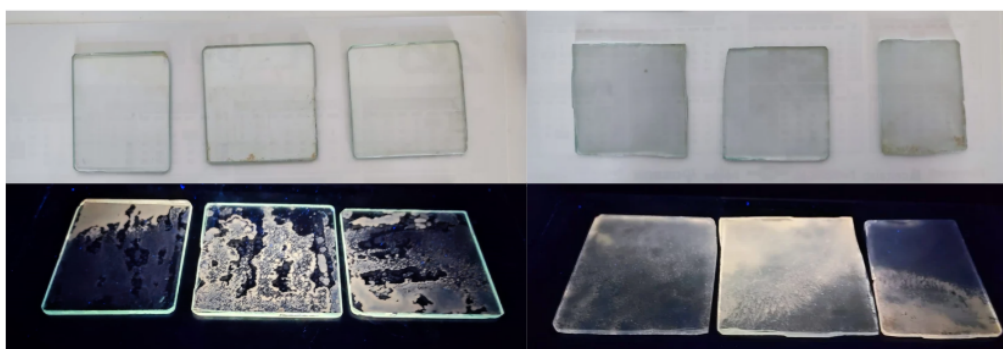


Figure 2.30: Spray test on normal (left) and frosted (right) soda lime glass at 360°C . $\text{AgNO}_3 = 0, 18 \text{ M}$ $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$.

The samples were later annealed to 450°C and 500°C , Figure 2.31, the glass showed yellowish and brown dots, being more visible at 500°C , these are due to the presence of silver np's.

Regarding luminescence intensity, visually it is noticed a stronger intensity of luminescence than on the samples annealed at 360°C .

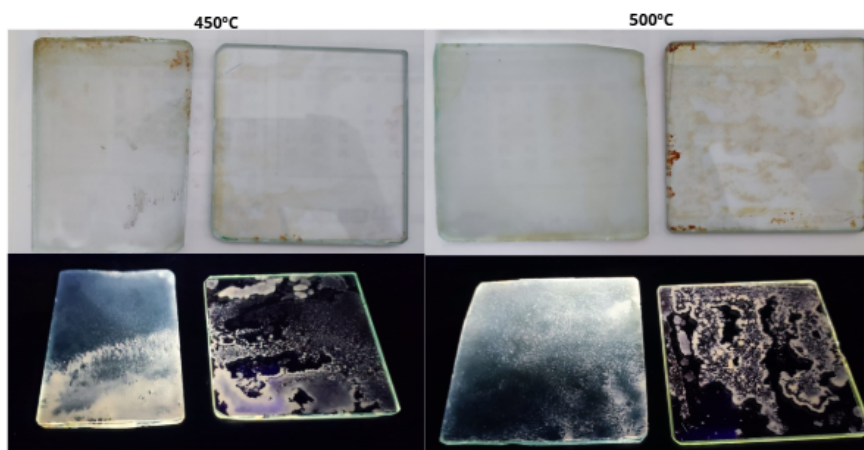


Figure 2.31: Spray test on normal (left) and frosted (right) soda lime glass at 450°C and 500°C. $\text{AgNO}_3 = 0$, 18 M $\text{NaNO}_3 = 0,73$ M. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366$ nm.

The frosted glass samples revealed more coverage than normal glass. The normal glass also appeared to exhibit surface contamination, likely from residual grease, as indicated by irregular luminescence dispersion.

To address this, further tests were conducted after cleaning the glass with nitric acid (HNO_3), followed by potassium hydroxide (KOH), to remove any impurities as well as negatively charge the glass surface and promote silver attachment, due to the negative charge of the hydroxide and the positive charge of the silver.

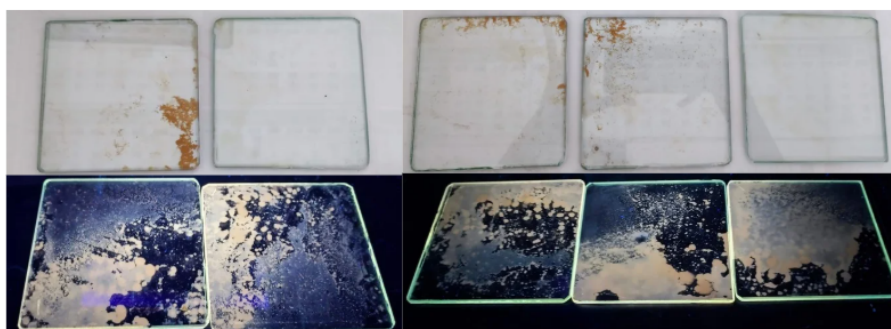


Figure 2.32: Spray test on soda lime glass at 360°C. $\text{AgNO}_3 = 0$, 18 M $\text{NaNO}_3 = 0,73$ M. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366$ nm.

After the glass have been cleaned the results on normal glass revealed to have better coverage, Figure 2.32 and 2.33, despite still not being a full coverage.

Having this in mind, further tests were made on frosted glass.

