

Pulsed Laser Deposition of Glass-Ceramic Thin Films for Computed Radiography

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Master of Science

Degree

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This thesis is dedicated to my family.

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ABSTRACT

For this work, a fluorochlorozirconate thin film storage phosphor was developed in a two-step process. In the first step, the synthesis and characterization of the glass portion of the storage plate was completed. The second step incorporated crystalline and dopant materials into the glass matrix to develop the glass-ceramic thin film. After synthesis was completed, characterization was conducted, including measurement of photostimulated emission after prior x-ray irradiation indicating the ability of the thin film to act as a storage phosphor plate.

The presence of reduced zirconium in fluorozirconate (FZ) glasses is highly unfavorable due to its detrimental effect on glass quality. Previous researchers have relied upon the use of a fluorine-containing processing gas to prevent the reduction of zirconium in FZ glasses deposited as thin films by pulsed laser deposition (PLD). However, the use of a fluorine-containing processing gas as an oxidizing agent is disadvantageous, due to its toxicity. Eliminating the need for the processing gas would lead to a significantly safer and simpler process. The approach presented within this thesis is to incorporate indium, which is multivalent, into the PLD ablation target in order to stabilize the zirconium and remove the need for a processing gas. Using a fluoride glass target, FZ glass films were successfully deposited on fused silica substrates by PLD, without the need for any processing gas.

In computed radiography applications using conventional granular storage phosphor materials, scattering of the stimulating laser light during read-out leads to decreased spatial resolution. The desire for high spatial resolution has led to imaging plates with thinner phosphor layers in order to reduce this scattering. The films produced in this study consist of multiple transparent layers of orthorhombic phase barium chloride nanocrystals doped with europium, separated by nanoscale layers of fluoride glass. The transparent nature of these films reduces blurring of the image due to scattering of the stimulating light during read-out. The films are deposited on fused silica substrates via pulsed laser deposition, utilizing a multicomponent target. This method allows for a higher concentration of luminescent centers compared to glass-ceramic imaging plates synthesized in bulk form.

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INTRODUCTION

Fluoride Glass and Glass Ceramics

Fluorozirconates were the first heavy metal fluoride (HMF) glass system discovered in 1974, using ZrF_4 as the primary constituent, BaF_2 as the principal modifier, and other metal fluorides as tertiary constituents [1]. Fluoride glass systems gained attention due to their low phonon energy and mid-infrared transparency [2-4]. The infrared transmission is a result of the weaker bond strengths in fluoride glass, relative to that of silica glass systems [4]. Most fluoride glass research is focused on fluoro-zirconate-type and rare earth fluoride glasses [1, 5]. Rare-earth fluoride glasses have been studied as candidates for applications of optical amplification, fiber laser, and wavelength shifters for solar cells and light emitting diodes [6, 7]. The most stable HMF is ZBLAN, consisting of the fluorides of zirconium, barium, lanthanum, aluminum, and sodium [4].

Substituting chlorine for a portion of the fluorine in the glass matrix results in systems deemed fluorochlorozirconates (FCZ); subsequent heat treatments allow for the precipitation of BaCl_2 nanocrystals, creating a novel, luminescent glass-ceramic material (see Figure 1). FCZ-based glass ceramics have been considered candidates for many applications including photovoltaics, nondestructive testing, and medical imaging [9-16]. The precipitation of Eu^{2+} doped orthorhombic phase barium chloride (BaCl_2) nanocrystals in the glass matrix results in a transparent storage phosphor plate for computed radiography [13]. Heat treatments above approximately 285°C on the FCZ glass ceramic transform the BaCl_2 nanocrystals to the orthorhombic phase, which is necessary for use as storage phosphors. The glass ceramic also has potential use as a scintillator when its nanocrystals are in the hexagonal phase, a state developed from heat treatments typically between $240\text{--}280^\circ\text{C}$ [17]. Sodium fluoride (NaF) content influences evaporative loss during synthesis and the magnitude of photostimulated (PSL) luminescence when used as a storage phosphor [11].

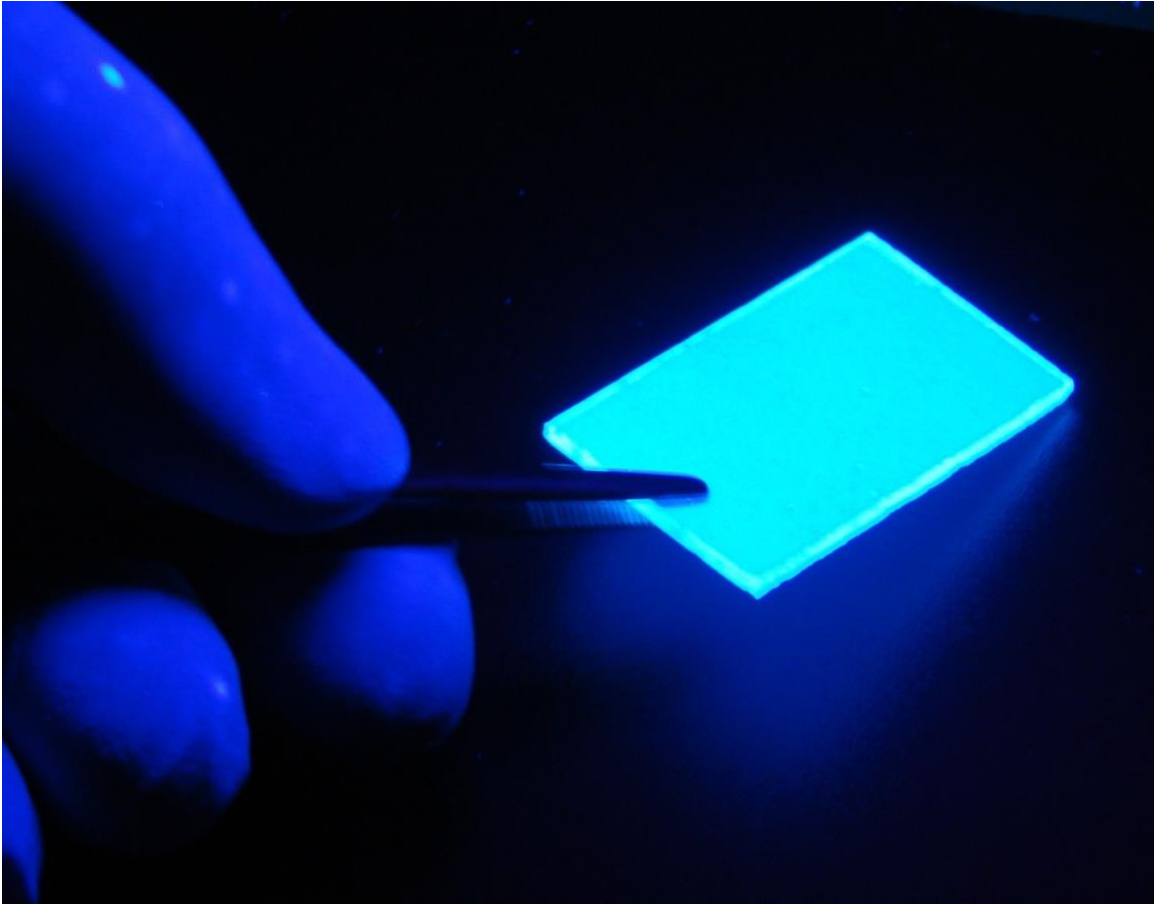


Figure 1. An FCZ glass ceramic exhibiting photoluminescence under UV excitation of 365 nm [10]. Used with permission.

Due to their transparency, FCZ glass ceramic storage plates have the potential to create computed radiography images with resolution superior to those of commercial plates [13]. An x-ray computed radiograph developed with an FCZ storage plate is shown in Figure 2 [8]. Although the resolution results show promise, the PSL characteristics illustrate that light output of FCZ is inferior to commercial storage plates [12, 15]. Attempts to increase PSL output of the FCZ storage plate has altered its transparency diminishing the high-resolution imaging capabilities [17]. An alternative method of synthesis is required to increase luminescent centers in the glass matrix without devitrification or clustering, which quenches emission.

Pulsed Laser Deposition

Thin films synthesized by pulsed laser deposition (PLD) were developed shortly following the invention of the pulsed ruby laser in the 1960s [18, 19]. The process gained popularity in scientific research in the late 1980s when development of thin film superconductor devices began. Although the physical ablation processes in PLD are highly complex and interrelated, PLD is experimentally and conceptually simple [18]. A simplified schematic diagram of a PLD apparatus is shown in Figure 3. PLD uses photonic energy in the form of an excimer laser that is coupled to a target material via electronic processes [20]. The excimer laser is focused in an optical window of a vacuum chamber onto a target surface that forms a plasma that elongates preferentially perpendicular to the surface [21, 22]. Film growth occurs on the surface of the substrate where material from the plume condenses; the substrate is typically located 5-10 cm away from the target [19]. The plume can be seen in the image of the inside of a PLD apparatus during operation in Figure 4.

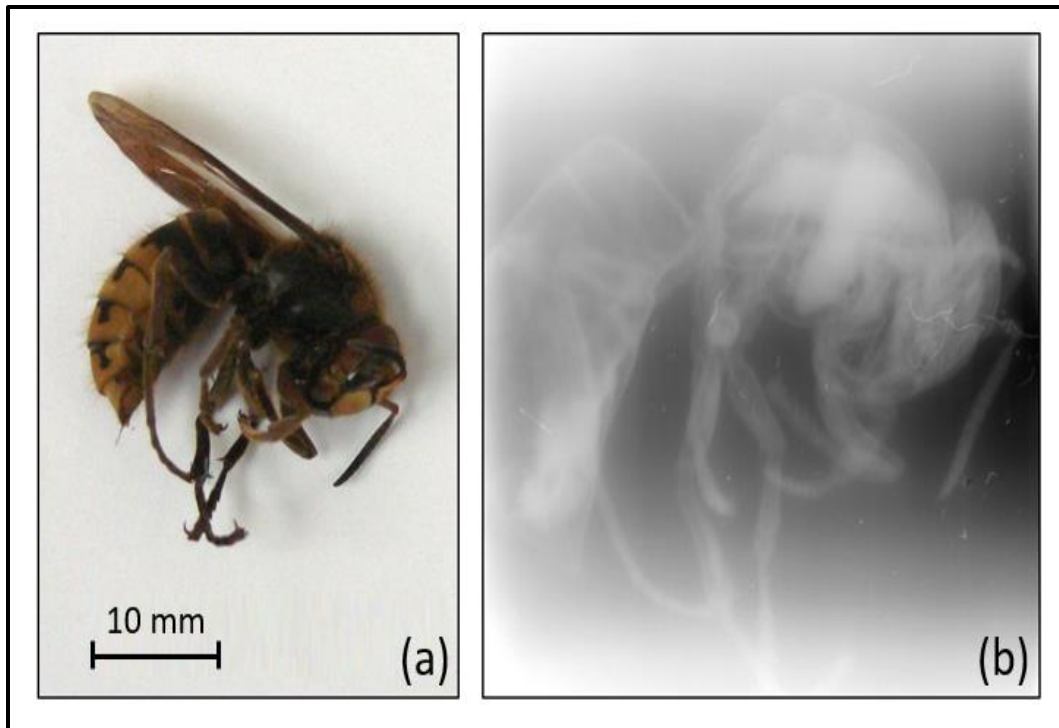


Figure 2. a) Photograph of a European hornet and b) an x-ray computed radiograph of the hornet produced using a glass-ceramic storage phosphor imaging plate. [8] Used with permission.

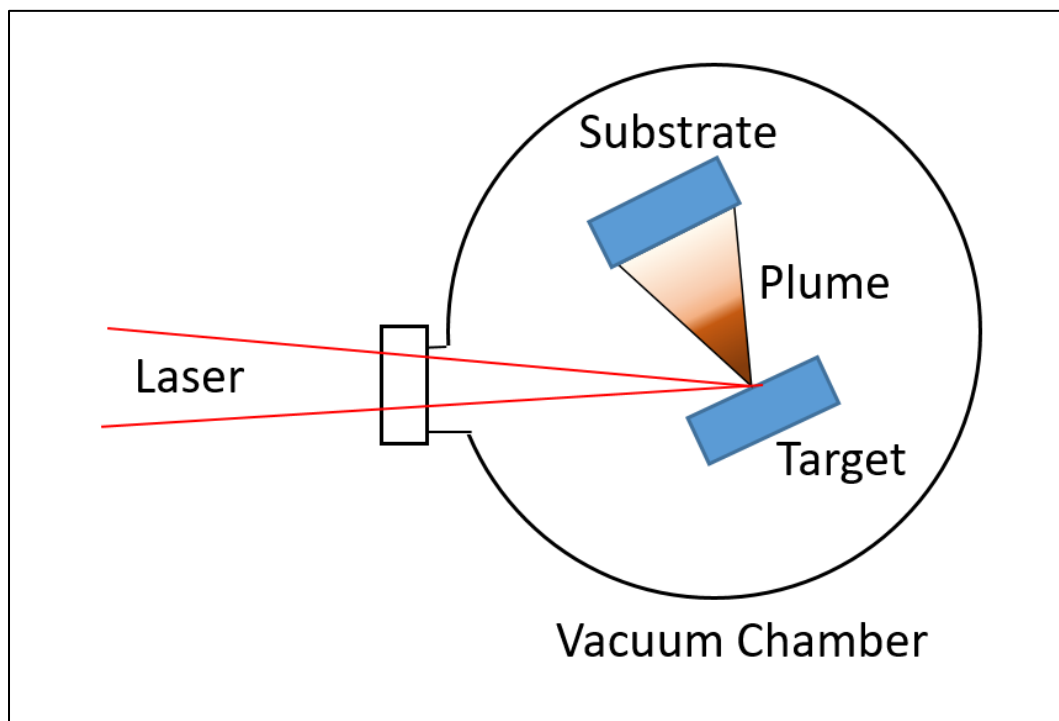


Figure 3. Schematic diagram of pulsed laser deposition apparatus.

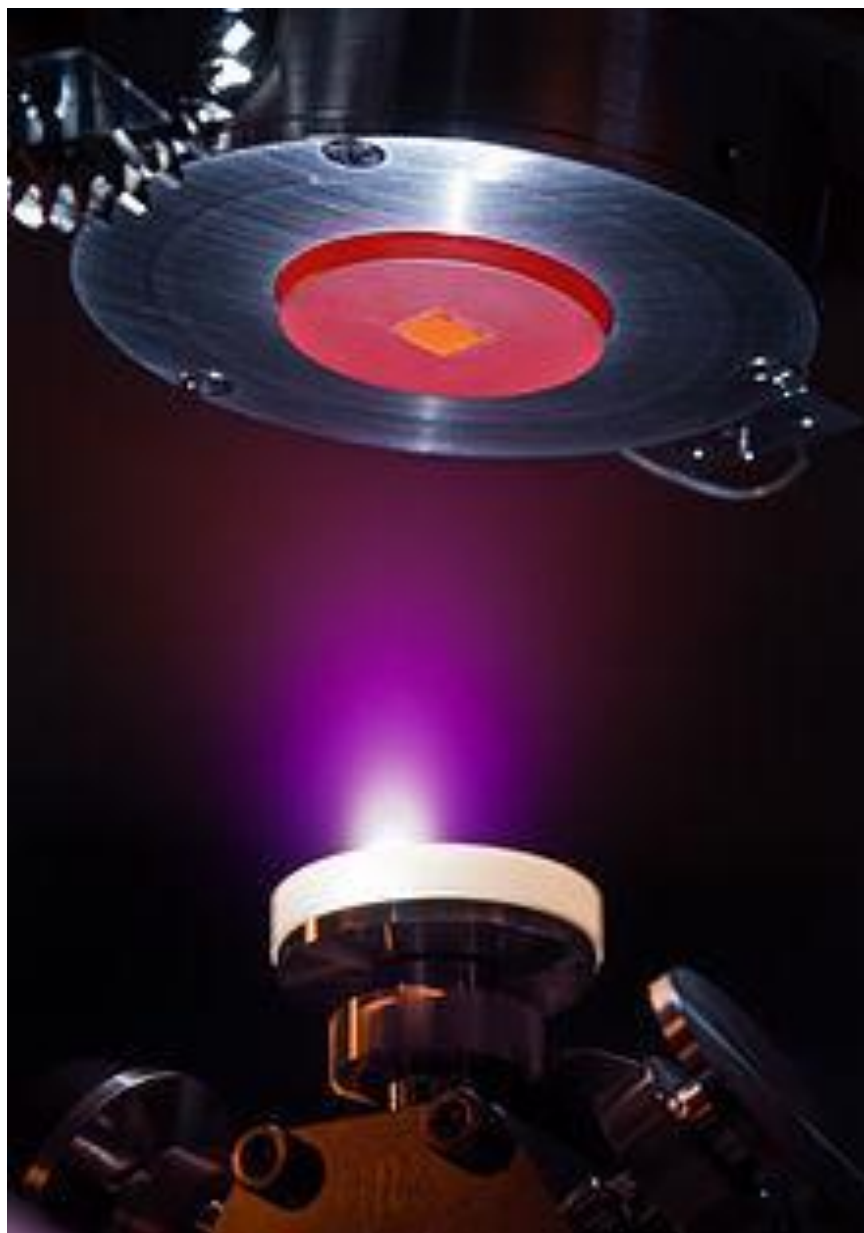


Figure 4. Pulsed laser deposition in action. Open access. Owner: Adam Andersen Laessoe.

PLD has many qualities that provide special advantages when compared to other film-growth methods [18]. There is a vast amount of materials that can be ablated allowing PLD to be utilized to transform many different types of condensed matter into thin films. Conditions can be optimized to grow films with the same elemental compositions as the target and allow the ability to promote electronic states within the film. Multilayered structures can be made to synthesize a film with different chemical compositions in a single continuous structure. This is accomplished via different targets being exchanged during film synthesis. Controlling the laser pulse repetition rate and laser pulse energy allow for controlled film growth on the atomic level.

Although this method of thin film synthesis has many advantages, there are characteristics that limit PLD both experimentally and commercially. The plasma of the target material becomes a highly directional plume consisting of some or all of the following: electrons, ions, energetically neutral atoms, molecules, atom clusters, micron sized particulates, and molten droplets [23]. Large particulates adhered by the substrate can disrupt thin film growth and result in rough films. Another limit of PLD is the lack of uniformity of film thickness due to varying density of the plume. The plume is most dense where it intersects the location of the laser hitting the target, and dissipates with proximity to that centralized spot. The narrow distribution of the plume and the resulting sample are illustrated in Figure 5.

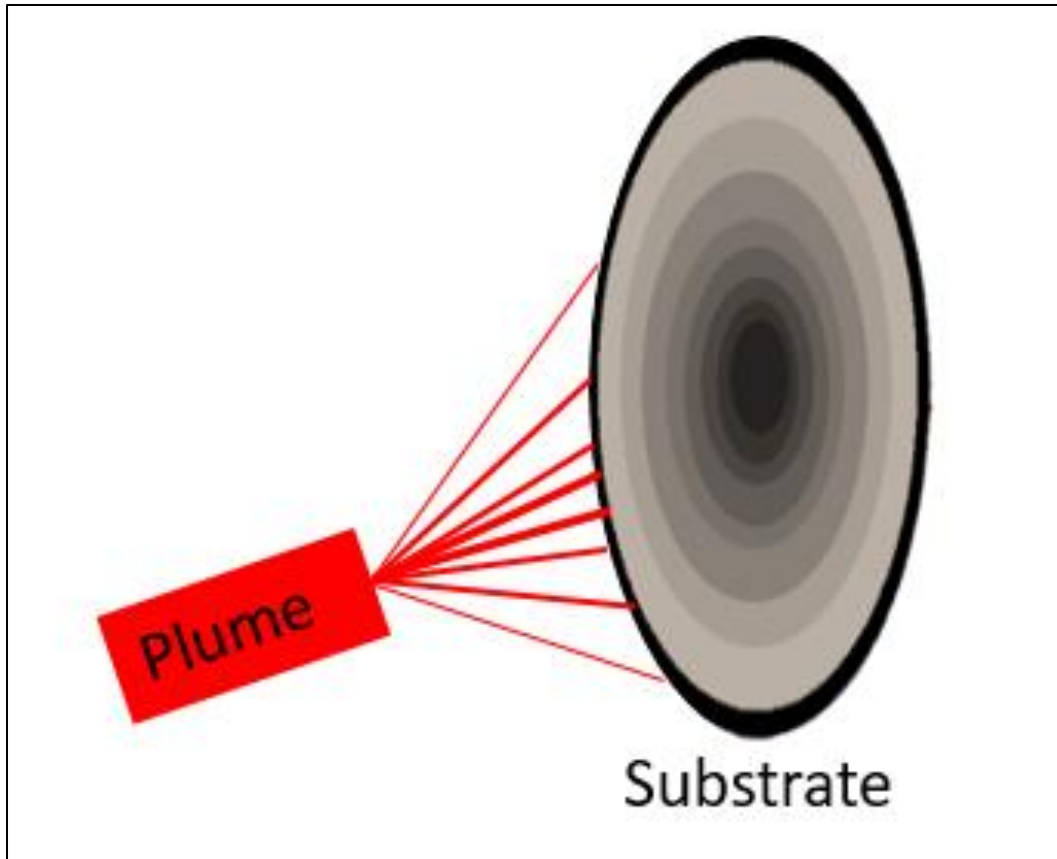


Figure 5. Illustration demonstrating the non-uniformity of a PLD thin film as a result of different densities of the plume.