The results presented in Figure 2.34 demonstrate that, following the cleaning treatment,

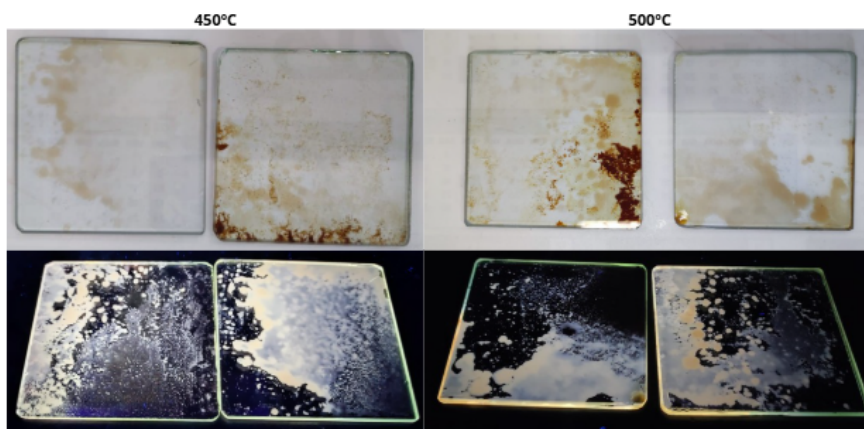


Figure 2.33: Spray test on soda lime glass at 450°C and 500°C. $\text{AgNO}_3 = 0,18 \text{ M}$, $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and UV-light lamp (below) at $\lambda = 366 \text{ nm}$.

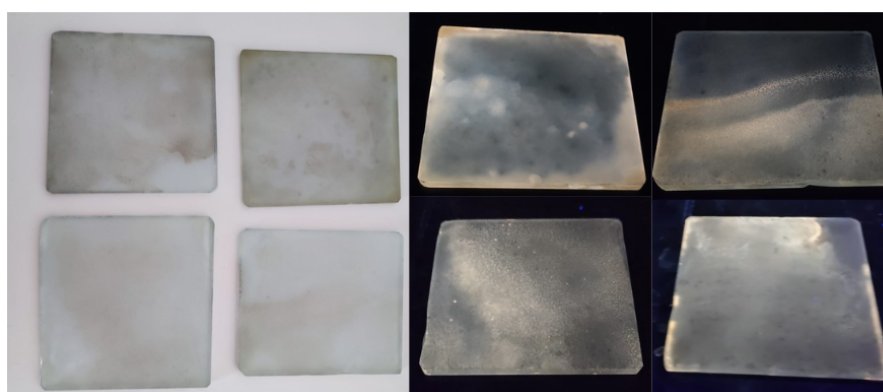


Figure 2.34: Spray test on frosted soda lime glass at 360°C. $\text{AgNO}_3 = 0,18 \text{ M}$, $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and UV-light lamp (right) at $\lambda = 366 \text{ nm}$.

the coatings exhibited improved surface coverage and greater homogeneity on frosted glass. These findings highlight the critical role of proper glass cleaning as a preparatory step for achieving effective spray deposition.

Frosted glass has a better response to spray deposition when achieving homogeneous luminescent coatings. Frosted glass samples were annealed at higher temperatures, such as 450°C and 500°C.

The samples annealed at 450°C, Figure 2.35, exhibited significantly higher luminescence intensity compared to those annealed at 360°C, Figure 2.34, approaching nearly complete surface coverage.

A fully homogeneous luminescent coating was achieved on the frosted glass sample annealed at 500°C, Figure 2.36, confirming the effectiveness of frosted glass and this temperature for uniform deposition.

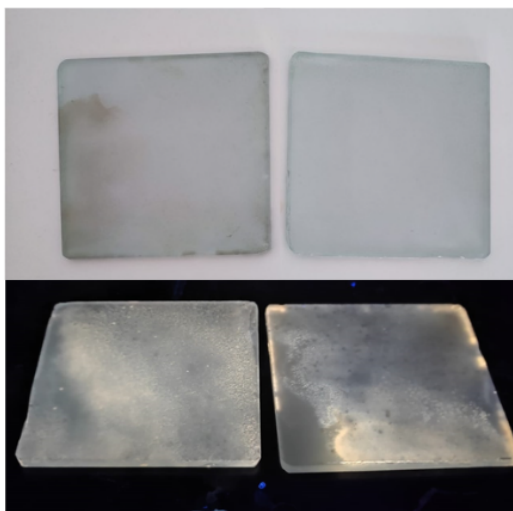


Figure 2.35: Spray test on frosted soda lime glass at 450°C. $\text{AgNO}_3 = 0,18 \text{ M}$
 $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (above) and
UV-light lamp (below) at $\lambda = 366 \text{ nm}$.

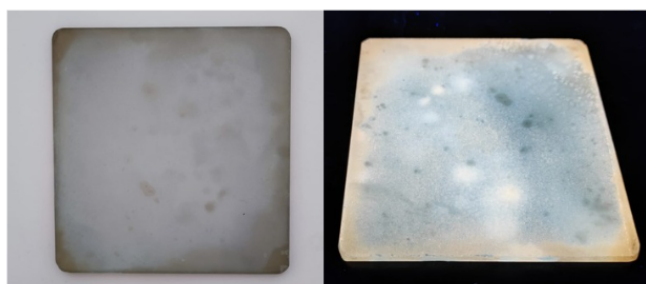


Figure 2.36: Spray test on frosted soda lime glass at 500°C. $\text{AgNO}_3 = 0,18 \text{ M}$
 $\text{NaNO}_3 = 0,73 \text{ M}$. The samples are shown under natural sunlight (left) and
UV-light lamp (right) at $\lambda = 366 \text{ nm}$.