Computed Radiography

Computed Radiography (CR) is the most commercially successful type of medical imaging when compared to screen/film methods and digital radiography [12]. Although the screen/film method has the greatest resolution of the three, it requires chemical processing and does not yield a digital readout. Digital radiography is a technique that uses either direct or indirect conversion to develop a radiograph simultaneously as x-ray exposure occurs. Direct conversion uses a photoconductor which converts the x-ray energy into an electronic signal while indirect conversion uses a scintillator to first convert the x-ray energy into visible light which is then detected and converted into an electronic signal [1]. Compared to CR, its digital counterpart is far more costly and positioning the readout sensor can be restrictive. CR uses a storage phosphor plate in which the image is gathered through a two-step process. First, the storage phosphor plate is positioned behind the object to be imaged that will be exposed to x-rays. The x-rays create metastable electron-hole pairs in the storage phosphor material. Different materials have different attenuation levels, resulting in differing densities of electron hole pairs in the storage phosphor plate, creating contrast. Following x-ray exposure, the storage phosphor plate is photostimulated, typically using a laser, allowing the electron hole pairs to recombine, yielding photostimulated light that is collected pixel-by-pixel to form a radiograph. Storage phosphor plates can be reused following optical bleaching.

Storage phosphor plates are typically composed of polycrystalline materials, such as europium doped barium fluorobromide, within an organic binder. Scattering of the stimulating light at crystalline grain boundaries can result in diminished image resolution, due to emission away from the desired pixel as illustrated in Figure 6(a). A storage plate transparent to the wavelength of the stimulating light source would minimize scattering, resulting in higher resolution radiographs. The anti-scattering characteristics of a transparent storage phosphor plate are illustrated in Figure 6(b). FCZ glass ceramics have been extensively researched as a candidate for transparent nanocrystalline storage phosphor plates.

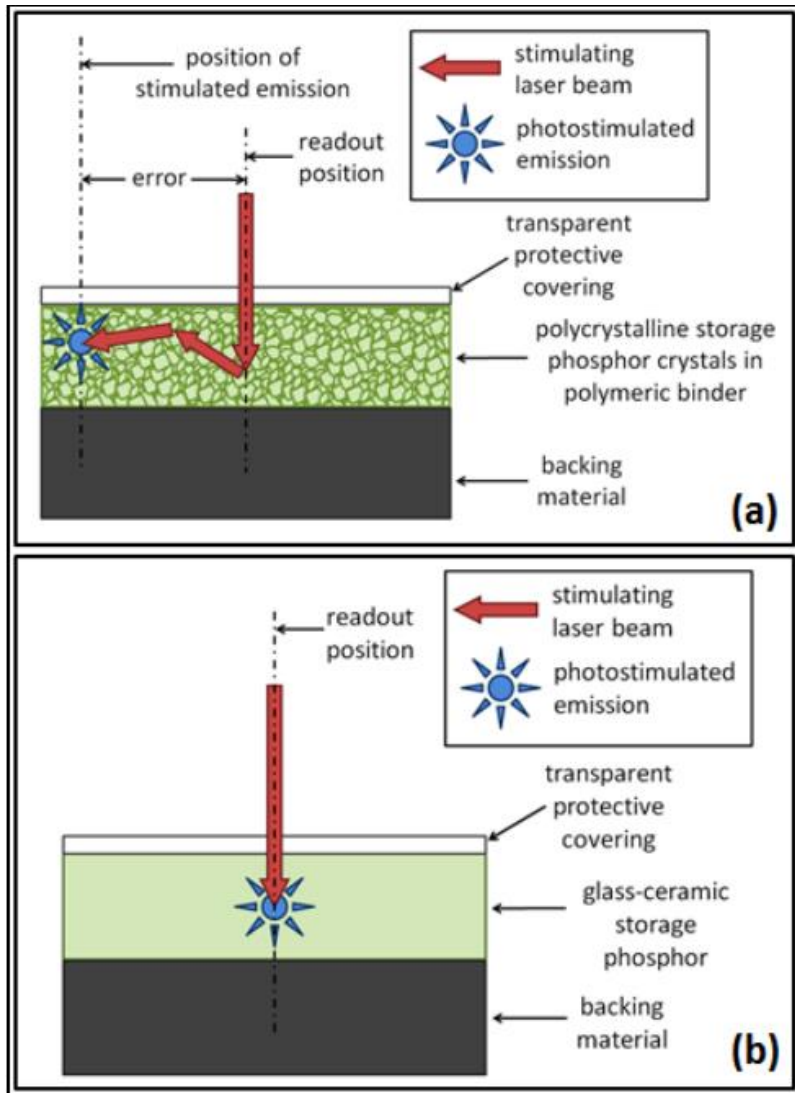


Figure 6. (a) Scattering of the stimulating laser beam at the grain boundaries of a polycrystalline storage phosphor causing a decrease in spatial resolution and (b) reduced scattering in a glass ceramic storage phosphor for improved spatial resolution. [2]. Used with permission.

Summary of Work

This work details the synthesis of a fluorochlorozirconate thin film storage phosphor plate for computed radiography applications. The plate was developed in two distinct stages. Chapter I focuses on the synthesis and characterization of the glass portion of the storage plate. Multiple samples were made, and the effect of thermal annealing on the samples was extensively studied. Chapter II describes the methods used to develop the glass-ceramic thin film, which contains the luminescent centers required for a storage phosphor plate. The synthesis of the target and control of target movement during thin film synthesis were highlighted. After synthesis was completed, characterization was conducted, including measurement of photostimulated emission after prior x-ray irradiation, indicative of the ability of the thin film to act as a storage phosphor.

CHAPTER I:
PULSED LASER DEPOSITION OF TRANSPARENT FLUORIDE GLASS

A version of this chapter was originally published by C.W. Bond, R.L. Leonard, R.A. Erck, A.Y. Terekhov, A.K. Petford-Long, and J.A. Johnson:

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C.W. Bond was responsible for all writing and research activities in the original article except as noted: A.Y. Terekhov assisted with PLD apparatus. R.A. Erck conducted optical profilometer measurements. R.A. Erck, A.K. Petford-Long, R.L. Leonard, and J.A. Johnson provided critical feedback. A.W. Evans synthesized the glass target. J.A. Johnson provided overall guidance.

Abstract

The presence of reduced zirconium in fluorozirconate (FZ) glasses is highly unfavorable due to its detrimental effect on glass quality. Previous researchers have relied upon the use of a fluorine-containing processing gas to prevent the reduction of zirconium in FZ glasses deposited as thin films by pulsed laser deposition (PLD). However, the use of a fluorine-containing processing gas as an oxidizing agent is disadvantageous, due to its toxicity. Eliminating the need for the processing gas would lead to a significantly safer and simpler process. Our approach is to incorporate indium, which is multivalent, into the PLD ablation target in order to stabilize the zirconium and remove the need for a processing gas. A ZLANI glass, based on the composition $60.24\text{ZrF}_4\text{-}4.13\text{LaF}_3\text{-}3.54\text{AlF}_3\text{-}31.49\text{NaF}\text{-}0.59\text{InF}_3$ (values are in mol%), was synthesized for use as an ablation target. Using the ZLANI target, FZ glass films were successfully deposited on fused silica substrates by PLD, without the need for any processing gas. Multiple depositions were performed to observe the effects of deposition duration on growth rate and on film roughness. The deposited films are transparent with a brownish coloration. The source of this coloration is postulated to be color centers that are created during synthesis. Thermal annealing increases light transmission through the films up to 400%, depending upon wavelength, in the UV and visible spectrum (350-600 nm), after a series of heat treatments culminating at 300°C. The fact

that the transparency of the films can be correlated to annealing temperature suggests that the films may be of use as passive temperature sensors.

Introduction

Fluoride glasses are notable for their extended transparency out to infrared wavelengths, with ultra-low loss of 0.001 dB/km in the infrared regions, which can be exploited for fiber optic applications [2, 3]. In addition, the low phonon energy of fluoride glass matrices makes them a favorable host for optically active rare earth elements, which can be employed for a variety of applications [5]. Rare earth-doped fluoride glasses have shown potential for such applications as optical amplification, fiber lasers, and wavelength shifters for solar cells and light emitting diodes [6, 7]. The addition of a second halide, such as chlorine, to the glass composition allows for the precipitation of halide crystals in the matrix, yielding novel glass ceramics with further applications, such as computed radiography and dosimetry [9, 12, 24, 25]. The most common fluoride glasses found in literature are ZBLAN compositions, consisting of the fluorides of zirconium, barium, lanthanum, aluminum, and sodium.

PLD deposition of fluorozirconate (FZ) glass thin films has utilized a fluorine-containing processing gas [26, 27], which is used to prevent the reduction of zirconium in the glass matrix during synthesis. Reduced zirconium is highly unfavorable in FZ glasses due to its detrimental effect on glass quality including the formation of black particulates in the matrix [28]. The use of a fluorine-containing processing gas as an oxidizing agent is disadvantageous due to its toxicity. Furthermore, removing the need for a processing gas would lead to a significantly safer and simpler process. It is hypothesized that the incorporation of indium, which is multivalent, into the PLD ablation target would stabilize the zirconium and remove the need for a processing gas. It has been shown that In^{3+} becomes reduced to In^+ , which allows reduced zirconium (Zr^{3+}) to oxidize to Zr^{4+} [29-31]. Reduced indium in the glass is colorless and does not negatively affect its transmission properties in the visible range.

This study presents preliminary work to an ultimate goal of synthesizing a multilayer ZBLAN designer glass ceramic. In this study, a series of transparent FZ glass thin films were deposited by PLD onto fused silica substrates using a ZLANI ablation target, consisting of the fluorides of zirconium, lanthanum, aluminum, sodium, and indium, and without a processing gas. Successful deposition of fluoride glass without an oxidizing process gas has not been reported in the literature and represents a significant process improvement. In future work, barium chloride and europium portions will be added to the ablation target. The vitreous nature of the films was confirmed by x-ray diffraction (XRD). Thermal characteristics were ascertained by differential scanning calorimetry (DSC). The optical transmission of the films, both as-made and after thermal annealing, was determined by spectrophotometry; the effects of heat treatments on the transparency of fluoride glass thin films have not been previously investigated. Surface roughness and film thickness were established by optical profilometry.

Materials and Methods

A ZLANI fluoride glass target was made with composition $60.24\text{ZrF}_4\text{-}4.13\text{LaF}_3\text{-}3.54\text{AlF}_3\text{-}31.49\text{NaF-}0.59\text{InF}_3$ (values are in mol%) via the melt-quench method. The synthesis was performed in an argon atmosphere glovebox with a connected furnace (Figure A1). The total weight for the sample mixture was approximately 20 grams. After mixing, the components were heated in the furnace at a temperature of 825°C for 20 minutes, within a platinum crucible. Following a 5-minute fining step at 750°C , the crucible was removed from the furnace and the molten glass was poured into a brass mold held at 200°C , which allowed the glass to cool gradually to ambient temperature over a period of four hours. An ablation target with dimensions $51 \times 38 \times 1.3$ mm was cut from the as-made glass, shown in Figure 7, with the remainder reserved for characterization. The same ablation target was utilized for the synthesis of all samples pertaining to this chapter.



Figure 7. ZLANI glass used as ablation target.

The ZLANI glass films were deposited via PLD on UV Grade fused silica substrates (University Wafer). Each deposition utilized four fused silica substrates that were approximately $25 \times 25 \times 0.5$ mm, mounted to a rotating substrate holder. Shown in Figure 8, the substrate holder secured the fused silica with a washer and screw, which created witness marks on the films during the deposition process. The witness marks were utilized for the various characterization techniques. Before deposition, the substrates were ultrasonically cleaned in high purity acetone (VWR Analytical, assay $\geq 99.5\%$) and methanol (VWR Analytical assay $\geq 99.8\%$) for ten minutes in each solution, respectively, followed by a 2-minute soak in piranha solution that consisted of a 1:1 volume ratio of H_2SO_4 (Fisher Scientific, 66 Be) and H_2O_2 (Acros Organics, 95% solution in H_2O).

Depositions were performed using a 193 nm ArF excimer laser with a repetition rate of 50 Hz and a rated pulse length of 15 ns. Five depositions were done with durations of 0.5, 1, 2, 3, and 4 hours over a 9-day period. During deposition, the background chamber pressure remained $< 7.0 \times 10^{-6}$ Torr, and the substrate temperature was $21 \pm 3^\circ\text{C}$. Details of the PLD deposition system are shown in Figure A3 the appendix. The incident laser pulse energy, measured before interaction with the focusing lens, was 6.82 ± 0.3 mJ during all depositions. This laser pulse energy is attenuated by the focusing lens, chamber window, and shielding glass before it interacts with the target. Although the energy at the target cannot be measured directly while the deposition chamber is closed, it can be estimated, based upon 50% attenuation and a focus spot size of 0.13 mm^2 , yielding an average fluence of 2.62 J/cm^2 . The films were kept in a light tight box within a vacuum desiccator when not being characterized.

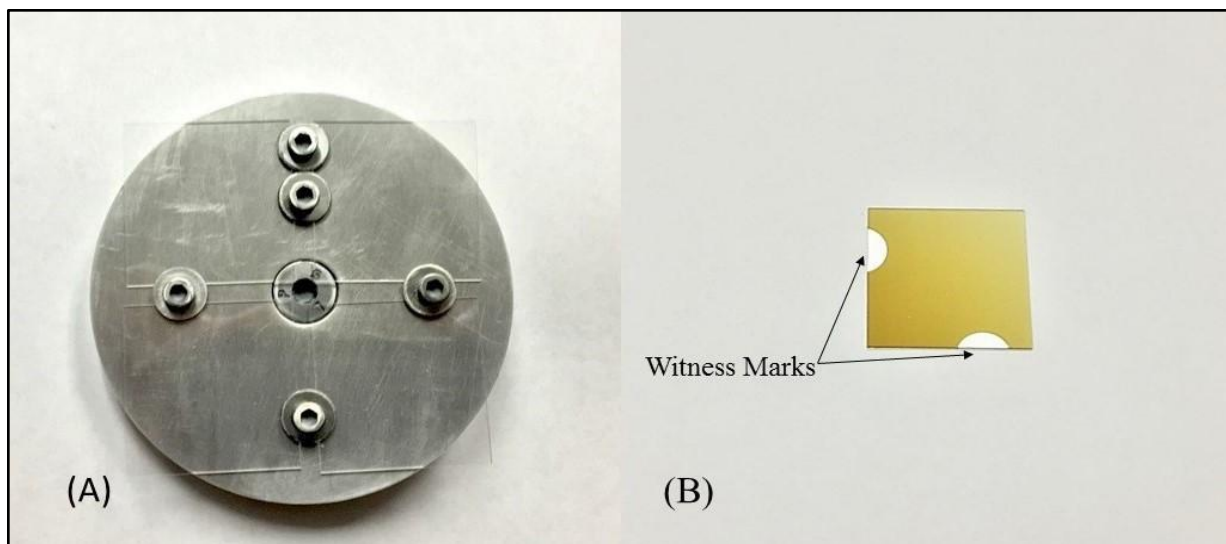


Figure 8. (A) Substrate holder used for PLD system with four transparent fused silica wafers. (B) Thin film demonstrating witness marks developed during a deposition.

The film thickness and surface roughness were measured with white light interferometry using a Bruker GTK 3-D optical microscope (Billerica, MA) and the Vison64 software. The roughness was measured over a 48 μm lateral field of view, while an 860 μm lateral field of view was used for thickness measurements. The film surface and exposed substrate were sputter coated with gold for uniform reflectivity, and the thickness measurement was made using the step height adjacent to the witness mark. The thickness of a film deposited using PLD will vary with proximity to the plume. While rotating the substrate holder provides for a more even coating, the film thickness will still vary radially; using the witness marks from the retaining screws allows for film thickness measurements to be made at a uniform radial distance for more meaningful comparison. The intrinsic machine uncertainty was determined to be 0.057 μm due to illumination variation during measurements.

The transmission properties of the films were observed using ultraviolet/visible light (UV/Vis) spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co.; Beijing, China) equipped with UVWin5.0 analysis software. Transmission was measured for incident light wavelengths between 350 nm and 600 nm at 1.0 nm spectral resolution. The measurements were performed using an uncoated fused silica reference. The witness marks were used to position the sample in

the spectrophotometer to ensure that the same region of the film was observed through multiple measurements.

The thermal characteristics of the films were determined by differential scanning calorimetry (DSC) (Netzsch DSC 200 F3; Selb, Germany). Scans were performed from 100°C to 550°C at a rate of 10°C /min. The deposited ZLANI films were scraped off the substrate (shown in Figure A5 in the appendix), and compared to the DSC data for the ZLANI glass target. The thickest deposited thin film (4-hour deposition) was used to ensure the largest possible DSC signal. Sample masses were 0.9 and 21.6 (± 0.1) mg for the thin film and target glass respectively.

X-ray diffraction measurement for the 4-hour deposition film was performed on a Philips X'Pert MRD X-ray Diffractometer (PANalytical Inc., Westborough, MA) with a Cu anode x-ray source. The x-ray diffraction spectrum was recorded over a 2θ range from 20° to 80° with a step size of 0.05° and a time step of 10 seconds. The amorphous nature of materials can be determined by x-ray or electron diffraction. The material is deemed to be vitreous if no crystals are detected [32].

Thermal annealing was performed in an argon atmosphere. The temperature in the sample chamber was proportional-integral-derivative (PID) controlled, using cartridge heaters as the heat source and thermocouples to monitor the temperature. The heat treatment apparatus is shown in the Figure A6. Two annealing protocols were used. In the first case, the sample was annealed at a temperature of 125°C for ten minutes, then removed and allowed to cool to ambient temperature, followed by transmittance measurement. The annealing/measurement process was repeated ten times on the same sample. In the second case the sample was annealed for one hour at temperatures from 75 to 300°C in 25°C increments; after each one hour anneal, the sample was removed from the chamber, allowed to cool to ambient temperature, and its transmittance was measured.

Results and Discussion

Structural Characterization

Examples of the deposited films are shown in Figure 9. An image of all of the films reported in the chapter is shown in Figure A2. No buckling or cracking was observed, indicating the films had adequately adhered to the substrate. With increasing deposition time, the samples become less transparent in visible light. The films exhibited a brown coloration, but no black particulates associated with reduced zirconium species [28]. A possible explanation for the brown coloration will be discussed in the upcoming Optical Characterization section.

The film roughness shows a direct correlation to deposition time, as seen in Figure 10. Using the kinetic roughening theory, the roughness can be related to growth time via a power law:

$$\omega \sim t^{\beta}, \quad (1)$$

where ω is the average roughness (R_A) of the film, t is the deposition time, and β is the scaling exponent, which shows the roughness development [33]. Based upon the data, the fitted β value for the fluoride glass roughness development is 1.07, indicating that roughness increases with respect to time at a near-linear growth. An alternate explanation to kinetic roughening, for the increase in roughness, is that there can be a buildup of relatively large particulates ejected from the ablation target over time [19].

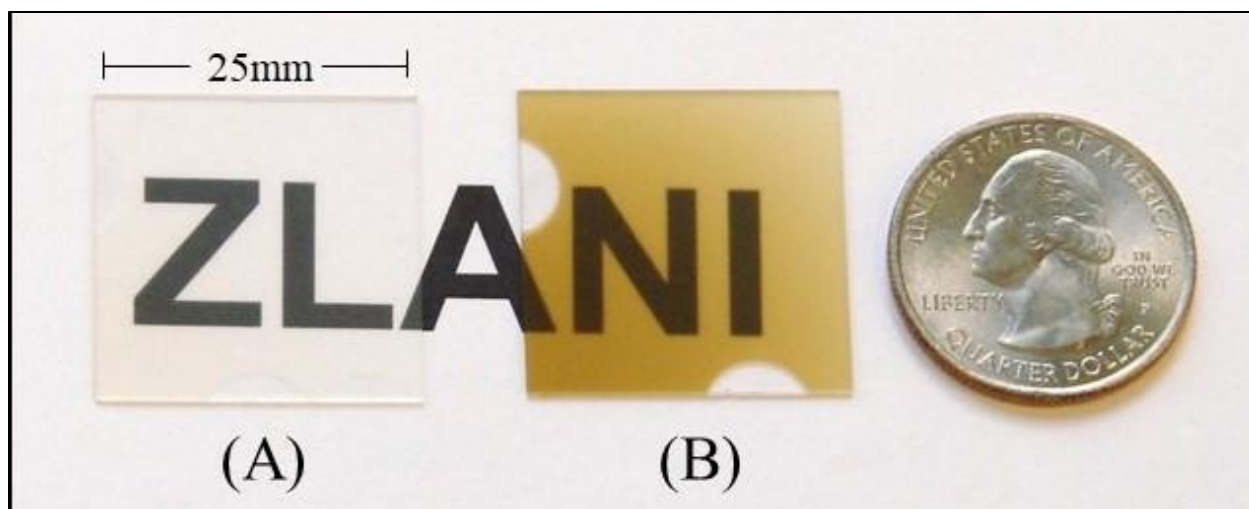


Figure 9. (A) ZLANI glass film deposited by PLD for 30 min. (B) ZLANI glass film deposited by PLD for 3 hours.