After the successful upscaling of spray deposition method on 2D glass substrates, the technique was subsequently extended to 3D glass pieces produced by VICARTE artists, to evaluate its applicability under more complex geometries and artistic contexts.

A MANUAL FOR ARTISTIC IMPLEMENTATION OF A SILVER LUMINESCENT COATING ON GLASS

Production manual of a silver luminescent coating on glass for the arts.

A protocol that empowers artists and makes chemistry accessible.

Warning: During all the procedures, the artists need to wear safety equipment such as a laboratory coat and gloves. And when applying the spray, a dust mask and protective glasses are essential. Silver nitrate is corrosive, please stay safe!

Step 1: The glass

Before applying the coating it is necessary to understand if the conservation of transparency or if some degree of unpredictability and staining is desired as shown in Figure 3.1.



Figure 3.1: Soda-lime glass pieces after deposition of the luminescent coating by spray, from artist Mayank Sahni, under natural sunlight. non-conservation of transparency (left) and conservation of transparency (right).

- **Conservation of transparency (Figure 3.1 (right)):** If it is necessary to preserve the transparency of the glass, the first step is to verify that the glass does not contain tin. Tin enables silver reduction, the visual reflection of this is yellow and brown stains on the glass surface. To verify tin presence, it is necessary to observe the glass under UV light at 254 nm, the presence of tin is indicated by a characteristic glow as indicated in Figure 3.2. Once confirmed, the piece should be cleaned before applying the coating. The cleaning begins by applying nitric acid (HNO_3) with a tissue to remove impurities, and then using a different tissue to apply potassium hydroxide (KOH) uniformly across the entire surface. Make sure this step is performed inside a hotte due to the use of nitric acid. Allow the piece to dry completely before proceeding.
- **Non conservation of transparency (Figure 3.1 (left)):** If preserving transparency is not required for the intended application, and some degree of staining or unpredictability is acceptable, this cleaning step may be skipped. However, it should be noted that in this case, brownish or yellowish stains may appear on the surface of the glass.



Figure 3.2: Soda-lime glass sample under UV light at a wavelength of 254 nm with tin (left) and without tin (right).

Step 2: Coating Production

These coatings consist of two solutions that will be made and applied separately so make sure that during their preparation, any material is mixed. Use different materials for the preparation of each solution.

- **The concentration of Silver Nitrate (AgNO_3) will be 0,18M; (Molar mass of AgNO_3 : 169,87 g/mol)**
- **The concentration of Sodium Nitrate (NaNO_3) will be 0,73M; (Molar mass of NaNO_3 : 84,99 g/mol)**

The required volume of solution depends on the surface area of the piece to be coated. To illustrate the procedure, a step by step calculation is provided below for determining the necessary volume, table 3.2, 3.1.

CHAPTER 3. A MANUAL FOR ARTISTIC IMPLEMENTATION OF A SILVER LUMINESCENT COATING ON GLASS

Example: Suppose that 25 mL (equivalent to 0.025 L) of each solution is required to adequately cover the surface of the piece.

Table 3.1: Table with solution calculation for a volume of 25 mL.

For AgNO_3	For NaNO_3
• n° of moles (mol) = concentration (M) $\times$ Volume (L) • n° of moles (mol) = $0,18 \text{ M} \times 0,025 \text{ L} = 0,0045 \text{ mol}$ • mass (g) = n° of moles (mol) $\times$ molar mass (g/mol) • mass (g) = $0,0045 \text{ mol} \times 169,87 \text{ g/mol} = 0,764 \text{ g of AgNO}_3$	• n° of moles (mol) = concentration (M) $\times$ Volume (L) • n° of moles (mol) = $0,73 \text{ M} \times 0,025 \text{ L} = 0,018 \text{ mol}$ • mass (g) = n° of moles (mol) $\times$ molar mass (g/mol) • mass (g) = $0,018 \text{ mol} \times 84,99 \text{ g/mol} = 1,53 \text{ g of NaNO}_3$

Table 3.2: Table with solution calculation for a desired volume.

For AgNO_3	For NaNO_3
• n° of moles (mol) = concentration (M) $\times$ Volume (L) • n° of moles (mol) = $0,18 \text{ M} \times \text{Volume desired (L)} = A$ • mass (g) = n° of moles (mol) $\times$ molar mass (g/mol) • mass (g) = $A \times 169,87 \text{ g/mol} = \text{mass of AgNO}_3 \text{ needed to weight}$	• n° of moles (mol) = concentration (M) $\times$ Volume (L) • n° of moles (mol) = $0,73 \text{ M} \times \text{Volume desired (L)} = B$ • mass (g) = n° of moles (mol) $\times$ molar mass (g/mol) • mass (g) = $B \times 84,99 \text{ g/mol} = \text{mass of NaNO}_3 \text{ needed to weight}$

- After calculating the required weights of silver nitrate (AgNO_3) and sodium nitrate (NaNO_3) for the piece, weigh the salts in separate precipitation cups. If necessary, grind the sodium nitrate in a mortar to facilitate dissolution, as shown in Figure 3.3 on steps 1, 2, 3, 4.
- To each cup containing the weighed AgNO_3 and NaNO_3 , add MilliQ water, ensuring that the added volume does not exceed the total solution volume to be prepared. If required, use an ultrasonic bath to assist in the dissolution process as shown in Figure 3.3 on steps 5, 6, 7.
- Once the salts are fully dissolved, transfer each solution to separate volumetric flasks and add MilliQ water, if necessary, until the calibration line of the flask is reached. (If precise concentrations of AgNO_3 and NaNO_3 are not required, this step may be

skipped. However, care should be taken to ensure that the final volume in the cups is as close as possible to the desired value). As it is shown on Figure 3.3 on step 8.