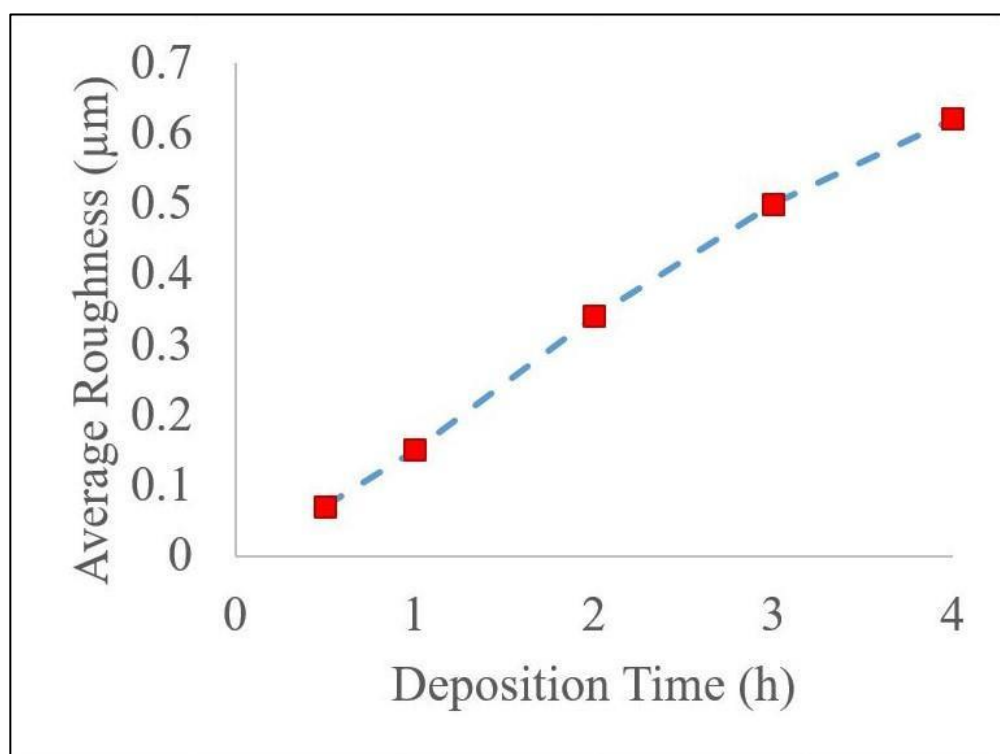


Figure 10. Average roughness (RA) of deposited fluoride glass determined by an optical profilometer compared to deposition time. A line is shown to guide the eye.

The thickness and calculated deposition rate for the five films are shown in Table 1. The deposition rate was not consistent from sample to sample. In general, the growth rate decreased with increasing order of deposition, i.e. the earlier samples had a higher growth rate than those that followed. There are several factors in the experiment which may account for this variation. Material build-up on the PLD system's rotating shield, which was observed after the experiment was completed increases absorption of the laser light, and can have a large effect on the laser fluence at the ablation target and affect deposition rate; because of this build-up, thin film interference effects, leading to changes in the intensity of the transmitted laser light, are also possible [34]. Furthermore, radiation damage, due to the UV laser, may have altered the transparency of the PLD system's focusing lens, optical window, and/or rotating shield, leading to a general reduction laser fluence at the target over time. Changes in the target-to-substrate distance, although small (≤ 4 mm), may also be a factor [35]. Further experimentation on ZLANI deposition rate is described in the second chapter.

Table 1. Thickness and calculated deposition rate for the five thin film samples.

Sample	Deposition Time/h	Laser Pulse Energy*/ mJ	Thickness/ μm	Deposition Rate/ $\mu\text{m h}^{-1}$	Deposition Sequence
CWB007	0.5	6.92 $\pm$ 0.3	0.21	0.42	5
CWB004	1	6.88 $\pm$ 0.3	0.61	0.61	2
CWB003	2	6.80 $\pm$ 0.3	1.7	0.85	1
CWB006	3	6.82 $\pm$ 0.3	1.8	0.60	4
CWB005	4	6.81 $\pm$ 0.3	3.0	0.75	3

*Laser pulse energy measured outside of deposition chamber.

X-ray diffraction (XRD) measurements on the 4-hour deposition film showed the sample to be amorphous as expected (see Figure 11). Because no crystalline particles are found within the film, the observed coloration is not believed to be a byproduct of scattering. DSC data for the 4-hour deposition film are shown in Figure 12 along with data for the ZLANI glass ablation target. There is a considerable difference in glass transition temperature between the deposited ZLANI thin film and the ZLANI glass target. The target glass has a well-defined glass transition temperature onset at $\sim 250^\circ\text{C}$, whereas the onset for the thin film is less defined and begins in a region from 125°C to 175°C . Crystallization of the thin film also occurs at a lower temperature, $\sim 250^\circ\text{C}$, compared to $\sim 300^\circ\text{C}$ for the ZLANI glass target. The observed glass transition region is indicative of an amorphous material, which parallels with the film's XRD results. The differences in thermal properties may be explained by the dissimilar synthesis methods involved i.e. melt-quench versus PLD [19]. With the melt-quench method, a glass-forming liquid is rapidly cooled so that crystallization does not occur with freezing, resulting in a disordered glass [36]. With PLD, the film is the result of the accumulation upon a substrate of various highly energetic species, which may include electrons, ions, energetically neutral atoms, molecules, atom clusters, micron sized particulates, and molten droplets [23]. Therefore, it is expected that differences in structure and possibly elemental composition and distribution would exist between the ablation target glass and the resulting thin film, which explains their disparate thermal properties [19]. It should be noted that physical differences in the compared samples might also contribute somewhat to the dissimilarities measured in the thermal characteristics. The mass of the target glass portion used

for DSC measurement, 21.6 ± 0.1 mg, was significantly greater than that of the thin film, 0.9 ± 0.1 mg, which was necessarily small. In addition, the target glass sample was one solid piece, while the thin film sample was many small shavings, resulting in discontinuities. These characteristics can influence heat transfer rate within the DSC cell.

Optical Characterization

The transparency of each film is quantified through the transmission percentage as a function of wavelength, which is shown in Figure 13. For longer deposition time, the increased film thickness lowers transparency. The overlapping curves for the films deposited for 2 hours and for 3 hours can be attributed to their similar thicknesses, suggesting that the difference in surface roughness between these two films does not have much effect on light attenuation.

Interestingly, it was observed that the films become slightly more transparent with time. The optical stability as a function of time for a film deposited for 1 hour is shown in Figure 14. There is an increase of $\sim 1.5\%$ in transmission during the first ten days, before the transmission reaches a plateau.

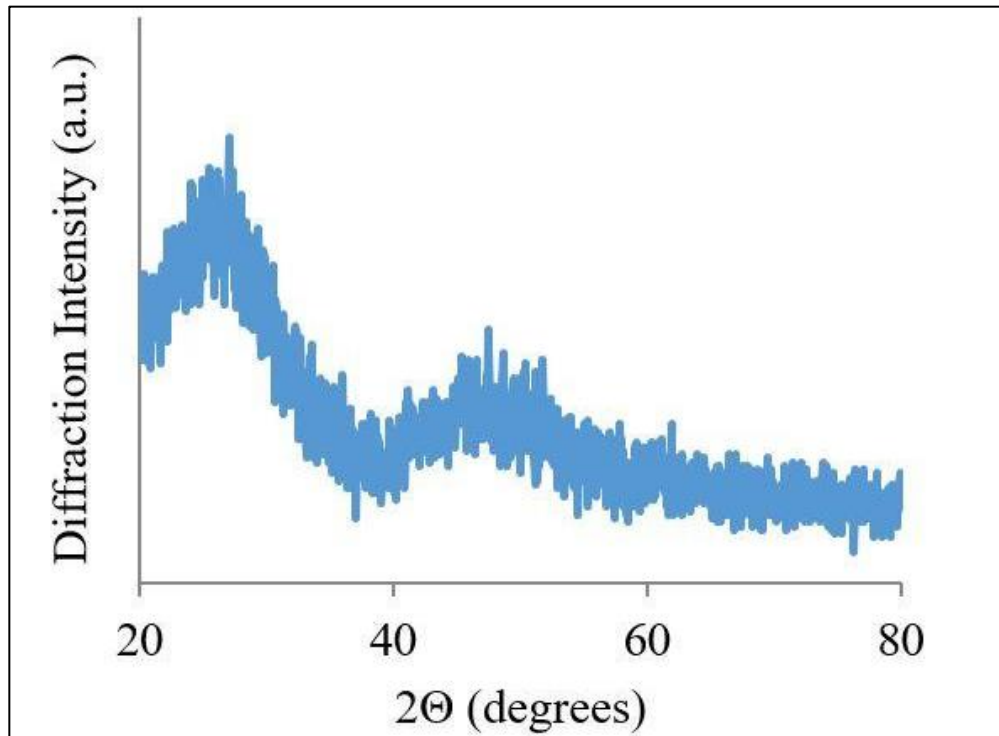


Figure 11. XRD diffractogram of a film deposited for 4 hours.

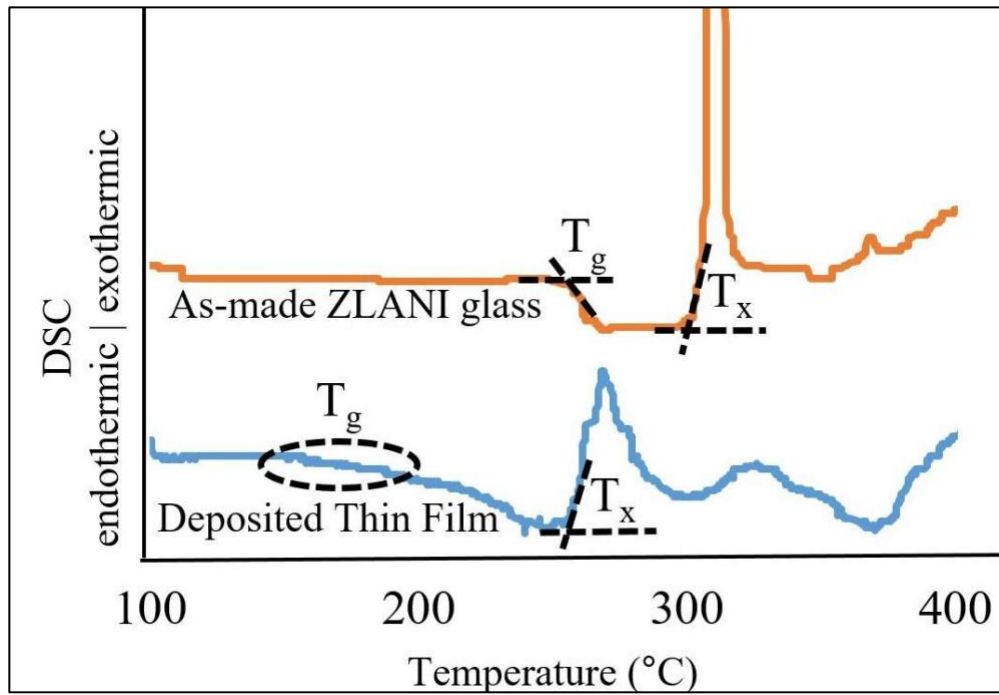


Figure 12. DSC data for a fluoride glass thin film (four-hour deposition time) compared to that of the ZLANI glass target. T_g is the glass transition temperature, T_x is the onset temperature of the crystallization exotherms.

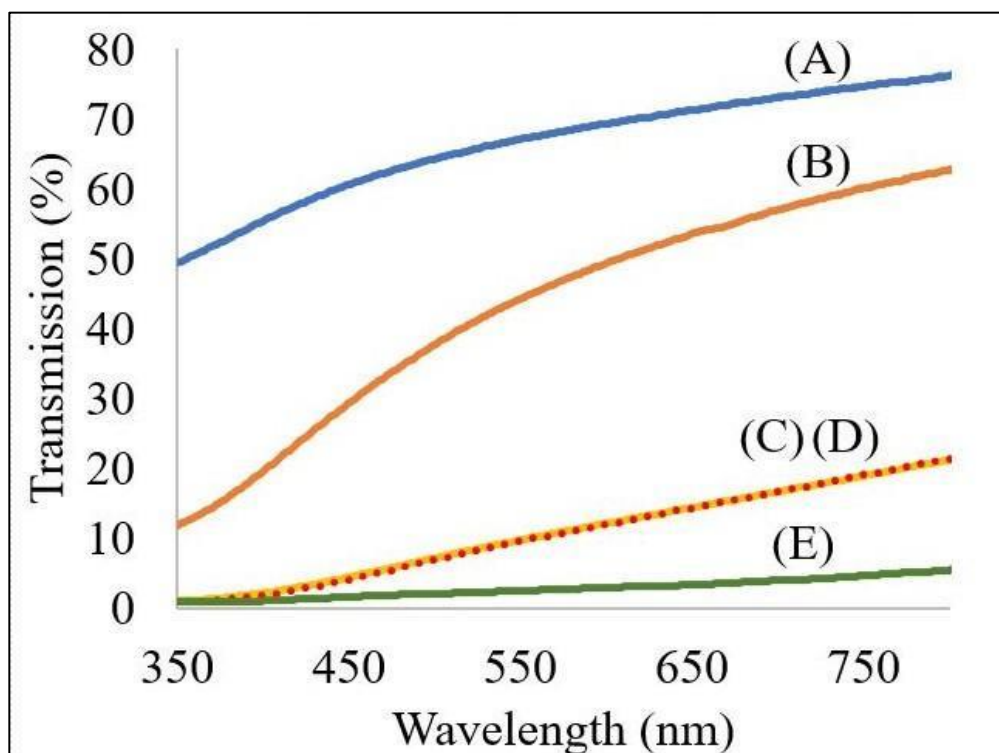


Figure 13. Transmittance of fluoride glass films as a function of deposition time. (A) 30 min, (B) 1 hour, (C) 2 hours, (D) 3 hours, (E) 4 hours. Note: There is considerable overlap of the data for (C) and (D).

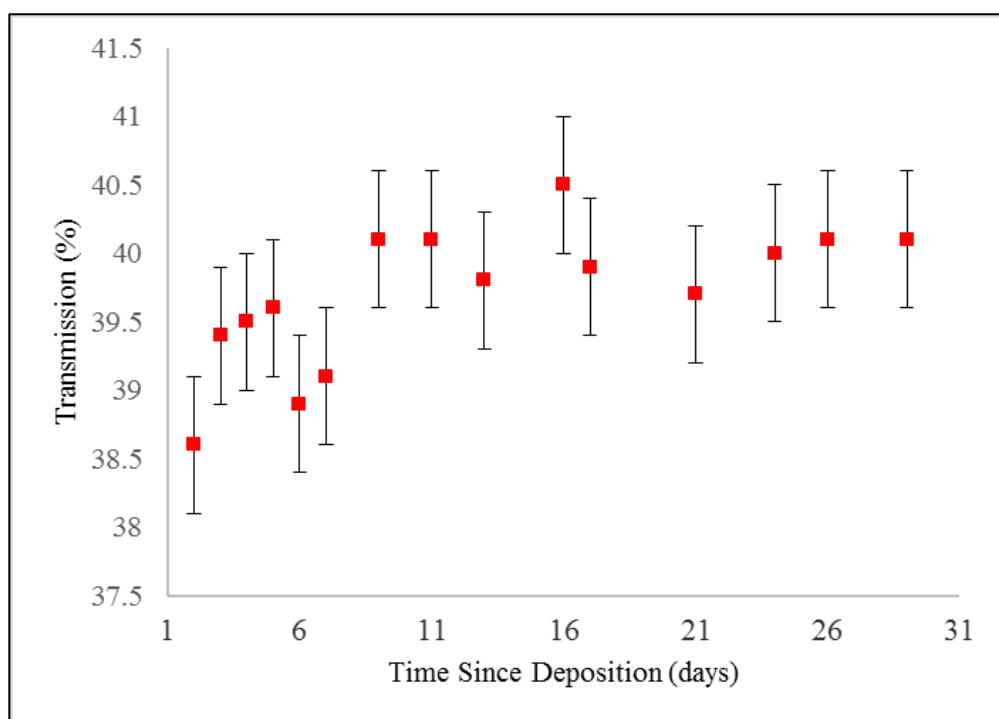


Figure 14. Transmittance at 550 nm of a film deposited for 1 hour, as a function of time.

Temperature has a significant effect on the films' transparency. Figure 15 shows the transmittance of a film deposited for 2 hours and subjected to successive one-hour anneals at gradually increasing temperatures. After each successive anneal, the film becomes increasingly transparent, generally across all wavelengths, with the greatest percentage change, 400%, occurring in the near UV. A transmission decrease is seen in the infrared tail after the 200 °C heat treatment, which is in the glass transition region. The decrease in transmittance at the infrared tail is speculated to be due to the changing of bonding geometry, i.e. a relaxation of intrinsic stresses in the glass matrix above the glass transition temperature.

One possible explanation for this increase in transparency and the initial brown coloration of the films, is the presence of color centers in the glass film, formed during synthesis. Many types of color centers have been identified in fluoride glasses including the well-known F-center, an electron occupying a halide vacancy [37]. The increase in transparency is attributed to a decrease in the number of color centers, which are quenched by thermal annealing. To explain the increase in transparency across the entire measured spectrum, it is hypothesized that there are many overlapping absorption bands due to variations in the local environment for the color centers, which may include any of the five different cations found in the target glass.

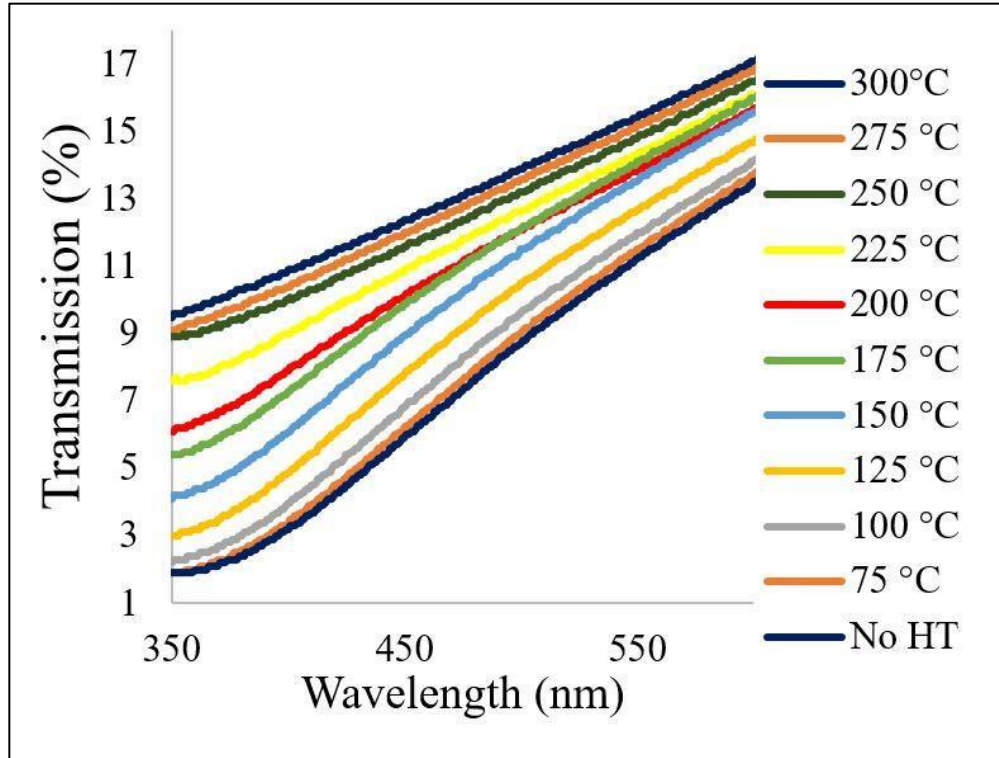


Figure 15. Transmittance of a 2-hour deposition film, after each successive anneal. Transmittance of the as-deposited sample is also shown.

The presence of color centers in the as-made films would also explain the slight increase in transparency over time for the as-made films. A small percentage of the color centers may be unstable at room temperature due to diffusion, which results in the filling of some of the vacancies. The mechanism for the color center bleaching is dependent on the type of color center; in the case of F-centers, an interstitial anion may fill the vacancy, with the free electron combining with a molecular ion present elsewhere in the glass film [37].

Typically, color centers are induced in glasses or crystals through exposure to ionizing radiation. Heating crystals in excess of their respective cation is another common method for the creation of color centers. The prospect of color centers is unusual because there are no reports in the literature of their intrinsic presence in glass thin films created by physical vapor deposition processes. However, due to the highly energetic nature of the PLD plume, which may contain

both electrons and ions, the formation of color centers during film synthesis is not beyond question [23].

Figure 16 shows the change in transparency of a film subjected to successive 10 minute anneals at 125°C. The transmittance increases significantly during the first ten minute anneal and reaches a plateau after ~30 minutes of total annealing time. These results show that the increase in transparency shown in Figure 15 with each successive anneal is due to the increase in temperature and is not due to the additional annealing time. These data, together with the data shown in Figure 15, indicate that there is a broad, continuous spectrum of energies required to quench the color centers present in the ZLANI thin films.

The source of the brown coloration will be investigated further in future work. Although the increases in optical transmission after annealing support the hypothesis that the brown coloration in the as-made glasses is due to color centers, additional techniques, such as electron spin resonance, will be required to verify their presence. Photochromism, due to the 193 nm ultraviolet light used in the process, is unlikely because the target glass does not change color during the ablation process. i.e. coloration is not photo induced in the target glass.

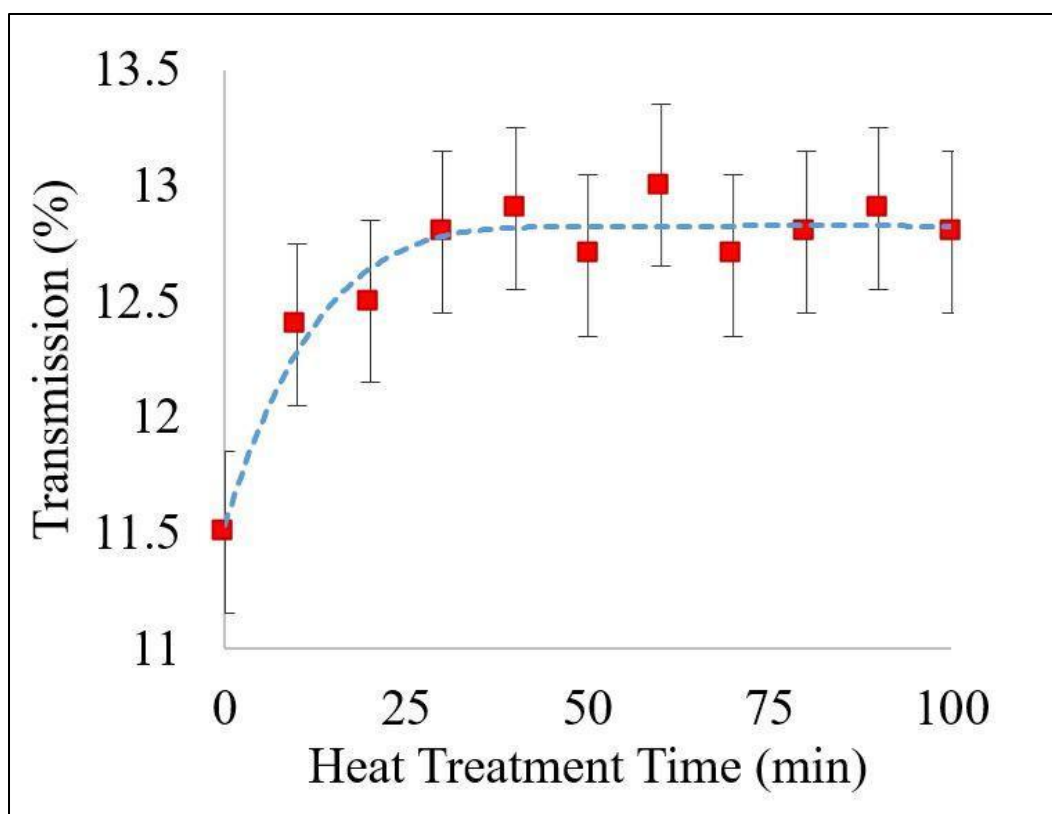


Figure 16. Transmittance at 550 nm of a film deposited for 2 hours as a function of increasing number of 10 minute anneals at 125 °C. A curve is shown to guide the eye.

The change in optical transmittance as a function of anneal temperature suggests that ZLANI films deposited by PLD may be useful as passive temperature sensors, which provide a record of the maximum temperature to which they are exposed. Readout can be achieved by a standard commercial visible light photometer or spectrophotometer, and a camera could be used to record the change in optical properties over time. The ZLANI films would possess many advantages as temperature sensors. First, they are passive, requiring no energy source to operate. Secondly, as thin films, they are lightweight, with the mass of the sensor being largely governed by the substrate onto which they are deposited. Thirdly, they can be made with small lateral dimensions, with minimum size determined by handling considerations and the beam size of the readout system. Lastly, unlike thermochromic materials, the ZLANI films will not revert to their original state after cooling, meaning they provide a non-volatile record of the maximum temperature to which they are exposed.

Conclusion

Pulsed laser deposition has been used to produce thin films of an amorphous transparent fluoride glass, without the need for a processing gas. The as-made films have a brownish hue, possibly due to light absorption by color centers, which will be investigated in future studies. Thermal annealing increases light transmission through the films up to 400%, depending upon wavelength, in the UV and visible spectrum (350-600 nm), after a series of heat treatments culminating at 300°C. The fact that the transparency of the films can be correlated to annealing temperature leads to potential applications of these films as passive temperature sensors.

CHAPTER II:
THIN FILM STORAGE PHOSPHORS FOR COMPUTED RADIOGRAPHY APPLICATIONS

Abstract

In computed radiography applications using conventional granular storage phosphor materials, scattering of the stimulating laser light during read-out leads to blurring of the image and decreased spatial resolution. Although x-ray absorption is reduced, the desire for high spatial resolution has led to imaging plates with thinner phosphor layers in order to reduce this scattering. The films produced in this study consist of multiple transparent layers of orthorhombic phase barium chloride nanocrystals doped with europium, separated by nanoscale layers of fluoride glass. The transparent nature of these films reduces blurring of the image due to scattering of the stimulating light during read-out. The films are deposited on fused silica substrates via pulsed laser deposition, utilizing a multicomponent target. This method allows for precision control of layer thickness and doping level for optimized performance. In addition, a higher concentration of luminescent centers can be produced leading to greater efficiencies, as compared to glass-ceramic imaging plates synthesized in bulk form.

Introduction

X-ray radiography can be used to screen for bone fractures, cancer, pneumonia, lung disease, heart disease, and vascular disease [38]. Three techniques for x-ray radiography are currently employed in medical imaging: screen/film (SF), computed radiography (CR), and digital radiography (DR). The advantages of CR are its dynamic range, inexpensive implementation, digital readout, and ease of image plate placement [11]. CR utilizes a storage phosphor material, such as BaFBr:Eu^{2+} , within an organic binder [39]. Scattering of the stimulating light at grain boundaries is one factor limiting the spatial resolution of these types of imaging plate [14]. A transparent glass ceramic plate could minimize scattering, resulting in improved resolution [8, 9, 12, 13, 40, 41].

Fluorochlorozirconate (FCZ) based glass ceramics have been extensively studied as a candidate for a transparent storage plates and have shown the potential to advance CR [11, 13]. Although

alternative compositions have been tested, Eu^{2+} doped FCZ storage plates have proven to be the most adequate [12]. BaCl_2 nanocrystals are precipitated throughout the FCZ glass matrix during heat treatments, with the orthorhombic phase acting as an ionizing radiation storage phosphor [17]. During nucleation of the nanocrystals, the dopant becomes incorporated in the crystalline structure resulting in $\text{BaCl}_2:\text{Eu}^{2+}$. Compared to commercial CR plates, FCZ storage plates have shown increased resolution but only a relative photostimulated luminescence (PSL) efficiency up to 80% [12, 15].

Increasing the size and/or number of luminescent centers in the glass matrix is an intuitive solution to the inferior light output of FCZ storage plates. However, increased crystal size results in an increase turbidity that annuls the anti-scattering advantage of the transparent storage plate [17]. The ratio of luminescent center to glass matrix volume needs to be increased while maintaining the high-resolution abilities of a transparent storage phosphor plate. To achieve this, an alternative synthesis method needs to be explored.

In this study, a transparent thin film storage phosphor was developed via physical vapor deposition. Three components of the FCZ storage plate (glass matrix, BaCl_2 , and rare-earth dopant, Eu) were separated and made into a target to be ablated by pulsed laser deposition. The composition of each sample was controlled by precise movement of the target using a programmable stepper motor. The glass-ceramic thin films were characterized by differential scanning calorimetry (DSC), and then heat treated to precipitate the BaCl_2 nanocrystals to the orthorhombic phase, which was determined by visual inspection under UV light. The europium dopant was deposited on the BaCl_2 film layers, and integrated in the crystalline structure during precipitation. After x-ray exposure, PSL characterization was conducted to determine the storage phosphor capabilities of the thin films.

Materials and Methods

An integrated stepper motor was installed on the PLD system to control rotational movement of the deposition target. The system utilized a 100:1 ratio planetary gearhead allowing the target movement to be controlled at lower speeds. The motor assembly was attached to the target

holder via a universal joint, and mechanical slides so that the vertical movement of the target was not inhibited. The target translates vertically so the laser creates multiple tracks and can ablate over the entirety of the target. The more area of the target that is used, the less the target is etched by the laser, resulting in a more uniform sample than if the laser ablated the same circular track throughout a deposition. All components of the stepper motor installation can be seen in Figure 17. The motor allowed the option to program the target to rotate to a particular position, resulting in the laser striking the desired material within a multicomponent target. The direction of the target's rotational movement could be programmed, moving the target clockwise and counter clockwise to ablate a particular target region, and then switch to another region when desired. The speed was adjustable, allowing rotations to be slow when focusing on ablating a region, but then increased when moving from one target region to another to decrease uncertainty of film compositions.

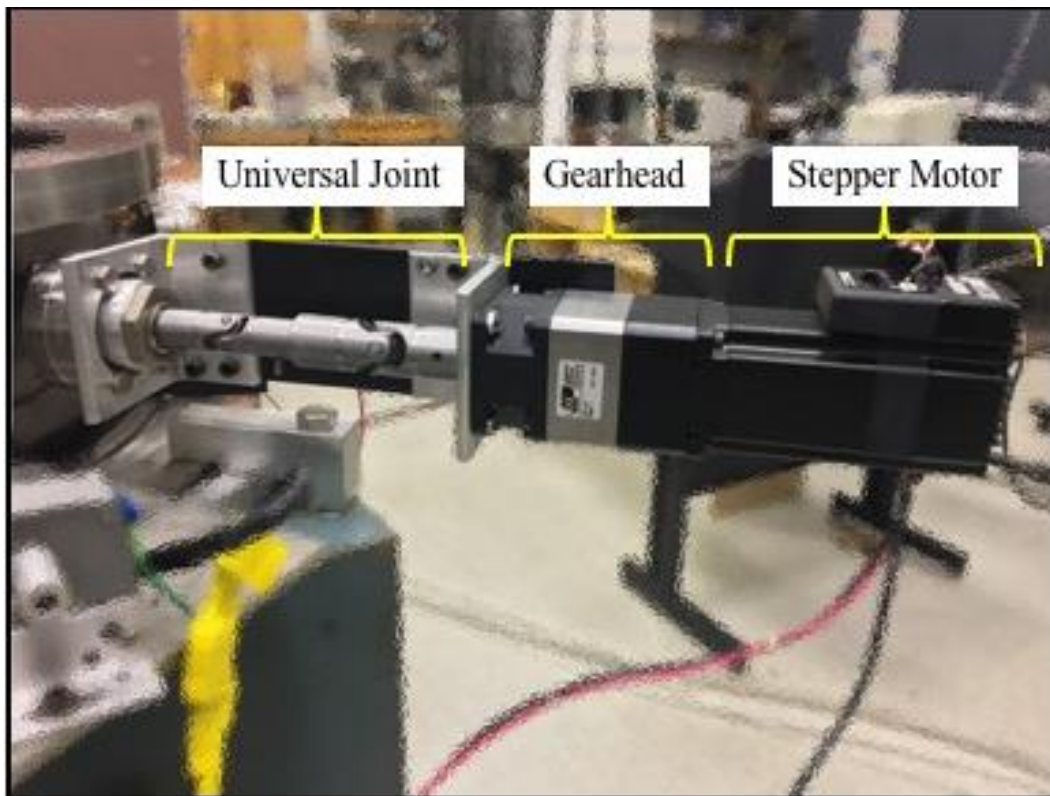


Figure 17. Integrated StepSERVO motor attached to PLD apparatus with different components labeled

The integrated stepper motor was controlled by Applied Motion's Q programmer software. The radial position of the motor was based on steps, where 200,000 steps equals a full 360-degree rotation. Although the Q programming coding is fairly intuitive, it is a language unique to the Applied Motion software. To further simplify the programming and lessen the chance of a coding error, a MATLAB program was created to produce the Q programming script after a series of prompts were answered. The MATLAB script is located in the appendix. The program was developed for a three-component target with each component being deposited in clockwise order of where the laser started. This program was employed to develop a script used for a mock ablation of laser paper with arbitrary markers representing a target with different materials in three different regions. The mock ablation confirmed the accuracy of the stepper motor. Although the laser ablation tracks stayed within the intended regions, it was determined to add uncertainty zones at the beginning and end portions of each region. The uncertainty regions allowed an area where the stepper motor speed could be increased traveling from one region to the other, resulting in a more precise sample composition. The regions of uncertainty are based upon an estimate accounting for the imperfect fit of the actual components of the target materials. The ablated laser paper, along with illustrated uncertainty regions can be seen in Figure 18.

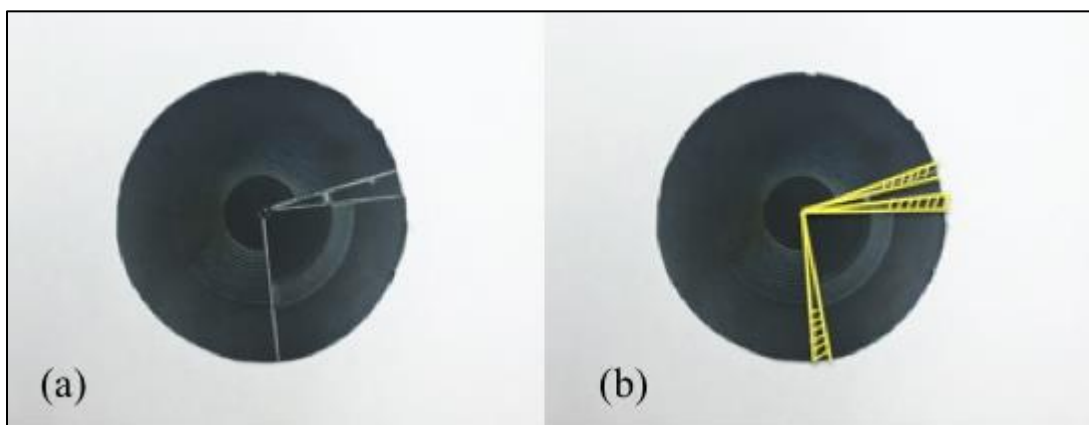


Figure 18. (a) Laser paper with three different regions and ablation tracks following mock ablation. (b) Laser paper with proposed uncertainty regions illustrated in.

A fluoride glass target was synthesized in an argon atmosphere glove box (MBRAUN Labmaster SP) with attached tube furnace (Figure A1). The target, deemed ZLANI, consisted of the fluorides of zirconium, lanthanum, aluminum, sodium, and indium. The composition in mole percentage was $60.24\text{ZrF}_4\text{-}4.13\text{LaF}_3\text{-}3.54\text{AlF}_3\text{-}31.49\text{NaF}\text{-}0.59\text{InF}_3$. Full synthesis details of the ZLANI glass target, along with its image, can be found in Chapter 1. The target was used in many PLD depositions prior to being part of the multicomponent target. Previous use resulted in cracks and ablation tracks on the surface of the glass. The target was polished to expose the glass bulk and smooth the ablation tracks off the surface. Note: Some imperfections were left on the opposite face and other regions outside the ablation path.

A barium chloride (BaCl_2) target was synthesized via a hydraulic press and a stainless-steel mold. 6.07 g of BaCl_2 power was placed in a stainless-steel mold and pressed with 5,000 pounds of force for 36 minutes. The resultant target was approximately 25 x 28 x 0.9 mm and 2.74 g. The synthesis process and resultant target are shown in Figure 19. Initially, the BaCl_2 targets were sintered with temperature controlled platens on a hydraulic press. The hygroscopic nature of BaCl_2 caused the target to crack when exposed to ambient air. The target synthesized without heat was stable in ambient air. Because of the increased robustness, the pressing method without heat was used to make the BaCl_2 portion of the multicomponent target.

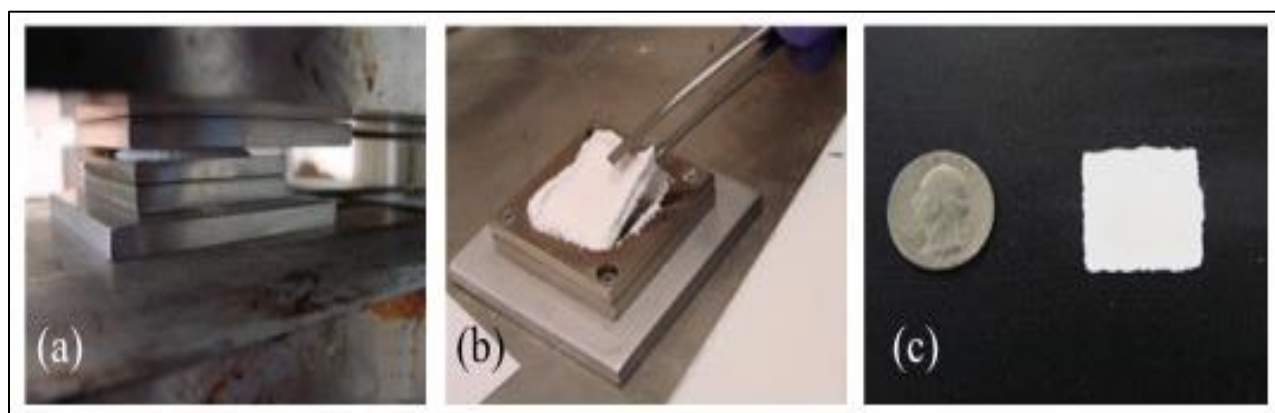


Figure 19. (a) Stainless steel mold containing BaCl_2 powder in a hydraulic press. (b) The BaCl_2 target being removed from the mold following the pressing. (c) The resultant BaCl_2 target.

The europium (Eu) target was purchased from Kurt J. Lesker (Jefferson Hills, PA). The target was circular with a diameter of 50.8 mm and a thickness of 3.28 mm. The target was shipped in a sealed container with mineral oil because exposure to air has a strong oxidizing effect on rare earths [42]. Only a small portion of the target was cut from the bulk circle, with the unused target placed back in mineral oil for future use. All work on the Eu target was conducted in argon, with the only air exposure occurring during transportation from the glovebox to the PLD chamber. To remove the mineral oil from the Eu, a cleaning protocol obtained from Kurt J. Lesker was followed. A series of three beakers were filled with enough lab grade hexane (Fisher Scientific) to fully submerge the Eu wedge. The Eu was placed in the hexane, agitated, removed, then dabbed dry with a lint free Kimwipe. This process was completed for all three beakers of lab grade hexane. Following the last drying step, the same procedure was performed with three beakers filled with high purity hexane (Fisher Scientific).

Two pieces of polished ZLANI were fixed to a stainless-steel disc made specifically for the PLD target holder. The pieces were positioned on the holder to make a circle with a 90° wedge missing so that the BaCl₂ and Eu portions could complete the circle. The BaCl₂ wedge was shaped so that the cut Eu wedge would fit together in the 90° portion. All components of the target were attached via double-sided carbon tape. The resultant three component target is pictured in Figure 20. An outline was made of the completed target and scanned so the exact dimensions of each component could be determined. An electronic compass placed over the scan revealed the space occupied in the ablation track by each component in degrees. The degrees were then converted to steps, and a Q program was developed for the stepper motor. The program accounted for uncertainty at the interfaces between the target components. A mock ablation was conducted on laser paper to ensure the program would line the laser up correctly with the components of the target.

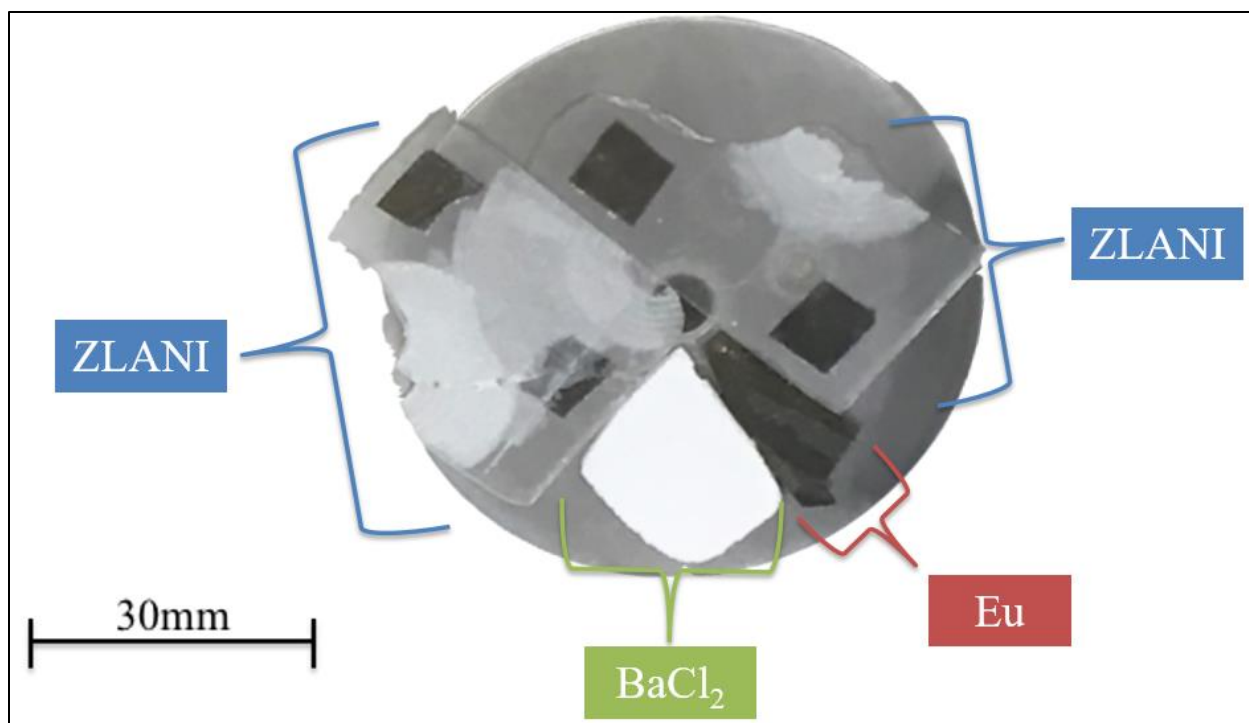


Figure 20. Three component target on stainless steel target holder with each component labeled.