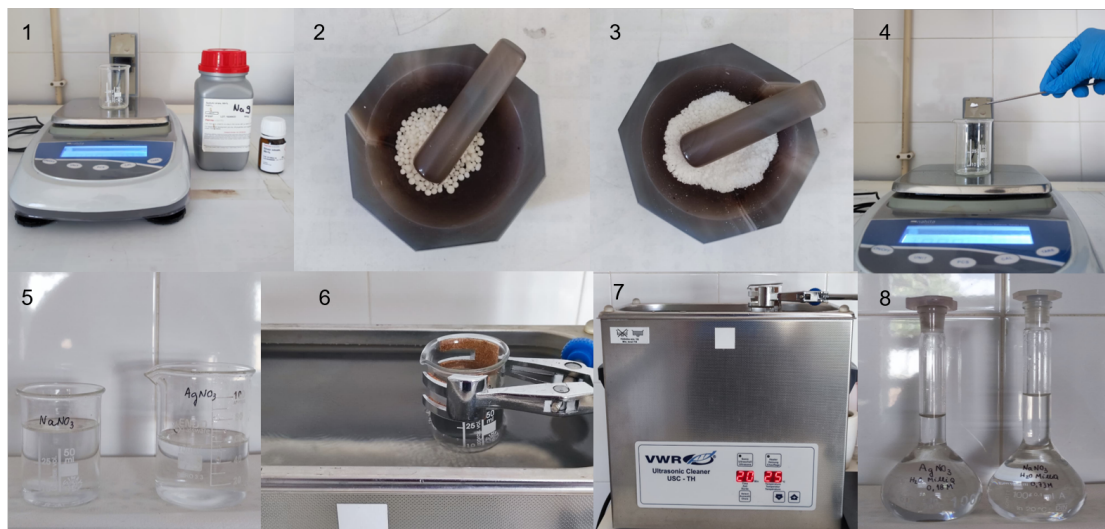


Figure 3.3: Steps for solution preparation 1- Weigh silver nitrate, 2/3- grind sodium nitrate, 4- weigh sodium nitrate, 5- add water milliQ to each precipitation cup, ensuring it does not surpass the total volume desired, 6/7 - use an ultrasound bath to help with the dissolution of the salts at 25°C, 8 - transport the solutions from the precipitation cups to volumetric balloons until the calibration line

Step 3: Coating Application

On the table below, the deposition procedure for either small scale pieces and large scale pieces is described, table 3.3.

Table 3.3: Deposition procedure for small scale and large scale applications.

Small Scale (Figure 3.4)	Large Scale Figure (3.5)
- Before deposition, it is recommended to place a support beneath the piece to facilitate both handling and transport. A separate plastic pipette should be used for each solution to avoid cross contamination. - Apply the NaNO_3 solution first, ensuring that the entire surface of the piece is uniformly covered. Subsequently, apply the same quantity of AgNO_3. Once the deposition is complete, carefully transport the piece to the kiln. - If a precise deposition volume is required, the use of a micropipette is recommended.	- Use a spray device connected to a compressed air system. Appropriate safety precautions must be followed at all times, including the use of a respirator, lab coat, and gloves, and ensuring that the deposition is carried out in a well ventilated environment. - Fill the sprayer with the NaNO_3 solution and apply it uniformly to the glass surface. After application, thoroughly rinse the sprayer with water before repeating the procedure with the AgNO_3 solution. Once both depositions are completed, carefully transport the coated piece to the kiln.

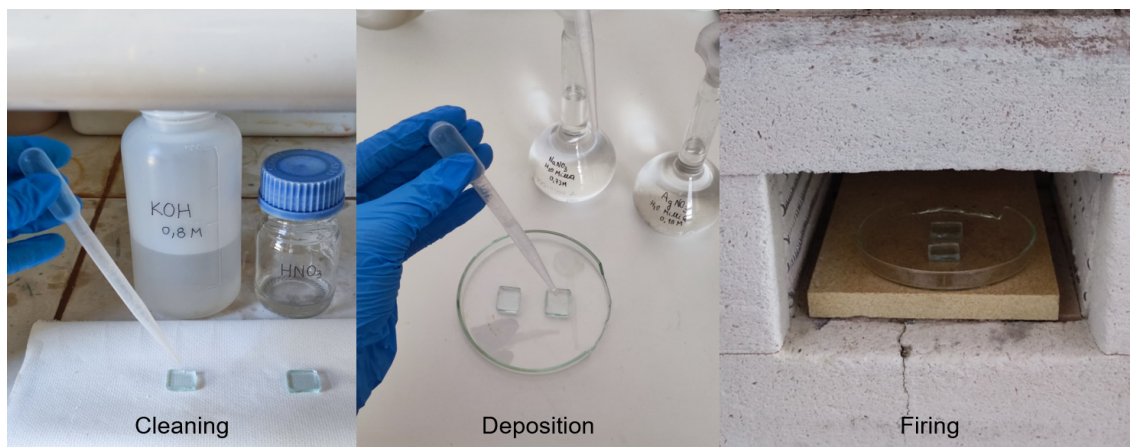


Figure 3.4: Sample cleaning with Potassium Hydroxide $[\text{KOH}] = 0,8 \text{ M}$ and Nitric Acid, (HNO_3), small scale deposition by drop casting using a plastic pipette, kiln transport and firing.