A 193 nm ArF excimer laser with a repetition rate of 10 Hz and a rated pulse length of 15 ns was used for the depositions. An image of the PLD apparatus, along with a dimensioned diagram can be seen in Figure A3 and Figure A4 in the appendix. The PLD chamber was a room temperature (23-25°C) vacuum environment that remained below 5.0×10^{-6} Torr. The measured spot size of the laser had an area of 0.13 mm^2 . The laser traveled through a focusing lens, PLD chamber window, and a shielding glass before hitting the target; each optical component contributed to a measurable attenuation of the laser beam at the target. The experiments in chapter 1 yielded results that brought the constancy of these attenuation factors into question. To determine the approximate fluence of the laser hitting the target during depositions, the incident laser pulse energy was measured outside of the deposition chamber periodically throughout the deposition. The attenuation effects were determined by measuring the laser pulsed energy outside the deposition chamber and inside the deposition chamber (before and after the sources of attenuation) prior to and following ablations. The attenuation measurements was used to determine the consistency of the laser fluence during depositions.

The thin films were deposited on UV grade fused silica substrates (Valley Design). The fused silica was received as 0.5 mm thick wafers and were diced into 25 x 25 mm squares. The substrate holder secured four substrates per deposition via screws and washers. The washer masks the substrate from the plume, resulting in witness marks that can be utilized in characterization. Prior to each deposition, the four substrates were ultrasonically cleaned in high purity acetone and methanol for 10 minutes in each solution respectively, followed by a 2-minute soak in piranha solution (1:1 volume ratio H_2SO_4 and H_2O_2), and a 1 minute soak in ultrapure H_2O . The sample was rinsed with ultrapure H_2O between each step.

A series of depositions (samples CWB010-CWB015) were performed to further understand the growth rate of ZLANI and BaCl_2 . Using a two-component target (Figure 21) and the deposition rates obtained from experiments in Chapter 1, 12 samples were synthesized with different compositions. The projected compositions can be found in Table 2. The thicknesses of the films in chapter 1 were higher than expected, so a more precise ZLANI deposition rate needed to be obtained for thinner films, along with a BaCl_2 deposition rate. Each deposition was done in a two-step process. Cleaned fused silica substrates were placed in the deposition chamber that was pumped to a vacuumed environment. The ZLANI portion was ablated on all four substrates. The deposition chamber was filled with nitrogen gas and opened. Two substrates were removed and two were left on the substrate holder, which was placed back in the deposition chamber. After the PLD chamber was again pumped down to an adequate pressure, the BaCl_2 component of the target ablated, adding an additional layer to the two remaining substrates. The resulting films allowed for a comparison that could determine the ZLANI and BaCl_2 deposition rates.

Table 2. Projected two-component compositions.

Sample Name	Projected Total Thickness (nm)	Projected ZLANI Thickness (nm)	Projected BaCl ₂ Thickness (nm)
CWB010	35	25	10
CWB011	175	125	50
CWB012	105	75	30
CWB013	70	50	20
CWB014	140	100	40
CWB015	210	150	60

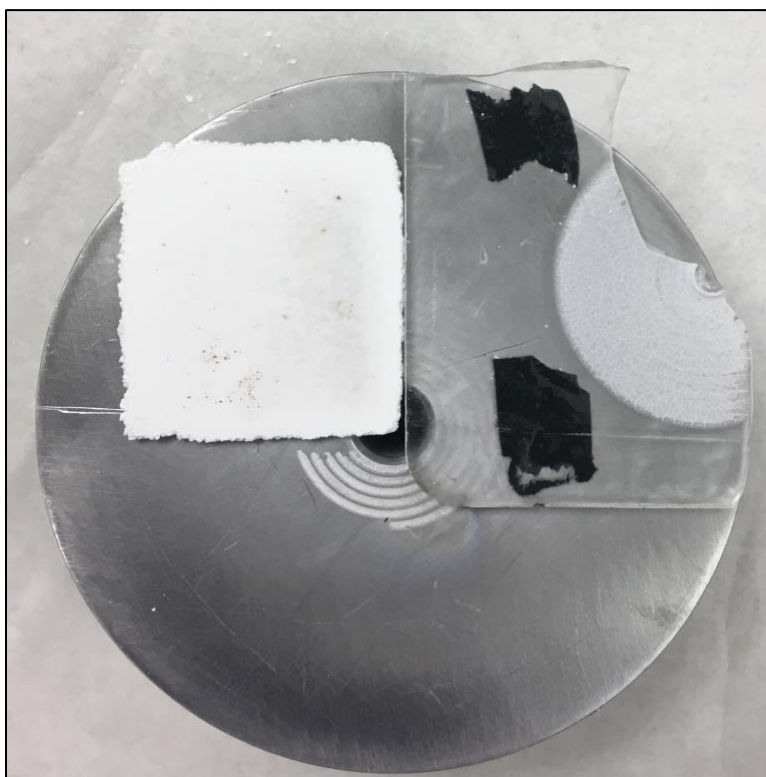


Figure 21. Two component ZLANI and BaCl₂ target used to determine film growth rate. The black carbon taped used fix the materials to the holder can be seen through the transparent ZLANI glass.

Three films were synthesized using a three-component target composed of ZLANI, BaCl₂, and Eu. The deposition rates used to determine the necessary laser pulses in each region for the desired thickness were found through the CWB010-CWB015 sample series. The average of ZLANI and BaCl₂ deposition rate was used as the Eu deposition rate, yielding 83.1 pulses/nm. The first three-component film (sample CWB017) was made with one sublayer of ZLANI, BaCl₂, and Eu and capped with a protective ZLANI layer. The projected thicknesses of the layers were 300 nm ZLANI, 150 nm BaCl₂, 50 nm Eu, and 100 nm ZLANI. After synthesis was complete, additional samples, both thicker and thinner, were made to aid characterization. Sample CWB019 was synthesized with four sublayers and finalized with a protective ZLANI cap. The sublayers and the protective cap followed the same projected thickness of 300 nm ZLANI, 150 nm BaCl₂, 50 nm Eu, and 100 nm ZLANI. Sample CWB018, the thinnest film, was synthesized for TEM analysis. An illustration of the composition of the three component films is shown in Figure 22.

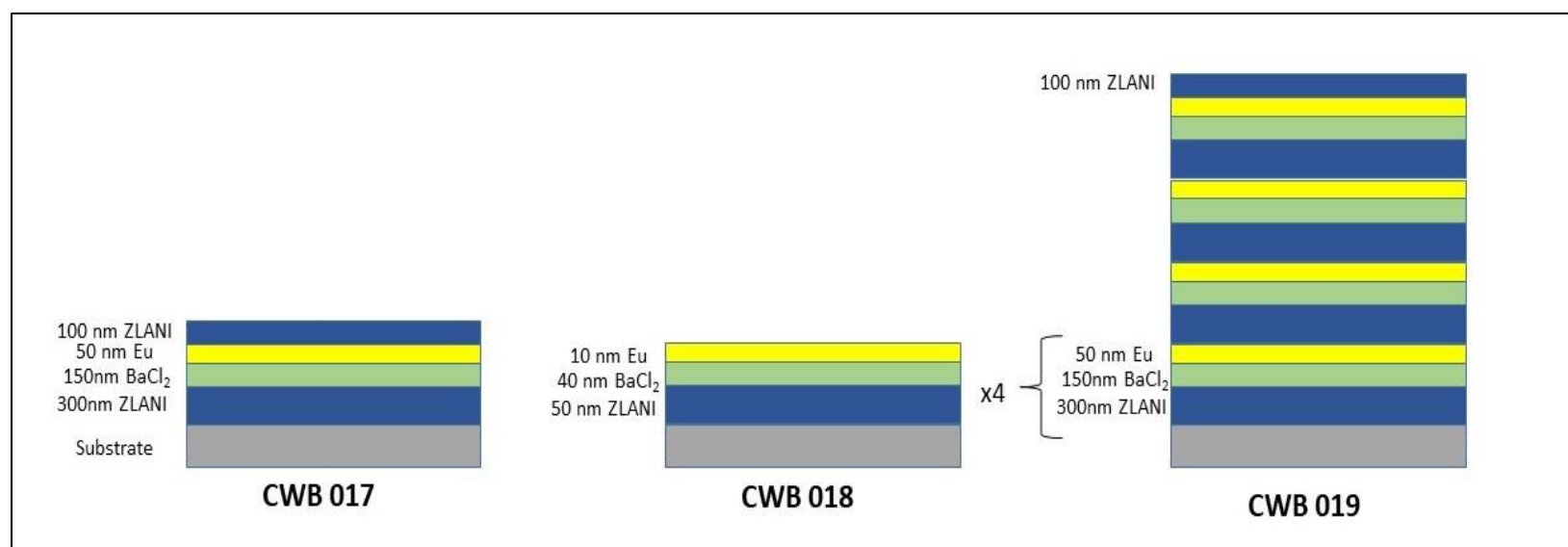


Figure 22. Illustration of the projected composition of samples CWB017-CWB019

Film thickness was determined by characterizing the step height of the witness mark using a stylus profilometer. A Veeco Dektak 150 Surface Profiler, equipped with a diamond-tipped stylus, was used at the Vanderbilt Institute for Nanoscale Science and Engineering (VINSE). The stylus started on the fused silica and moved on the film during the scan. The length of the scans was 1000 μm with a duration of 120 seconds resulting in a resolution of 0.028 $\mu\text{m}/\text{sample}$. Multiple measurements of different radial distances in proximity to the plume were conducted on each sample. Only measurements with the same proximity to the plume can be compared due to the differing density of material deposited. The different measurements conducted on each sample can be seen in Figure 23, with an illustrated arrow representing the path of the stylus.

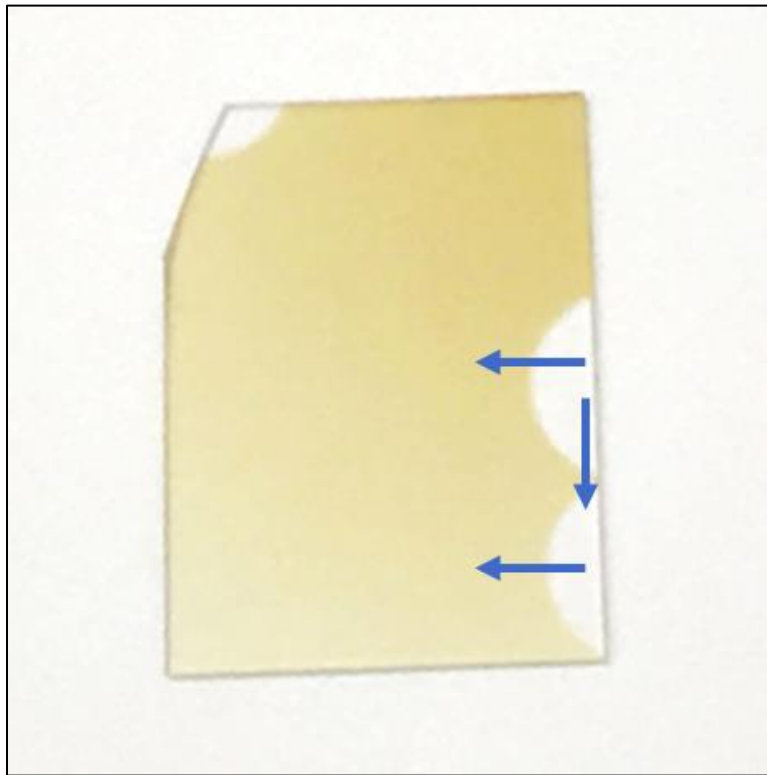


Figure 23. Fluoride glass thin film with arrows illustrated to represent the different paths of the stylus during stylus profilometer step height analysis.

An ultraviolet/visible light (UV/Vis) spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co.; Beijing, China) equipped with UVWin5.0 analysis software was used to determine the transmittance of the films. Measurements were determined for incident light wavelengths between 400 nm and 700 nm at 1.0 nm spectral resolution. A custom stainless-steel holder was fabricated to accommodate the thin film samples. A fused silica substrate of identical optical grade as the film substrate was used as a reference. Samples were aligned using the witness marks to ensure the same area of each sample was measured.

Differential scanning calorimetry (DSC) was employed to determine the thermal characteristics of a three-component sample, CWB019. Two films were scraped off the substrate using a razor blade resulting in 2.1 mg of sample. The scan was performed from 100°C to 550°C at a rate of 10°C/min. The resultant data was used to estimate an experimental heat treatment temperature range necessary to transition BaCl_2 from its hexagonal to orthorhombic phase.

Heat treatments were performed within a custom heat treatment system that employed cartridge heaters as a heat source for the sample chamber, and thermocouples to measure chamber temperature. The heat treatment apparatus is shown in Figure A6 in the appendix. All heat treatments were conducted in argon atmosphere glovebox. Each heat treatment was brought to 150°C, held for 5 minutes, then ramped to the desired temperature at 1°C/min, held for 5 minutes, then allowed to cool to 25°C slowly over time. A 25 x 25 mm sample of the CWB017 and CWB019 deposition was scribed into four pieces, and each piece received a different maximum temperature. The four CWB017 samples received maximum heat treatment temperatures of 250, 275, 288, and 300°C. The four CWB019 samples received maximum heat treatments temperatures of 270, 275, 280, and 285°C.

After heat treatments, the samples were inspected for emission both visually and via phosphorimetry. The samples were visually inspected under 254 nm UV excitation, and the perceived hue of the luminescence, indicative of the phase of the BaCl_2 , was recorded. A PTI QM30 model 810/840 phosphorescence/fluorescence spectrofluorometer (Birmingham, NJ) connected to a PC equipped with PTI Felix32 software was used to measure the excitation and emission spectra. The scan was conducted with a step size of 1 nm, 50 μs integration time, and a

lamp frequency of 100Hz. Each scan was repeated three times and averaged. The background was acquired before each measurement was taken. Emission scans were measured from an excitation of 270 nm and 360 nm. The 270 nm emission was measured from 280-700 nm and the 360 nm emission was measured from 370-700 nm. Excitation scans were measured for a 410 nm and 470 nm emission, for wavelengths 225-400 nm and 225-460 nm respectively.

The ability of the films to be utilized as storage phosphors was determined by measuring the photostimulated (PSL) emission characteristics for sample CWB019 after heat treatments. A custom experimental set-up was used consisting of a 532 nm pumped diode Nd/YAG laser, a collector cone, a photomultiplier tube, a data acquisition card (National instruments NIUSB-6215), and a power supply (Hamamatsu HC124-06 and C7169). The experimental set-up is shown in Figure 24. The films were optically bleached then placed in a light tight x-ray envelope. The envelope is designed so that the x-ray can penetrate the films, but visible light, capable of bleaching the samples, is inhibited. The x-ray source used to expose the film was a Philips 65 kVp DENS-O-MAT (Amsterdam, Netherlands) at Pediatric Dental Centers P.C. (Tullahoma, TN). The x-ray source is shown directed at an imaging plate within an x-ray in Figure 25. Each film was exposed to 65 kVp x-ray radiation at 6.4 mAs five times (32 s total). The films were then transported to UTSI, removed from the x-ray envelopes in a dark room and PSL characterization was conducted within one hour of exposure. A MATLAB function was used to acquire 30 seconds of data, where the film was stimulated with the laser 5 seconds following the start of data collection.

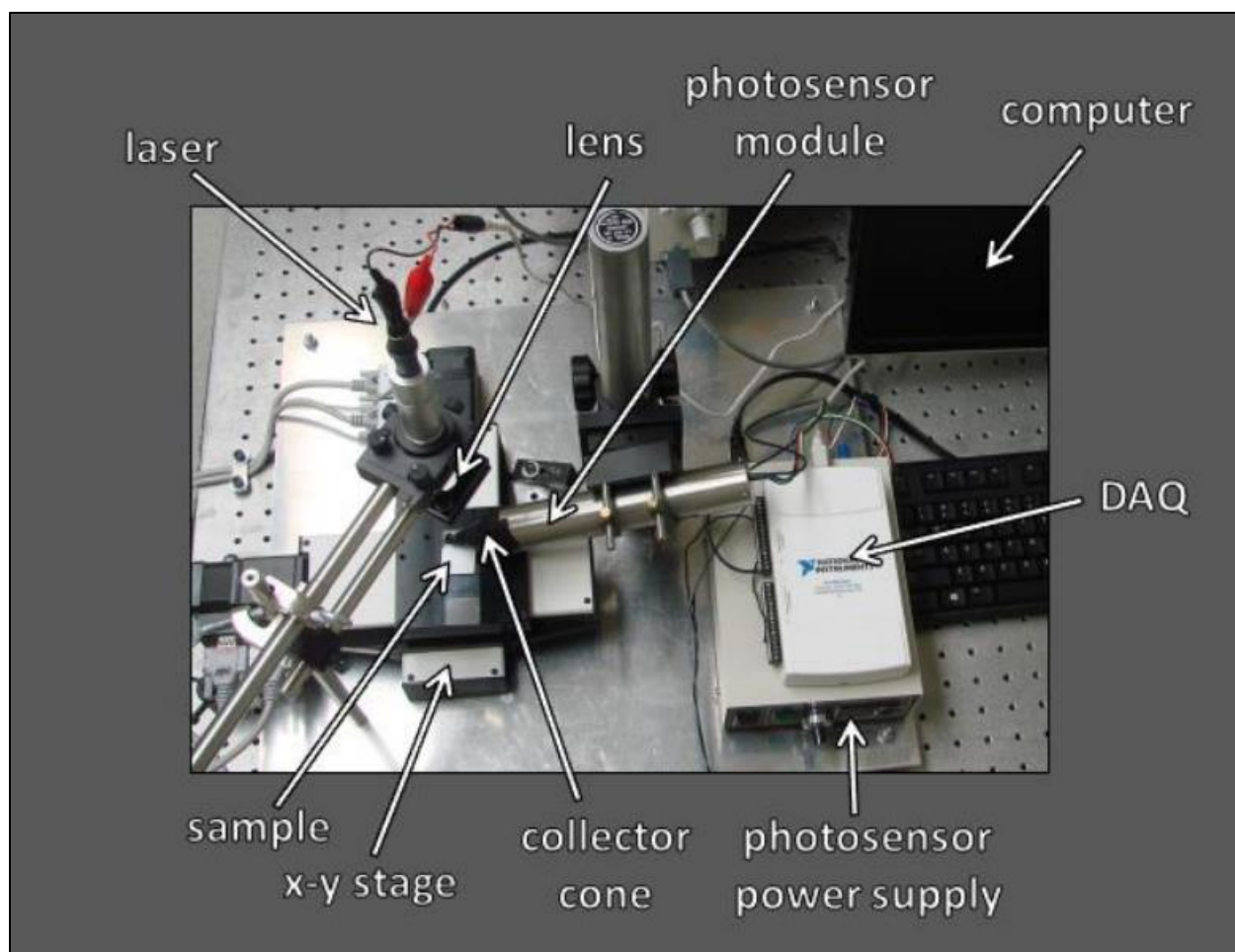


Figure 24. Apparatus used to achieve photostimulated light output measurements [2]. Used with permission.



Figure 25. X-ray tube utilized for reported experiments. It is shown here directed at image phantom overlaying a medical imaging plate within a light tight envelope.

Results and Discussion

Two-Component Samples

The two-component deposition series resulted in four samples: two composed of ZLANI (samples A and D), and two composed of ZLANI and BaCl₂ (samples B and C). Samples A and C of depositions CWB010-CWB015 were compared to determine ZLANI and BaCl₂ growth rate. Stylus profilometer thickness measurements can be seen in Table 3. Although multiple thickness measurements were taken on each sample, moving the profilometer's stylus across the double witness mark away from the proximity of the plume proved to render the most reliable readings. The average deposition rate from the six samples with only ZLANI is 0.0202 nm/pulse. The average BaCl₂ growth rate is 0.0073 nm/pulse.

Table 3. Stylus profilometer results of samples CWB010-CWB014.

Sample	Thickness (nm)				Deposition Rate (nm/pulse)	
	Profilometer Measurement	Projected Total Thickness	Projected ZLANI Thickness	Projected BaCl ₂ Thickness	ZLANI	BaCl ₂
CWB010A	161.95	25	25		0.0306	
CWB010C	183.47	35		10		0.0102
CWB011A	477.14	125	125		0.0180	
CWB011C	507.22	175		50		0.0028
CWB012A	295.87	75	75		0.0186	
CWB012C	375.81	105		30		0.0126
CWB013A	248.66	50	50		0.0235	
CWB013C	289.60	70		20		0.0097
CWB014A	324.02	100	100		0.0153	
CWB014C	350.34	140		40		0.0031
CWB015A	490.51	150	150		0.0154	
CWB015C	556.91	210		60		0.0052

When the CWB010-CWB015 sample series is combined with the samples series featured in Chapter 1 (samples CWB003-CWB007), the ZLANI growth rate can be fit to a linear regression, shown in Figure 26. Sample CWB006 was not considered in the graph because of reasons described in the previous chapter. Although the series were synthesized with two different laser frequencies, 50Hz and 10Hz, samples were compared as thickness per pulse, so the different frequencies are relative. The R-squared value of 0.9296 proves the linear trend is suitable to be considered indicative of the deposition rate. It should be noted that this is only indicative of the thickness between the two witness marks.

The Beer-Lambert law states that absorbance of the material is directly proportional to thickness of the material [43]. The law is written in equation form as:

$$A = \log_{10} \left(\frac{I_0}{I} \right) \quad (2)$$

where A is absorbance, I_0 is the incident intensity, and I is the transmitted intensity. Because all samples were deposited on an identical substrate the absorbance, or its inverse the transmission, is based on how thick the deposited film is. Figure 27 shows transmission measurements of sample A (ZLANI) for the CWB010-CWB015 sample series, while Figure 28 shows sample C (ZLANI/BaCl₂). The spectrophotometer results show expected trends for both series samples A and C. The more pulses from the laser, the more material is ablated from the target that results in a thicker film. As the film becomes thicker, more light is absorbed and the transmission decreases.