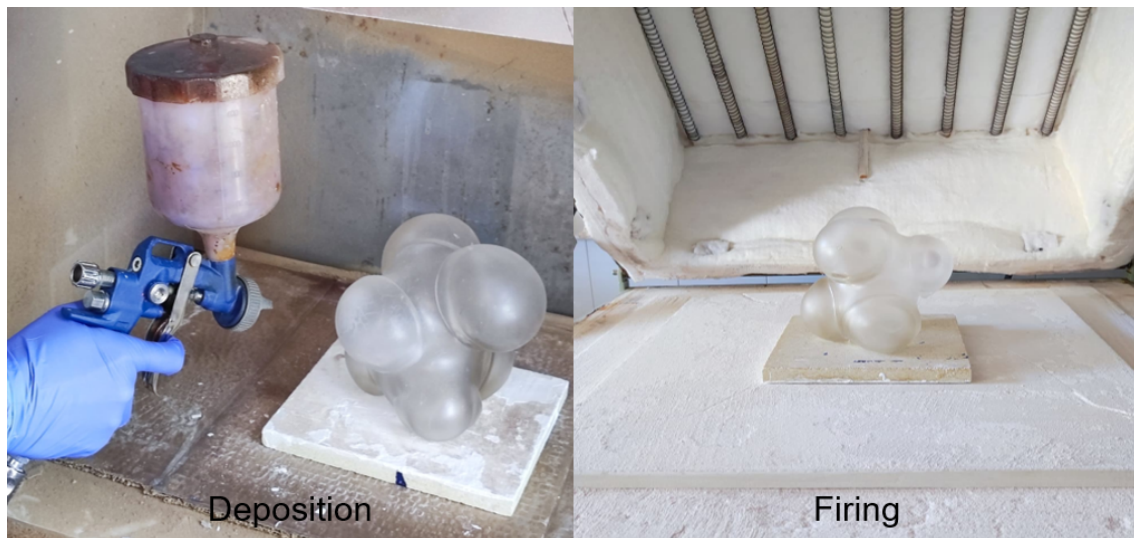


Figure 3.5: Large scale deposition by spray, kiln transport and firing

Step 4: Firing

On the the table below, table 3.4, the firing programmes for the pieces are shown and on Figure 3.6, the influence of temperature in staining and luminescence intensity is shown.

Table 3.4: Firing programmes and their effect on luminescent and visual properties of the coated glass pieces.

Firing step	Programme	Resulting effect
First firing	Ramp: 360°C/h → 360°C; hold 1 h; natural cooling to room temperature	Initial stabilization of coating. Required for all pieces regardless of final aspect.
Second firing	Ramp: 360°C/h → 450°C; hold 1 h; natural cooling	Enhanced luminescence; stained appearance with yellowish tones.
Second firing	Ramp: 360°C/h → 500°C; hold 1 h; natural cooling	Enhanced luminescence; darker yellow tones.
Second firing	Ramp: 360°C/h → 550°C; hold 1 h; natural cooling	Enhanced luminescence; darker stains with brownish tones.

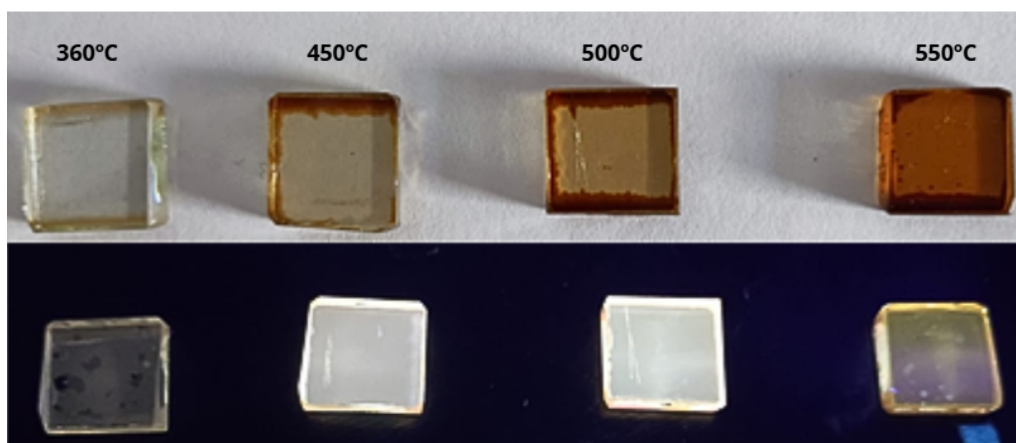


Figure 3.6: Soda lime luminescent glass samples produced by ion exchange bath with AgNO_3 and NaNO_3 , on a weight (%wt/%wt) proportion of 1 AgNO_3 : 2 NaNO_3 , and fired at 360°C/450°C/500°C and 550°C. On top the samples are shown under natural sunlight, below the samples are shown under UV-light lamp at $\lambda = 366$ nm.