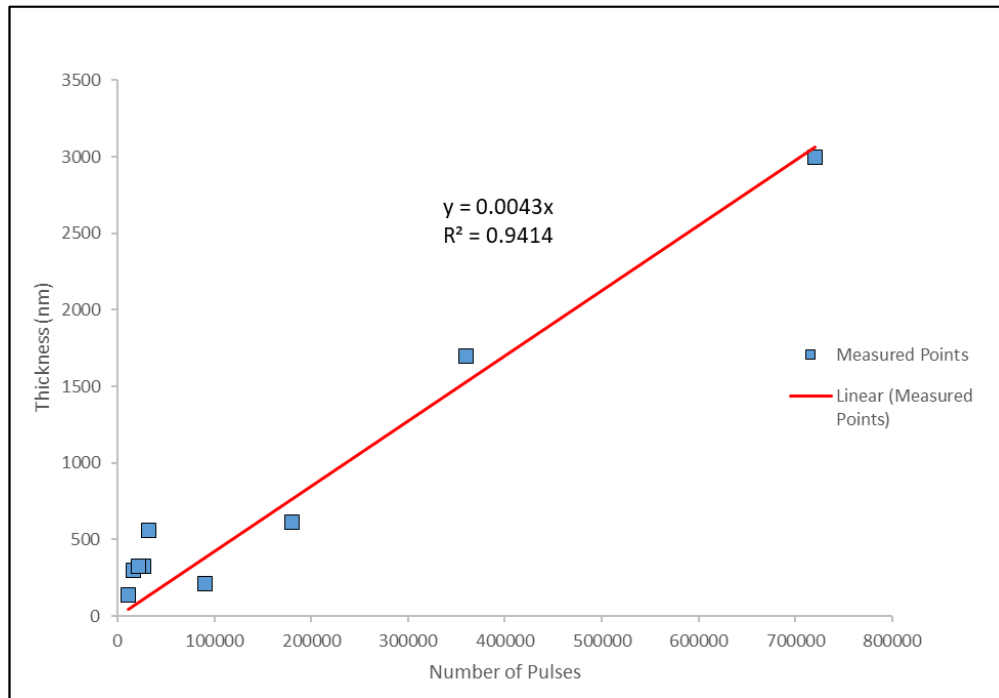


Figure 26. Thickness of ZLANI films compared to number of laser pulsed on target with a linear trend line fit to the data.

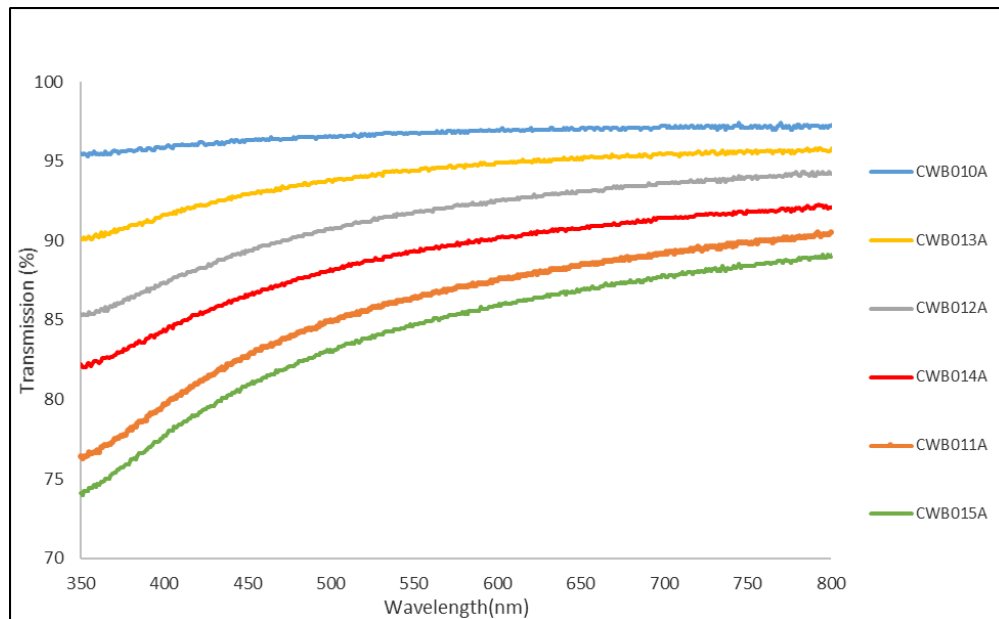


Figure 27. Transmission spectra of samples CWB010-CWB015 with only ZLANI glass deposited as a film.

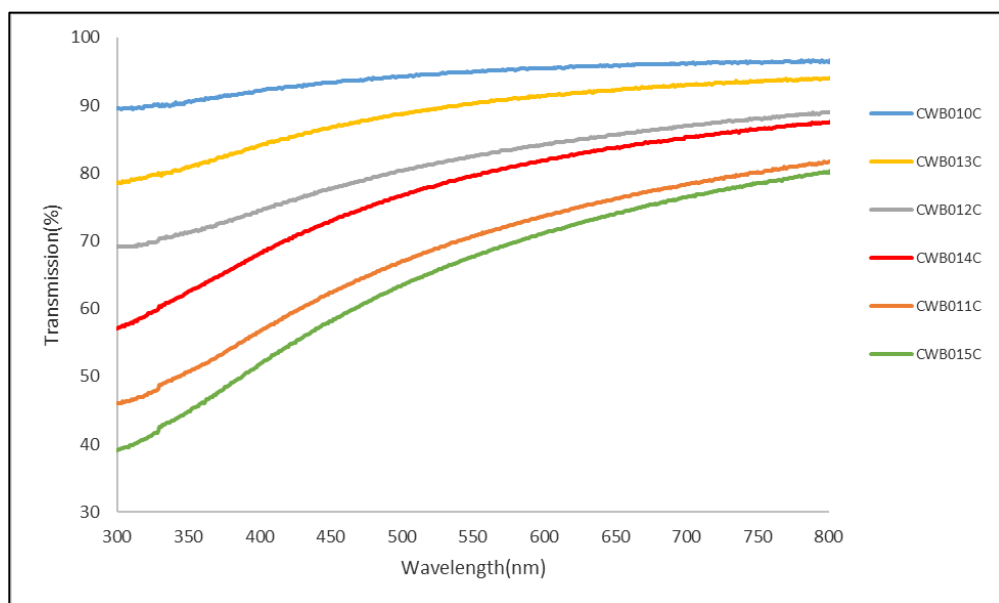


Figure 28. Transmission spectra of samples CWB010-CWB015 with ZLANI glass and BaCl₂ layer deposited on substrate.

To determine the effect BaCl₂ had on the transmission, the transmission percentage at 400 nm of sample A was subtracted from Sample C. The results were plotted in order of increasing BaCl₂ amount in Figure 29. With increasing BaCl₂, more light is attenuated following the Beer-Lambert law.

Three-Component Samples

All reported three-component films can be seen in Figure 30. In the thinnest sample, 100 nm CWB018, it is difficult to distinguish the film from the substrate. The witness marks are noticeable on sample CWB017, and become evident with the thickest sample, CWB019. As with the previous two-component samples, the spectrophotometer results are in agreement with the Beer-Lambert law, with increased thickness resulting in increased absorbance. The transmission spectra of the three component films can be seen in Figure 31. For each sample, the transmission spectrum is indicative of what is seen via visual inspection.

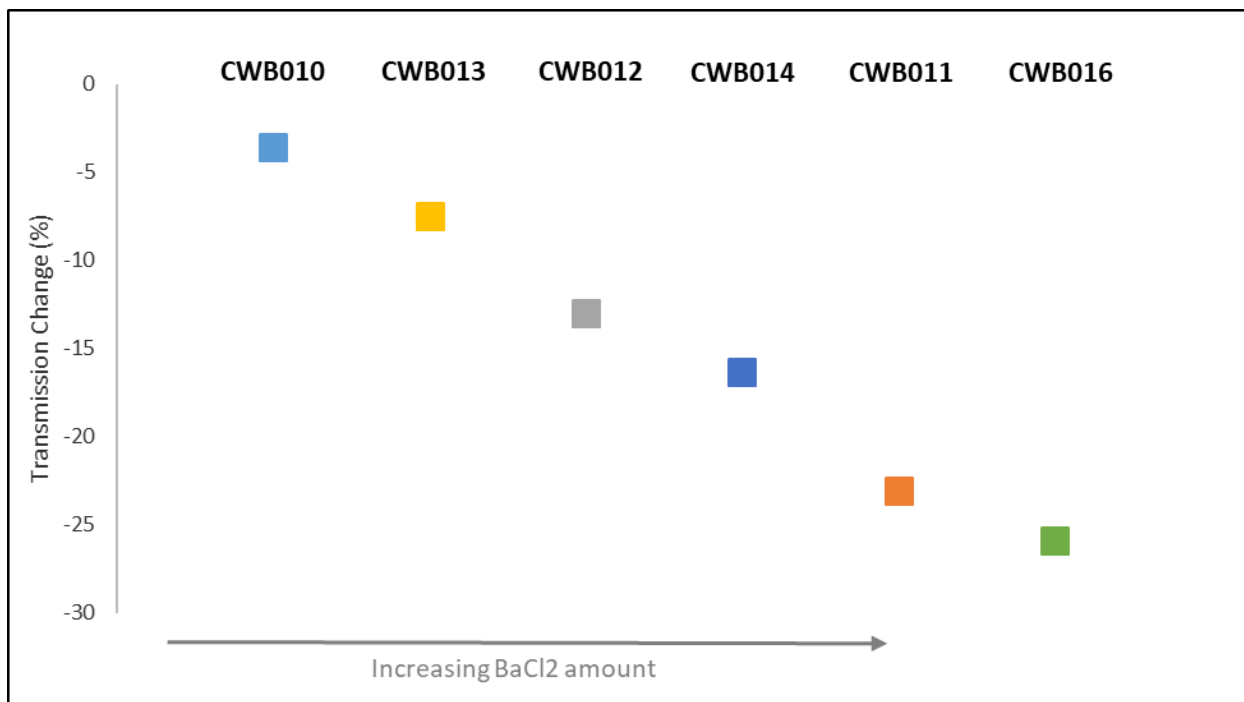


Figure 29. Effect of BaCl₂ on transmission percentage at 400 nm wavelength.

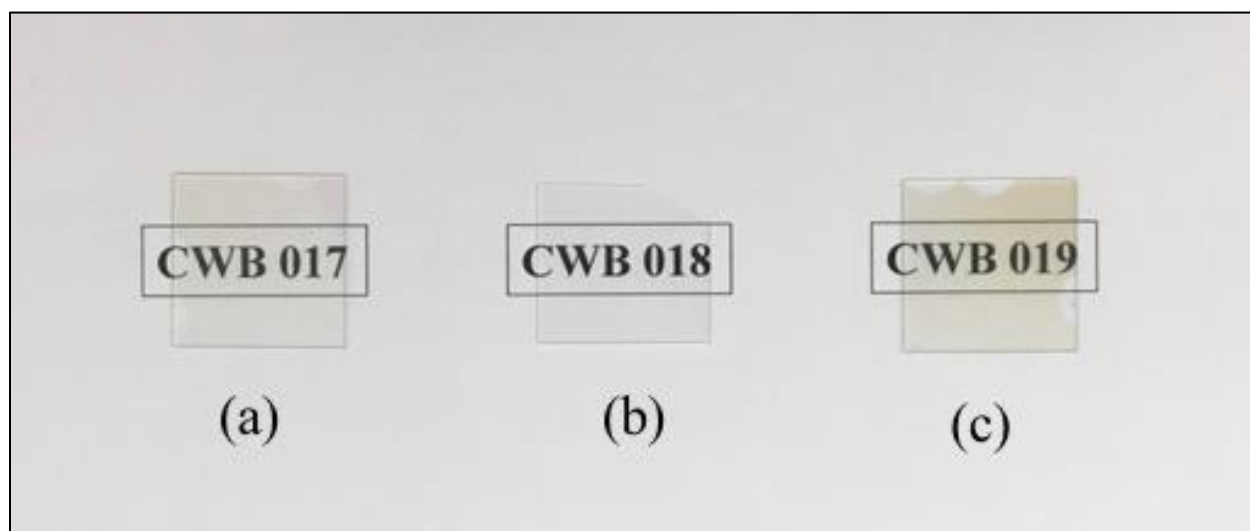


Figure 30. (a) Sample CWB 017 with a project thickness of 600nm. (b) Sample CWB 018 with a projected thickness of 100nm. (c) Sample CWB 019 with a projected thickness of 2100nm.

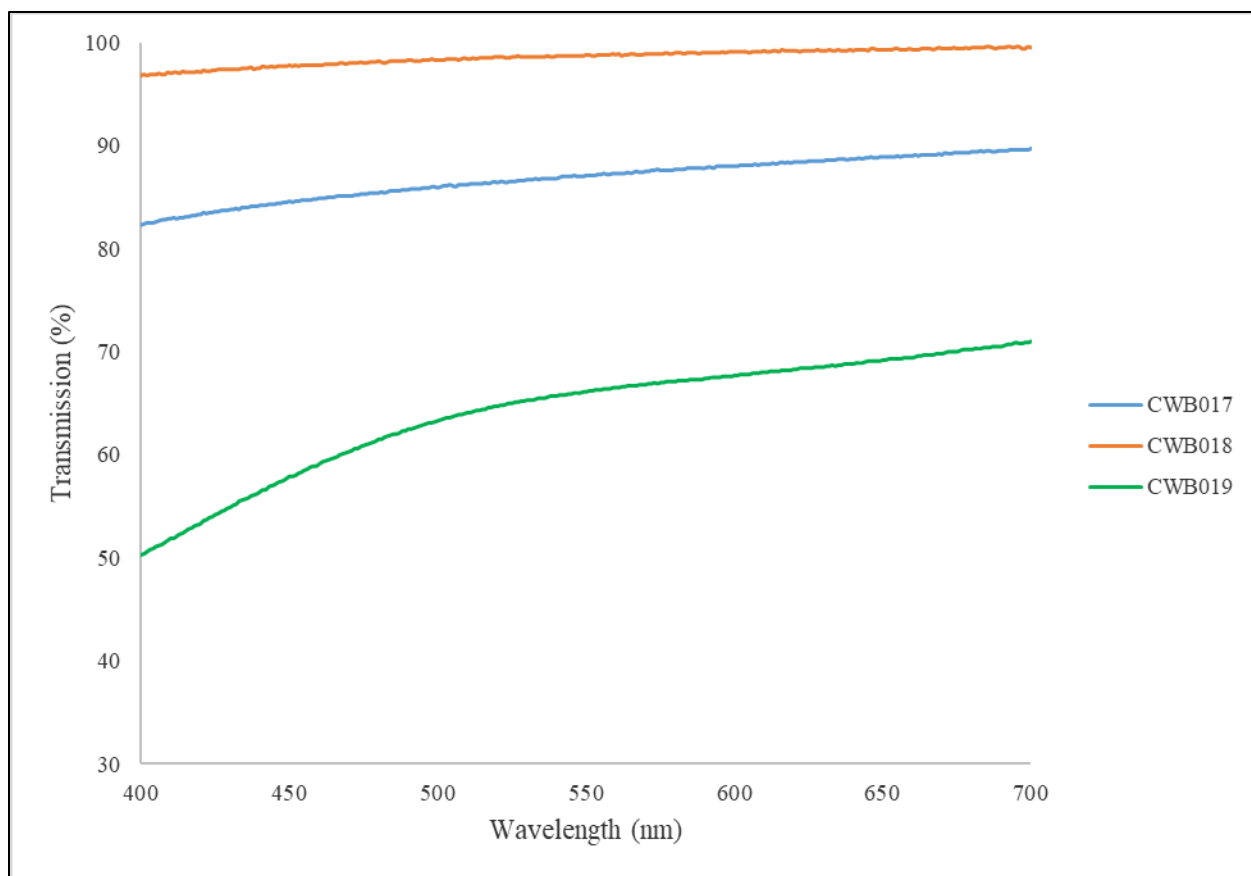


Figure 31. Transmission spectra of each three-component sample, samples CWB017-019.

DSC data from the scrapings of the three-component film, sample CWB 019, are shown in Figure 32. The data is compared to sample CWB005, which is the scrapings of a thin film composed of only ZLANI glass. The two samples are very similar with only a slight variation occurring after crystallization. For both samples, the glass transition temperature is in a region from 125°C to 175°C and partial crystallization occurs at approximately 250°C. The exotherm beginning at 300°C is attributed to crystallization of the glass matrix. From the data obtained in the DSC, an experimental heat treatment temperature range of 250°C to 300°C was determined adequate to attempt to transition the BaCl_2 in the films to the orthorhombic phase. The lack of thermal events, along with previous experiments [17], indicate that temperatures below 250°C will have no effect on the BaCl_2 . Temperatures above 300°C will cause the glass matrix of the samples to crystallize, diminishing their value for storage phosphor applications.

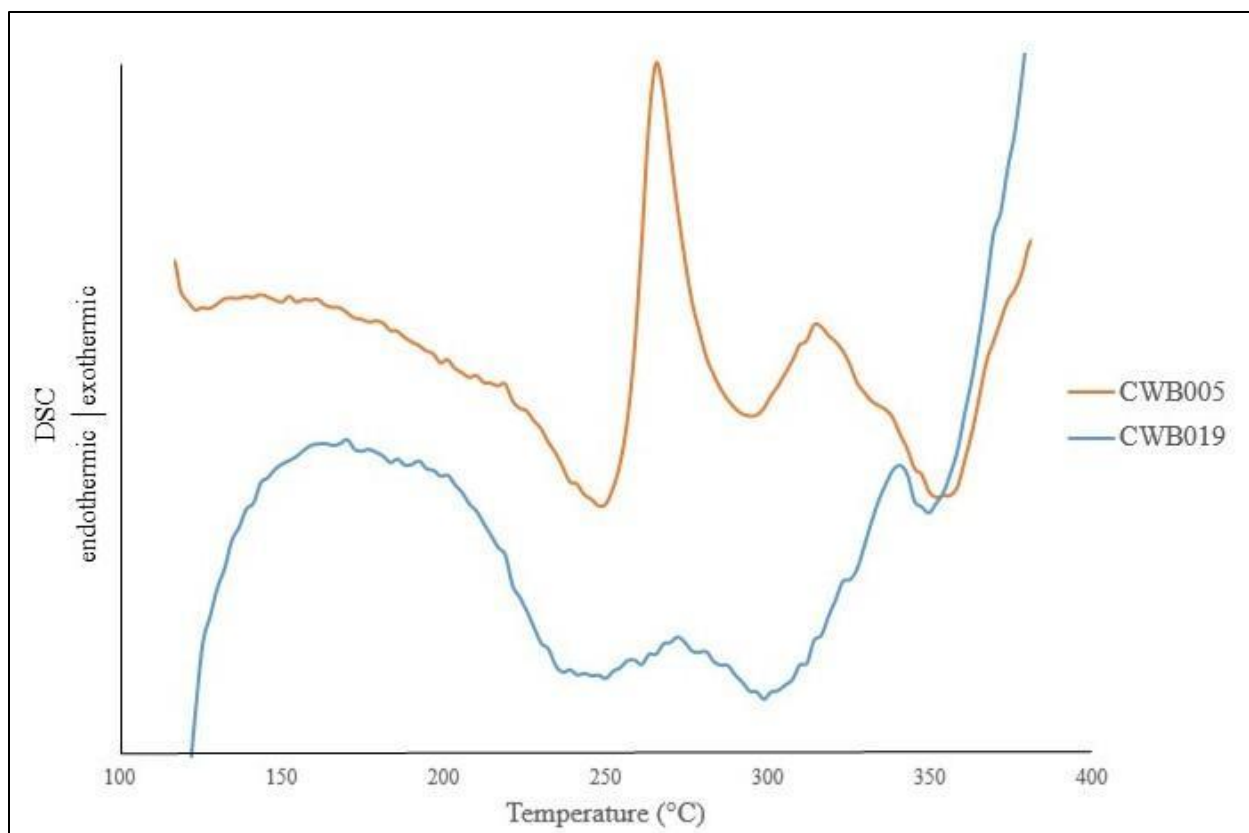


Figure 32. DSC results of CWB005, a ZLANI thin film and CWB 019, a ZLANI/BaCl₂/Eu film.

Initial heat treatments were conducted on sample CWB017 with maximum temperatures of 250, 275, and 300°C. Visual inspection revealed luminescence properties of the sample following the 250°C and 275°C heat treatments. Each of these films exhibited a blue luminescence when exposed to a 254 nm light, indicative of hexagonal BaCl₂. No luminescence was seen following the 300°C heat treatment. Following the observation of the 300°C heat treatment, a fourth heat treatment was conducted at 288°C. The 288°C heat treatment yielded a sample that did not luminesce under UV light. Due to the transparent nature of the sample, most of the light emitted from the film was seen on the edges of the sample, a phenomenon known as light trapping. Phosphorimetry produced results with a low signal-to-noise ratio due to low emission from the sample surface.

The heat treatment maximum temperatures for sample CWB019 were determined with the results of the CWB 017 heat treatments in consideration. The sample before heat treatments,

and following 270, 275, 280, and 285°C heat treatments can be seen in Figure 33. Similar to sample CWB017, phosphorimetry results for sample CWB019 had a small signal-to-noise ratio. A peak in the emission scan from 270 nm excitation can be seen following heat treatments, but the different heat treatments cannot be differentiated. The emission scan from 280-700 nm (excited at 270 nm) of a sample with and without heat treatment can be seen in Figure 34.

Although visual inspection of sample CWB017 proved challenging, sample CWB019 yielded more apparent results when excited by the 254 nm light. The samples of each CWB019 heat treatment are shown being excited by a 254 nm light in Figure 35. While the sample that was not heat treated demonstrated no luminescence, each heat treatment sample luminesced under UV light. The 270 and 275°C heat treated samples show similar results, both having an emission that is a royal blue color. It is hypothesized that these two samples have a mixture of hexagonal and orthorhombic BaCl_2 . The 280°C heat treatment sample luminesces a cyan color that is noticeably different. The color change is indicative of a sample that contains mostly hexagonal BaCl_2 [2]. The 285°C heat treatment sample reveals a violet luminescence, which is indicative of a sample that contains mostly orthorhombic BaCl_2 [2].

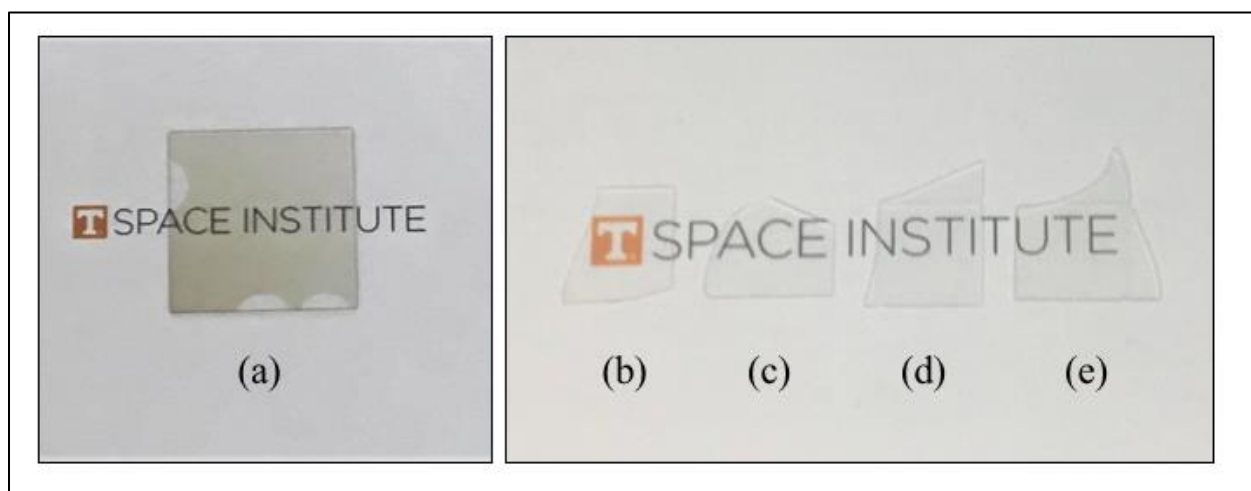


Figure 33. Picture of glass ceramic thin film sample CWB019 with different heat treatment temperatures. Different maximum temperatures: (a) No heat treatment. (b) 270°C (c) 275°C (d) 280°C (e) 285°C.

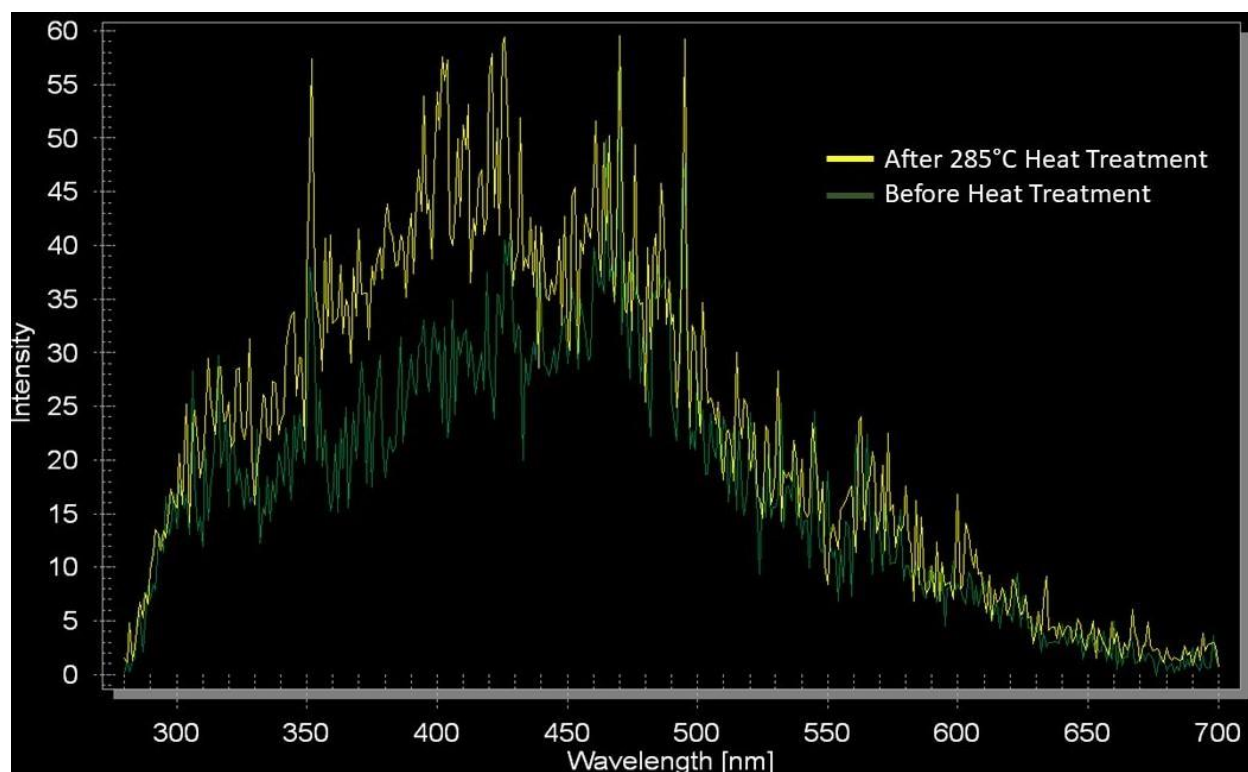


Figure 34. PL emission spectra of sample CWB019 before and after heat treatment of 285°C. Samples were excited at 270 nm and observed between 280 and 700 nm.

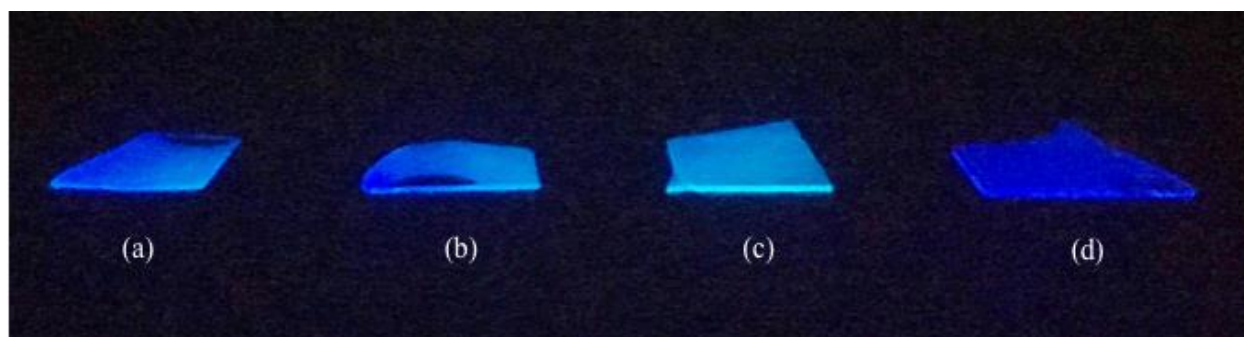


Figure 35. Samples CWB019 that were heat treated to four different maximum temperatures excited by a 254 nm light. Different temperatures: (a) 270°C (b) 275°C (c) 280°C (d) 285°C.

The emission of a storage phosphor will decay exponentially over time when irradiated with x-rays and subsequently stimulated with a laser. The glass ceramic film uses $\text{BaCl}_2\text{:Eu}^{2+}$ as luminescent centers, which needs to be in the orthorhombic phase to exhibit storage phosphor capabilities [3]. Based on the visual inspection results, the only sample that had primarily orthorhombic BaCl_2 was the sample heat treated with a maximum temperature of 285°C . The PSL characterization results corresponded with this determination with the 285°C heat treated sample being the only sample whose emission followed an exponential decay curve. The PSL results are shown in Figure 36 with a decay curve fit plotted on the data.

Conclusion

A method for creating layered glass-ceramic thin films via PLD using a multicomponent target was developed. Mock ablations on laser paper show that precision control of target movement was achieved and can be used for multicomponent targets. Stylus profilometer and optical profilometer results show that the ZLANI deposition rate can be predicted via a linear regression equation. The newly developed method was used to create an imaging plate for computed radiography, which contained a higher percentage of Eu-doped orthorhombic BaCl_2 luminescent centers than could be achieved through conventional techniques. PSL results indicate the developed samples can be used as storage phosphor plates with potential applications in high-resolution computed radiography.

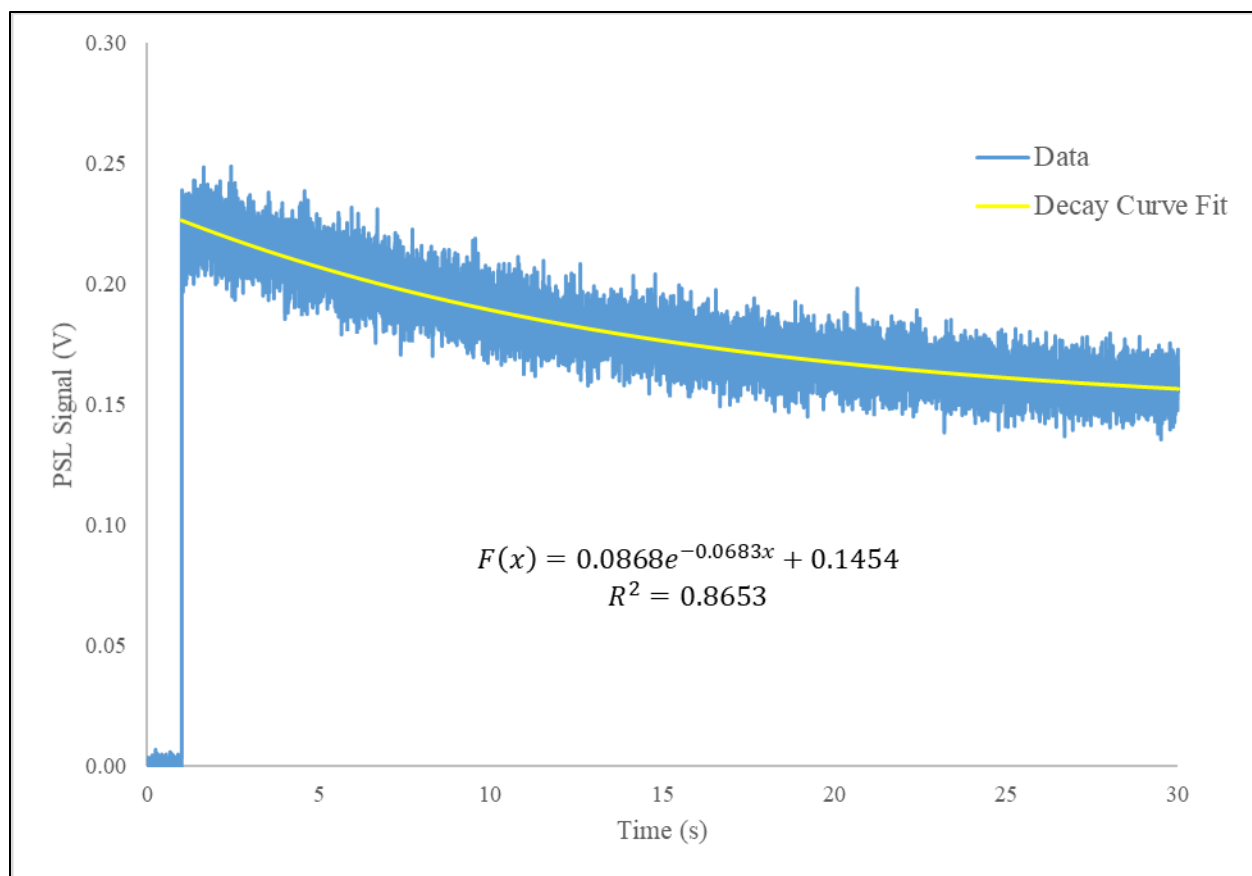


Figure 36. PSL curve form sample CWB 019 following a 285°C heat treatment.

CONCLUSION

Fluoride glass thin films were successfully synthesized via PLD without a fluorine processing gas, a result not found previously in literature. Circumventing a toxic processing gas leads to a safer and simpler experimental procedure. The films were used as a glass matrix to enclose rare earth doped BaCl_2 nanocrystals resulting in a transparent thin film storage phosphor plate.

The fluoride glass thin films were deposited with a slight coloration, which is hypothesized to be due to color centers. When energy was applied in the form of heat, the films became colorless while transparency was maintained. The maximum temperature experienced by the films can be correlated to the transmission, suggesting their potential use as passive temperature sensors.

A method for creating transparent thin film storage phosphor plates, with a higher percentage of Eu-doped orthorhombic BaCl_2 luminescent centers has been demonstrated. Optimization of this method could lead to storage phosphor plates with resolution and PSL light output superior to commercial plates.

REFERENCES

1. Tran, D.C., G.H. Sigel, and B. Bendow, HEAVY-METAL FLUORIDE GLASSES AND FIBERS - A REVIEW. *Journal of Lightwave Technology*, 1984. 2(5): p. 566-586.
2. Torres, A. and R. Barr, A quantitative characterization of micro-gravity and unit-gravity processed ZBLAN glass. *Materials Characterization*, 2015. 107: p. 386-397.
3. Harrington, J.A., *Infrared Fibers and Their Applications*. 2004: SPIE Press.
4. Zhu, X. and N. Peyghambarian, High-Power ZBLAN Glass Fiber Lasers: Review and Prospect. *Advances in OptoElectronics*, 2010. 2010.
5. Dejneka, M., The luminescence and structure of novel transparent oxyfluoride glass-ceramics *JOURNAL OF NON-CRYSTALLINE SOLIDS* 1998. 239(1-3): p. 149-155.
6. Leonard, R.L., et al., Rare earth doped downshifting glass ceramics for photovoltaic applications. *Journal of Non-Crystalline Solids*, 2013. 366: p. 1-5.
7. El-Agmy, R.M. and N.M. Al-Hosiny, 870 mW blue laser emission at 480 nm in a large core thulium doped ZBLAN fiber laser. *Laser Physics*, 2010. 20(4): p. 838-841.
8. Evans, A.W., *Fluorochlorozirconate Glass Ceramics for Computed Radiography*. 2016, University of Tennessee.
9. Leonard, R.L., et al., Evaluation of a Fluorochlorozirconate Glass-Ceramic Storage Phosphor Plate for Gamma-Ray Computed Radiography *JOURNAL OF THE AMERICAN CERAMIC SOCIETY* 2015. 98(8): p. 2541-2547.
10. Leonard, R.L., *Fluorochlorozirconate Glass Ceramics for Photovoltaic and Computed Radiography Applications*. 2015, University of Tennessee.
11. Leonard, R.L., A.R. Lubinsky, and J.A. Johnson, The effects of sodium fluoride content on the properties of fluorochlorozirconate glass-ceramic storage phosphors. *Journal of the American Ceramic Society*, 2017. 100(4): p. 1551-1560.
12. Chen, G.C., et al., Fluorozirconate-based nanophase glass ceramics for high-resolution medical X-ray imaging *JOURNAL OF NON-CRYSTALLINE SOLIDS* 2006. 352(6-7): p. 610-614.
13. Johnson, J.A., S. Schweizer, and A.R. Lubinsky, A glass-ceramic plate for mammography. *Journal of the American Ceramic Society*, 2007. 90(3): p. 693-698.
14. Schweizer, S., Physics and current understanding of X-ray storage phosphors *PHYSICA STATUS SOLIDI A-APPLICATIONS AND MATERIALS SCIENCE* 2001. 187(2): p. 335-393.
15. Schweizer, S., et al., Photostimulated luminescence in Eu-doped fluorochlorozirconate glass ceramics. *Applied Physics Letters*, 2003. 83(3): p. 449-451.
16. Schweizer, S., A.R. Lubinsky, and J.A. Johnson, Fluorozirconate-based glass-ceramic storage phosphors for digital mammography, in *Medical Imaging 2007: Physics of Medical Imaging*, Pts 1-3, J. Hsieh and M.J. Flynn, Editors. 2007.
17. Alvarez, C.J., et al., Structural and Kinetic Analysis of BaCl₂ Nanocrystals in Fluorochlorozirconate Glass-Ceramics. *Journal of the American Ceramic Society*, 2015. 98(4): p. 1099-1104.
18. Lowndes, D.H., et al., Synthesis of novel thin-film materials by pulsed laser deposition. *Science*, 1996. 273(5277): p. 898-903.

19. Chrisey, D.B. and G.K. Hubler, Pulsed Laser Deposition of Thin Films. 1994: Wiley.
20. Willmott, P.R. and J.R. Huber, Pulsed laser vaporization and deposition. Reviews of Modern Physics, 2000. 72(1): p. 315-328.
21. Singh, R.K. and J. Narayan, PULSED-LASER EVAPORATION TECHNIQUE FOR DEPOSITION OF THIN-FILMS - PHYSICS AND THEORETICAL-MODEL. Physical Review B, 1990. 41(13): p. 8843-8859.
22. Desantolo, A.M., et al., PREPARATION OF HIGH-TC AND JC FILMS OF BA₂YCU₃O₇ USING LASER EVAPORATION OF A COMPOSITE TARGET CONTAINING BAF₂. Applied Physics Letters, 1988. 52(23): p. 1995-1997.
23. Ohring, M., Chapter 1 - A Review of Materials Science, in Materials Science of Thin Films (Second Edition). 2002, Academic Press: San Diego. p. 1-56.
24. Lanca, L. and A. Silva, Digital Imaging Systems for Plain Radiography. 2012: Springer New York.
25. Johnson, J.J., et al., Eu-activated fluorochlorozirconate glass-ceramic scintillators JOURNAL OF APPLIED PHYSICS 2006. 100(3).
26. Evans, A.W., et al., The effect of trivalent iron on the properties of fluorochlorozirconate glass ceramics. Journal of Non-Crystalline Solids, 2018. 484: p. 8-13.
27. Dimitri Ganser, J.G., Uwe Mackens, Ulrich Weichmann, Pulsed laser deposition of fluoride glass thin films. Applied Surface Science, 2010. 257(3): p. 954-959.
28. Jens Gottman, et al., Laser deposition and structuring of laser active planar waveguides of Er : ZBLAN, Nd : YAG and Nd : GGG for integrated waveguide lasers in PROCEEDINGS OF THE SOCIETY OF PHOTO-OPTICAL INSTRUMENTATION ENGINEERS (SPIE) W.L. Pfleging, Y; Washio, K; Bachmann, FG; Hoving, W Editor. 2007. p. W4590-W4590.
29. France, P.W., Fluoride Glass Optical Fibres. 2012: Springer Netherlands.
30. Hehlen, M.H., et al., Synthesis of ultrapure ZBLAN glass for laser refrigeration Proceedings of SPIE ed. R.S. Epstein, M Vol. 6907. 2008.
31. L.J. Andrews, B.T.H., Robert C. Folweiler, Cornelius T. Moynihan, In Situ Oxidation of Heavy Metal Fluoride Glasses. Materials Science Forum, 1991. 32-33: p. 43-48.
32. Bruce T. Hall, G.L.J., W.R.C. Andrews, and B. Folweiler, all of Mass., METHOD FOR PREPARING FLUORIDE GLASSES. 1991, GTE Laboratories Incorporated, Waltham, Mass. p. 6.
33. James Shelby, M.L., Introduction to Glass Science and Technology. 2005: Royal Society of Chemistry.
34. Wang, L., et al., Kinetic surface roughening and wafer bow control in heteroepitaxial growth of 3C-SiC on Si(111) substrates. Scientific Reports, 2015. 5.
35. Greer, J., Large-Area Commercial Pulsed Laser Deposition, in Pulsed Laser Deposition of Thin Films. 2006, John Wiley & Sons, Inc. p. 191-213.
36. Kim, H.S. and H.S. Kwok, Correlation between target-substrate distance and oxygen pressure in pulsed laser deposition of YBa₂Cu₃O₇. Applied Physics Letters, 1992. 61(18): p. 2234-2236.

37. Aasland, S. and T. Grande, Crystallization of ZBLAN Glass. *Journal of the American Ceramic Society*, 1996. 79(8): p. 2205-2206.
38. Griscom, D.L., DEFECT CENTERS IN HEAVY-METAL FLUORIDE GLASSES - A REVIEW. *Journal of Non-Crystalline Solids*, 1993. 161: p. 45-51.
39. Prince, J.L. and J.M. Links, *Medical Imaging Signals and Systems*. 2012: PRENTICE HALL.
40. Leonard, R.L., et al., Evaluation of a Fluorochlorozirconate Glass-Ceramic Storage Phosphor Plate for Gamma-Ray Computed Radiography. *Journal of the American Ceramic Society*, 2015. 98(8): p. 2541-2547.
41. King, J.E., Doping of Fluorochlorozirconate and Borate-Silica Glass Ceramics for Medical Imaging and Fast Neutron Scintillation. 2015, University of Tennessee.
42. Gray, S.K., An Investigation of Rare Earth Co-doping in Fluorochlorozirconate Glass-Ceramic Imaging Plates to Improve the Storage Phosphor Properties for Computed Radiography. 2013, University of Tennessee.
43. David Hamric, M., Inc. Rare-Earth Metal Long-Term Air Exposure Test. 2007; Available from: http://www.elementsales.com/re_exp/.
44. Hollas, J.M., *Modern Spectroscopy*. 2004: Wiley.
45. R.L. Leonard, A.Y.T., C. Thompson, R.A. Erck, J.A. Johnson, Antifog coating for bronchoscope lens. *Surface Engineering*, 2012. 28(6): p. 468-472.
46. Leonard, R.L., *Synthesis and Characterization of Diamond-like Carbon Thin Films for Biomedical Applications*. 2010, University of Tennessee.