APPLICATION OF THE LUMINESCENT COATING BY ARTISTS AT VICARTE

The coating was later tested and applied by VICARTE artists. The glass pieces were normal soda-lime silicate glasses. The pieces were cleaned with Nitric Acid followed by Potassium Hydroxide and let it dry. Afterwards the pieces were sprayed with Silver Nitrate ($[\text{AgNO}_3] = 0,18 \text{ M}$) and Sodium Nitrate ($[\text{NaNO}_3] = 0,73 \text{ M}$) solutions. The volume deposited was not measured, it was applied until the entire piece was covered.

To complement the technical development of the luminescent coating, a short interview framework was designed to gather qualitative insights from artists who applied the coating to their work. The interview focused on five key aspects: (i) **Practicality**: assessing the ease of application of the coating; (ii) **Aesthetics**: evaluating the visual impact of the luminescence under different lighting conditions; (iii) **Stability**: identifying any changes in appearance or performance of the glass piece after firing; (iv) **Comparison**: comparing this coating with other luminescent or enamel materials previously used by the artists; and (v) **Future Work**: exploring potential applications of this material in future artistic projects.

4.0.1 Interview with artist Wai In Chan

To evaluate the practical applicability of the developed coating in an artistic context, an interview was conducted with artist Wai In Chan, who tested the coating using spray deposition on her glass artworks as shown in Figures 4.1 and 4.2. Her feedback was structured around five key aspects: practicality, aesthetics, stability, comparison with other materials, and potential for future use.



Figure 4.1: Soda-lime glass luminescence piece by Wai in Chan. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.



Figure 4.2: Soda-lime glass luminescence piece by Wai in Chan. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.

Practicality: Wai In Chan reported that the application process was extremely straightforward. The material spread evenly, and full coverage was achieved with one or two spray applications, without visible streaks or excessive buildup. Unlike traditional enamel coatings that require careful, repetitive brush layering, which is time consuming, the spray method significantly reduces preparation and application time. She emphasized that this technique was particularly effective for coating complex surfaces and larger pieces, allowing more time to be devoted to the creative process.

Aesthetics: From a visual perspective, the artist highlighted that this luminescent coating differs markedly from traditional enamels. Whereas conventional enamels often behave like watercolors, requiring manual placement to achieve uniform coverage, the spray-deposited coating produced a unique and consistent surface finish. Under both natural and artificial light, the luminescent effect was described as “striking,” offering new aesthetic possibilities and allowing for homogeneous luminescence across large areas, which is challenging to achieve with other techniques.

Stability: Following firing, the coating adhered well and retained its luminescent properties. However, Wai In Chan observed a slightly visible, uniformly distributed yellowish

tint, which she considered a limitation for certain applications requiring complete optical neutrality. She suggested that future iterations of the material could focus on improving color clarity and transparency, which would enable seamless integration with different glass compositions.

Comparison with Other Materials: When compared with conventional luminescent powders and enamel-based materials, the coating was considered superior in terms of ease of use and efficiency. Traditional approaches require manual mixing, slow application, and precise firing schedules, whereas the spray application provided a more user-friendly and time-efficient process. Nonetheless, the artist noted that improvements in optical transparency and color neutrality could make the coating even more competitive with existing commercial materials.

Future Applications: Wai In Chan expressed strong interest in exploring further applications of the coating in future projects. In particular, she mentioned its potential for luminescent enamel jewelry, such as *plique-à-jour* pieces, where achieving consistent luminescence over intricate surfaces is typically challenging. She indicated that resolving the slight yellowish coloration would broaden the coating's applicability, enabling it to integrate harmoniously with a wider palette of artistic designs.

Overall, the artist concluded that this coating has significant potential as a material for creative applications, combining efficiency of deposition with visually compelling luminescent properties. She expressed enthusiasm for continued experimentation to exploit both its technical and aesthetic potential.

Another artist, Mayank Sahni had the opportunity of also applying this luminescent coating to his pieces.

4.0.2 Interview with artist Mayank Sahni

Another interview was conducted with artist Mayank Sahni, who tested the coating using spray deposition on his glass pieces, as possible to observe below in Figures 4.3 and 4.4.

His feedback on the coating applicability also followed the same structure as the previous interview, practicality, aesthetics, stability, comparison with other materials, and potential for future use.



Figure 4.3: Soda-lime glass luminescence piece by Mayank Sahni. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under UV-light lamp at $\lambda = 366$ nm.