APPENDIX



Figure A1. Glovebox and adjacent tube furnace for bulk glass synthesis.



Figure A2. ZLANI glass films deposited by PLD for (A) 30 min, (B) 1 hour, (C) 2 hours, (D) 3 hours, (E) 4 hours). The witness marks where the substrates were mounted to the substrate holder can be seen in images B-E.

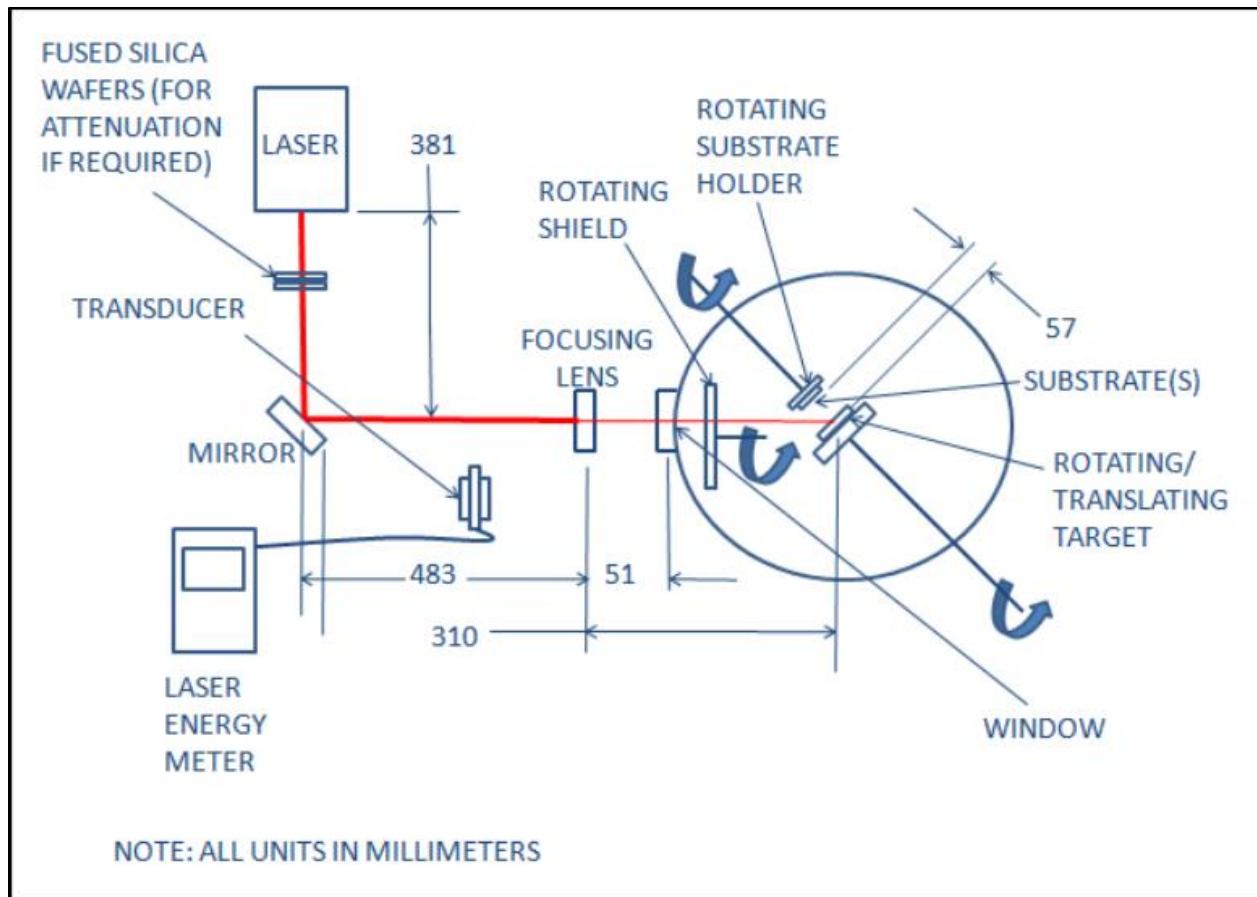


Figure A3. Schematic of the Laser and System Optic with Relevant Dimensions. [44, 45]. Used with permission.

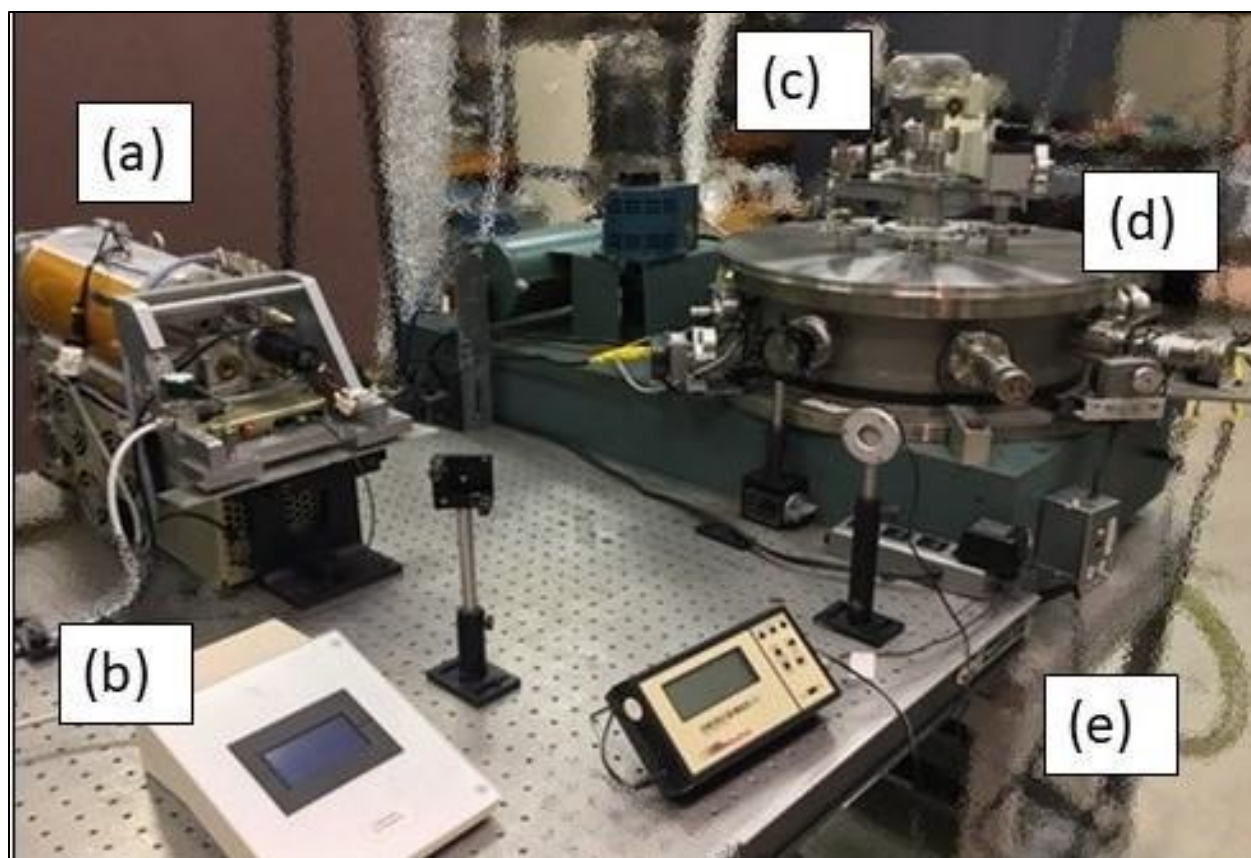


Figure A4. Pulsed laser deposition system at UTSI. (a) 193nm excimer laser (b) laser controller (c) ion gauge (d) vacuum chamber (e) vacuum system.

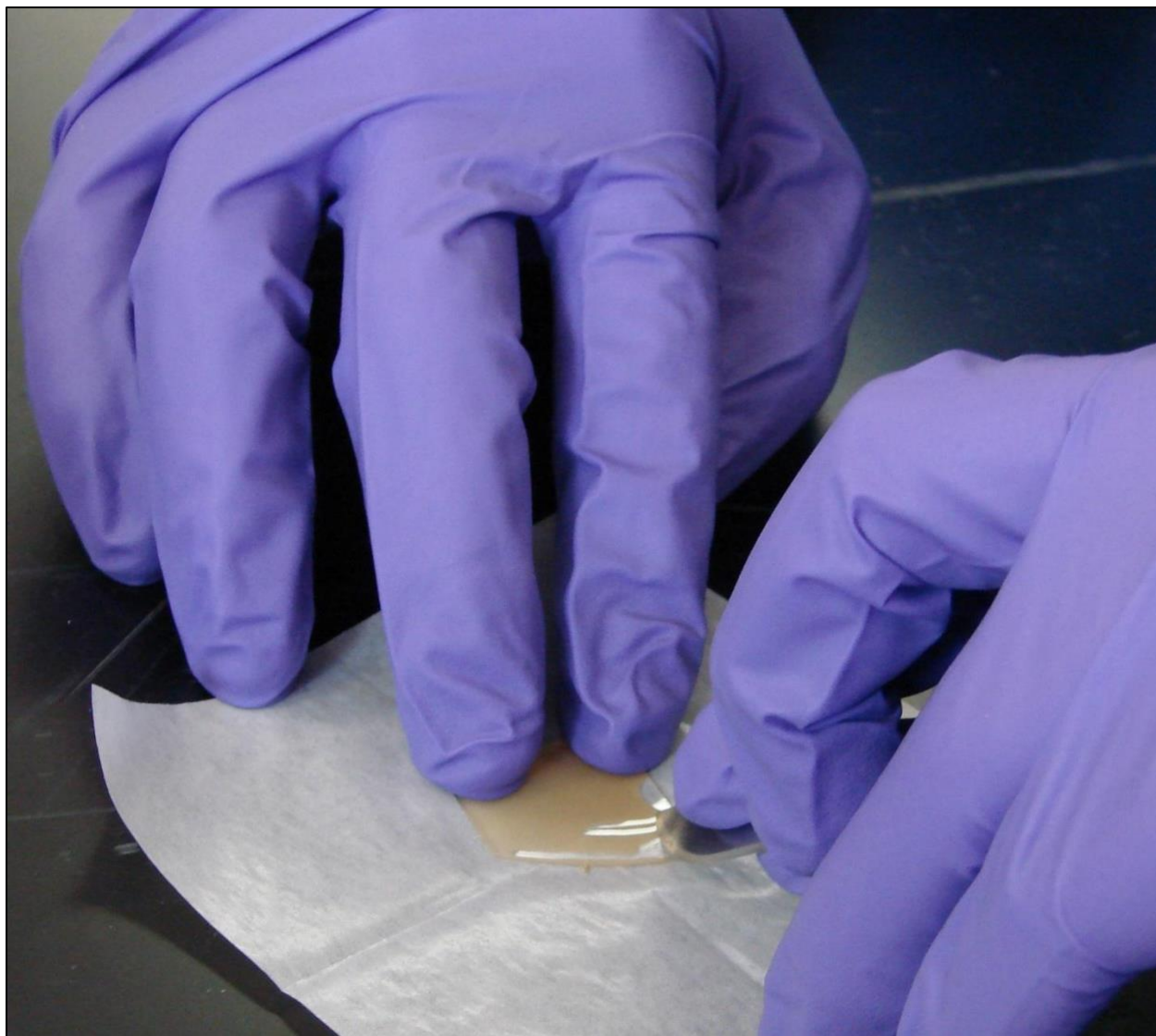


Figure A5. Scrapping film off fused silica substrate to obtain sample material for DSC characterization.

MATLAB script used to develop Qprogram for target motor movement:

```
close all; clear all; clc; clear vars;

%Degrees to Steps Conversion
Convert= 2e6/360;

%Laser Frequency
LaserFreq= 10;

%Inverse Deposition Rates (Pulses/Meter)
    %Zone 1 Rate
R1= %input ZLANI deposition rate;
    %Zone 2 Rate
R2= %input BaCl2 deposition rate;
    %Zone 3 Rate
R3= (R1+R2)/2;

%Zone 1 (ZLANI)
prompt= 'Size of ZLANI wedge (degrees): ';
Z1= input(prompt);
prompt= 'Thickness of ZLANI layer (nm): ';
T1= input(prompt);
prompt= 'Number of passes through ZLANI layer: ';
P1= input(prompt);
%Zone 2 (BaCl)
prompt= 'Size of BaCl wedge (degrees): ';
Z2= input(prompt);
prompt= 'Thickness of BaCl layer (nm): ';
T2= input(prompt);
prompt= 'Number of passes through BaCl layer: ';
P2= input(prompt);
%Zone 3 (Eu)
prompt= 'Size of Eu wedge (degrees): ';
Z3= input(prompt);
prompt= 'Thickness of Eu layer (nm): ';
T3= input(prompt);
prompt= 'Number of passes through Eu layer: ';
P3= input(prompt);

%Size of Uncertainty
prompt= 'Total Size of Uncertainty for 1 wedge (degrees): ';
Unc= input(prompt);
%Unc=4;

%Zones After Uncertainty
Z1= Z1-Unc;
Z2= Z2-Unc;
Z3= Z3-Unc;

%Speed Per Zone
Speed1= ((Z1/((R1*(T1/1e9))/LaserFreq)/P1))/360)*100;
```

```

Speed2= (((Z2/((R2*(T2/1e9))/LaserFreq)/P2))/360)*100;
Speed3= (((Z3/((R3*(T3/1e9))/LaserFreq)/P3))/360)*100;

%Steps Per Zone
Z1= Z1*Convert;
Z2= Z2*Convert;
Z3= Z3*Convert;
Z1= round(Z1);
Z2= round(Z2);
Z3= round(Z3);

%%Begin Q Program Code%
clc

%Initial Movement
disp('VE 50')
InitialMovement= Unc/2;
InitialMovement= InitialMovement*Convert;
InitialMovement= round(InitialMovement);
fprintf('DI %d',InitialMovement); disp(' ')
disp('FL')
disp('WT 5')

%Zone 1
fprintf('VE %d',Speed1); disp(' ')
fprintf('RX 1 %d', round((P1-1)/2)); disp(' ')
fprintf('DI %d',Z1); disp(' ')
disp('FL')
fprintf('DI %d',-Z1); disp(' ')
disp('FL')
disp('QR 1 7')
fprintf('VE %d',Speed1); disp(' ')
fprintf('DI %d',Z1); disp(' ')
disp('FL')

%Uncertainty Region 1
disp('VE 50')
Unc= Unc*Convert;
fprintf('DI %d',round(Unc)); disp(' ')
disp('FL')

%Zone 2
fprintf('VE %d',Speed2); disp(' ')
fprintf('RX 2 %d', round((P2-1)/2)); disp(' ')
fprintf('DI %d',Z2); disp(' ')
disp('FL')
fprintf('DI %d',-Z2); disp(' ')
disp('FL')
disp('QR 2 20')
fprintf('VE %d',Speed2); disp(' ')
fprintf('DI %d',Z2); disp(' ')
disp('FL')

%Uncertainty Region 2
disp('VE 50')

```

```

fprintf('DI %d',round(Unc)); disp(' ')
disp('FL')

%Zone 3
fprintf('VE %d',Speed3); disp(' ')
fprintf('RX 3 %d', round((P3-1)/2)); disp(' ')
fprintf('DI %d',Z3); disp(' ')
disp('FL')
fprintf('DI %d',-Z3); disp(' ')
disp('FL')
disp('QR 3 33')
fprintf('VE %d',Speed3); disp(' ')
fprintf('DI %d',Z3); disp(' ')
disp('FL')

%Place back to zero point
disp('VE 50')
%Unc= Unc*Convert;
fprintf('DI %d',InitialMovement+1); disp(' ')
disp('FL')

%Error Check
Check= (InitialMovement*2)+(round(Unc)*2)+Z1+Z2+Z3+1;

if Check < 2e6
    clc
    disp('ERROR: Program does not complete full circle')
end

```

Example of resultant Q program:

VE	50	
DI	83333	
FL		
WT	5	
VE	1.012	
RX	1	2
DI	1455556	
FL		
DI	-1455556	
FL		
QR	1	7
VE	1.012	
DI	1455556	
FL		

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VE	50	
DI	88889	
FL		
VE	1.062	
RX	2	19
DI	205556	
FL		
DI	-205556	
FL		
QR	2	20
VE	1.062	
DI	205556	
FL		
VE	50	
DI	44444	
FL		
VE	1.103	
RX	3	7
DI	122222	
FL		
DI	-122222	
FL		
QR	3	33
VE	1.103	
DI	122222	
FL		
VE	50	
DI	83333	
FL		

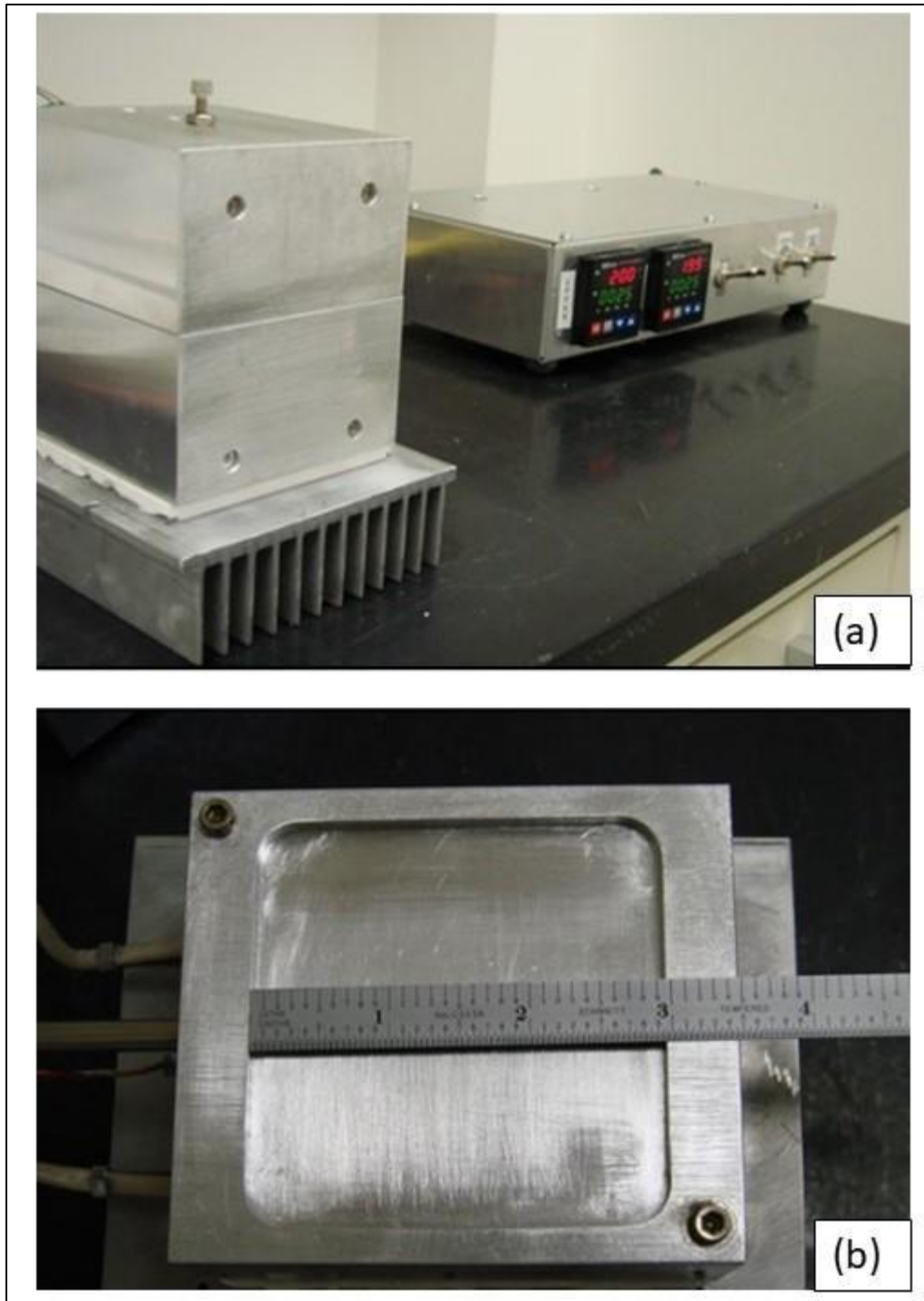


Figure A6. (a) A programmable heat treatment system and (b) the interior of the heat treatment chamber.[10]
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VITA

Charles William Bond was born in Tullahoma, Tennessee on January 17, 1993 to David and Tina Bond. He has a younger sister, Paige, and an older brother, Chris. He was raised in Tullahoma, Tennessee and graduated from Tullahoma High School in 2011. He graduated from University of the Cumberlands in Williamsburg, KY with a Bachelor of Science Degree in Chemistry in 2015. In 2016, Charles accepted a graduate research assistantship at the University of Tennessee Space Institute to pursue a Master's of Science degree in Biomedical Engineering under Dr. Jacqueline Johnson. After obtaining his Master's Degree, he will be continuing his education towards a Doctor of Philosophy at The University of Tennessee Space Institute in the same group.