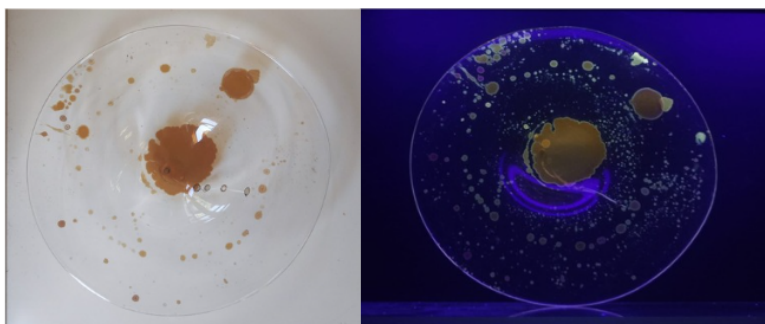


Figure 4.4: Soda-lime glass luminescence piece by Mayank Sahni. On the left, the piece is shown under natural sunlight and, on the right, the piece is shown under a UV-light lamp at $\lambda = 366$ nm.

Practicality: According to Mayank Sahni, the application of the coating was straightforward and easy to perform, with the spray method allowing for efficient coverage of the glass surfaces. He expressed interest in exploring alternative application methods, such as brush application or scenography techniques, to expand the possibilities for different artistic effects and finishes.

Aesthetics: Mayank reported experiencing a sense of curiosity and surprise when observing the luminescent effect under different lighting conditions. He noted that the material's behavior was dynamic, producing unique outcomes even when applied carefully and consistently. This variability was perceived as both intriguing and somewhat uncontrollable, as the exact regions of luminescence on the pieces could not be fully predicted.

Stability: He observed no visible changes in the appearance or stability of the pieces after firing, describing them as visually consistent with their pre firing state while maintaining their luminescent properties.

Comparison: Mayank mentioned that he used other luminescent enamels before and they start to degrade after four months and that he was curious to see if this one could be more resistant

Future Work: He highlighted significant potential for incorporating this material into artistic installations aimed at shifting viewers' perceptions. Mayank emphasized that the material has the capacity to transform ordinary glass into a surprising, interactive experience: under normal lighting, it appears as a conventional material, but under specific illumination, it becomes a luminescent work of art, prompting viewers to reconsider its identity and meaning.

4.0.3 Artists feedback

Both artists, Wai In Chan and Mayank Sahni, highlighted the practicality and efficiency of applying the luminescent coating using the spray method, noting its ability to achieve uniform coverage with minimal effort and preparation. From an aesthetic perspective, they emphasized the unique and striking luminescent effect, which remains visually engaging under different lighting conditions and adds a layer of unpredictability to the final outcome. This unpredictability was perceived not as a limitation but as a creative opportunity, introducing an element of spontaneity that can enrich artistic expression.

Regarding stability, both artists reported that the coating maintained its adherence and luminescent properties after firing, though slight coloration or surface tint was noted, which could be refined in future iterations for improved transparency. Importantly, both identified significant potential for this material in future artistic projects, particularly in installations and works where light-material interaction plays a central role. The ability of the coating to transform ordinary glass into a luminescent surface under UV or specific lighting conditions opens possibilities for creating dynamic, perception shifting artworks that engage viewers in new ways and expand the expressive vocabulary of glass.

EXHIBITION - SHALL WE MEET BY THE FIRE

Shall We Meet by the Fire originated from an intimate encounter with luminescent glass observed under UV light in a dark room. In this environment, the interaction between darkness and glowing glass generated a profound sense of stillness, a pause that momentarily suspended external distractions. This experience became the conceptual foundation of the work, aiming to translate the sensation of quiet awareness into a shared, embodied experience.

The project draws inspiration from ancestral rituals centered around fire as a gathering point. Historically, fire functioned not only as a source of warmth and light but also as a social and symbolic nucleus, enabling moments of collective presence, reflection, and exchange [46]. In these rituals, sharing did not only require verbal communication, sometimes silence, attentiveness, and presence were equally meaningful forms of connection. Shall We Meet by the Fire revisits this archetypal scenario as a framework for contemporary reflection, as shown in Figure 5.1.



Figure 5.1: Metaphorical fire installation with 2D and 3D glass pieces under natural light.

In contrast to this ancestral way of being, the work responds critically to the conditions

of contemporary life. Fast paced rhythms, continuous productivity, and the demands of digital platforms contribute to a state of chronic distraction and individualization. Within this context, the capacity for collective awareness and empathy is diminished, as attention is increasingly directed toward performance, efficiency, and the virtual world. The installation addresses this tension by proposing a space of stillness, where presence replaces productivity and contemplation resists consumption.



Figure 5.2: Metaphorical fire installation with 2D and 3D glass pieces under UV light.

The installation materializes as a metaphorical fire composed of silver luminescent glass elements that emit a warm glow under UV light, as possible to observe in Figure 5.2. Surrounding the luminous core, cushions are arranged to invite visitors to sit and engage in observation. A five minute guided meditation accompanies the experience, serving as a temporal anchor that encourages slowing down, grounding attention, and cultivating awareness of the present moment.

Through material, light, and spatial arrangement, *Shall We Meet by the Fire* seeks to reintroduce stillness as a shared moment and to remind us of the humanity that every human being carries within. The work positions contemplation not as withdrawal, but as a form of resistance, an intentional pause that reopens space for empathy, reflection, and embodied presence within contemporary society.

CONCLUSION

This thesis focused on the development of a silver based luminescent coating designed to function as a “paint” for artistic applications, with the goal of providing artists with a versatile, reproducible, and accessible material.

The coating itself are two solutions that were achieved through an extensive study and test of solvents, being water MilliQ the solvent with the best response. The coating was prepared using two separate solutions, one containing silver nitrate ($\text{AgNO}_3 = 0.18 \text{ M}$) and the other sodium nitrate ($\text{NaNO}_3 = 0.73 \text{ M}$) in water MilliQ. The solutions were kept separate due to the high sensitivity of silver nitrate, which easily reduces in the presence of sodium nitrate and other viscous solvents such as PEG and decoflux. The solutions were deposited on commercial float glass samples by drop casting, followed by heat treatment at 360°C and 450°C , which allowed the formation of silver clusters through ion exchange, giving rise to luminescence layers on the glass.

These tests with drop casting deposition aimed to understand the behaviour of the solutions on the glass surface and the effect of silver concentration on luminescence intensity. Although homogeneous luminescent layers were achieved on soda–lime glass, the effect of silver nitrate on luminescence intensity could not be determined. This deposition process also resulted in unwanted brown stains caused by silver nanoparticle formation that were confirmed by the band on the absorption spectra near 430 nm . The stains formed on the tin on the glass, which facilitated silver reduction. To minimize this effect, a layer of kaolin was placed beneath the samples to absorb excess solution and prevent dripping into the tin side. This approach successfully produced transparent, luminescent glass, with minimized staining, although luminescence homogeneity was not fully consistent. As the role of silver nitrate was not clear during these depositions, it was tested to apply only silver nitrate to the glass surface with increasing volume to evaluate the ability of silver alone to form a homogeneous luminescence layer and therefore clusters. This test showed that silver nitrate alone can give rise to luminescence in glass, but very heterogeneously, and that forms metallic stains that are very hard to remove, confirming that the role of sodium nitrate is indispensable for homogeneous luminescence layers.

Spectroscopic analysis suggested that the observed emission was due to silver clusters,

including $\text{Ag}^+ - \text{Ag}^+$ pairs (480–550 nm), Ag_2 dimers (440–450 nm), and Ag_3 trimers (590 nm). The overall luminescence intensity was therefore the result of the combined contributions of these species. Alternative precursors, such as silver sulfate and sodium sulfate in PEG, were explored to improve solution viscosity and deposition behavior, aiming to apply it on scale up pieces, however, these tests resulted in weak luminescence at 500°C.

For scaling up, two alternative deposition techniques were tested, screen printing and spray deposition. Screen printing was found to be ineffective for achieving good surface coverage, but spray deposition produced promising results with good coverage and easy application. Optimization of the spraying process revealed that cleaning the glass surface using nitric acid and potassium hydroxide before deposition was essential for better adhesion. Furthermore, frosted glass substrates provided superior coating adhesion and uniform coverage compared to clear glass, achieving optimal results when fired at 500 °C. The findings of this study culminated in the development of a step by step manual for artists, enabling them to prepare, apply, and fire the luminescent coating independently. Collaborative testing with VICARTE artists on mouth blown glass pieces demonstrated the practical and aesthetic potential of the material, bridging scientific research and creative practice. The work culminated with an exhibition named "Shall We Meet by the Fire?" that included the luminescent pieces in an immersive and meditative experience.

Overall, this work successfully developed and optimized a silver luminescent coating that can be applied using an artist friendly manual, while addressing challenges such as silver nanoparticle staining. The work highlights the potential of ion exchange coatings for use in glass art. Future work may focus on improving luminescence uniformity by exploring alternative solvents.

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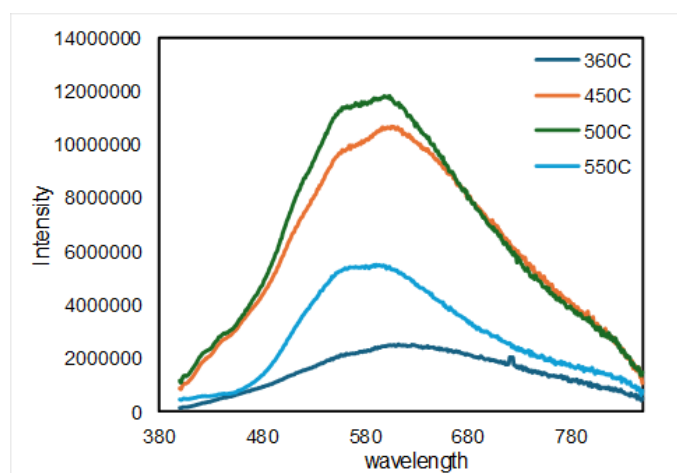


Figure I.1: Emission (excitation wavelength of 360 nm) spectra from ion exchange bath soda lime glass samples fired at 360°C, 450°C, 500°C, 550°C.

Table I.1: Reagents brand and purity

Reagents	Brand	Purity
Silver Nitrate (AgNO_3)	thermo scientific	>+99%
Sodium Nitrate (NaNO_3)	thermo scientific	>98%
Silver Sulfate (Ag_2SO_4)	thermo scientific	>98%
Sodium Sulfate anhydrous (Na_2SO_4)	sigma aldrich	>99%

Table I.2: Reading equipments

Equipment	Brand
Spectrophotometer	Varian, Cary-5000
Fluorescence Spectrophotometer	SPEX©Fluorolog©-3 HORIBA , FL3-22



2025

Optimization of silver luminescent coatings for artistic purposes

Matilde Serra