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Increased conductivity of fluoride glass due to mixed-valent rare-earth ions

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**INCREASED CONDUCTIVITY OF FLUORIDE GLASS DUE TO MIXED-VALENT
RARE-EARTH IONS**

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Mischa Ann Plesha

December 2002

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A handwritten signature in black ink, appearing to read "Roger H. Terrill", written over a horizontal line.

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ABSTRACT

INCREASED CONDUCTIVITY OF FLUORIDE GLASS DUE TO MIXED-VALENT RARE-EARTH IONS

By Mischa Ann Plesha

Adding mixed-valent rare-earth ions increases the total conductivity of fluoride-containing glasses. This was demonstrated by establishing baseline conductivity due to F^- ion conductivity and creating glasses with variable amounts of Eu^{3+} and Eu^{2+} to measure the increased conductivity due to electron hopping. The host material is a fluorozirconate glass, ZBLAN, which contained 53% ZrF_4 , 20% BaF_2 , 4% LaF_3 , 3% AlF_3 , and 20% NaF . The most successful methods of maintaining EuF_2 concentrations include heating in a reducing atmosphere and adding chemical reductants to the starting components. Samples were created with EuF_2 present ranging from 0.1 mol% to 3.48 mol%. Samples were characterized using quantitative and qualitative forms of analysis to include differential scanning calorimetry, cyclic voltammetry, and Ultraviolet-Visible and IR spectra. The solid-state conductivity was performed using a 2-probe, open face configuration. The conductivity increased at the lower temperature range for the mixed-valent species containing the highest concentration of EuF_2 .

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1. Introduction

1.1 Research Objective

The long-term goal of this research project is to create luminescent materials from fluoride-containing glasses. This thesis deals with a subset of the above stated objective, namely, to introduce electronic conductivity into a member of the fluoride glass family of materials by the substitution of mixed-valent Europium (i.e., $\text{Eu}^{2+/3+}$) centers for La^{3+} and Ba^{2+} ions respectively in a well-known glass forming composition. In this case, electron transfers between Eu centers are expected to be the charge transport mechanism. In a simple bimolecular kinetic theory [1], the concentration product ($[\text{Eu}^{2+}][\text{Eu}^{3+}]$) of the mixed-valent species should dictate the electron-hopping based contribution to the glass conductivity, so the experiments have been directed at preparing glass samples that have a range of known amounts of Eu^{2+} and Eu^{3+} . In addition to well-characterized ZBLAN control samples, a series of samples were prepared with 4 mol% Eu^{3+} , thus replacing all of the La^{3+} with a close structural analog. The strategy from that point was to chemically reduce a portion of the Eu^{3+} to Eu^{2+} to form what will be termed a “mixed-valent” sample. Mixed-valent compositions are expected to exhibit greater conductivity than pure Eu^{3+} or pure Eu^{2+} containing glasses because of an electronic conduction contribution attributable to electron hopping or self-exchange between EuF_2 and EuF_3 :

Once electron transfers can be established in the desired fluoride glass, then the long term

goal of luminescence can be approached in a fashion similar to electrogenerated chemiluminescence – where energetic cross electron transfers create luminescent products.

Measurements of the temperature dependence of the glass conductivity are key to unraveling the relative contributions of electron transfers and ion motions to charge transport. Specifically, it will be argued that the observed elevation of the near-room temperature conductivity for those samples with substantial $[\text{Eu}^{2+}][\text{Eu}^{3+}]$ is due to electron-transfer based conduction. In this model, electrons “hop” from Eu^{2+} to Eu^{3+} species throughout the sample, and evidently electrons are able to move more rapidly than fluoride ions at lower temperatures. This may be understood as a difference in the activation energies for ion and electron transfers – the former being more strongly activated (and more abundant) naturally dominates at higher temperature, while the less abundant, and less impeded electron transfers exceed the ions contributions below a certain threshold temperature.

1.2 Properties of Fluoride Glasses

A material that does not scatter light is the phenomenological way to describe a glass. The bulk optical properties of heavy metal fluoride glasses make them particularly useful for many applications such as optical fibers, laser hosts and ultra-low thermal distortion optics. Some notable properties of fluoride glasses include extended infrared (IR) transmission, low to moderate refractive index, good ultraviolet (UV) transmission

and much lower absorption and scattering losses than standard SiO_2 based glasses, especially in the near infrared [2-3]. Fluorozirconate glasses in particular are known to be quite stable and hence are employed in this study.

Although in many cases the addition of new components to the base composition can spoil glass formation, the most stable glasses are formed from multi-component mixtures. For example, most ternary glasses are more stable than binary compositions and likewise, quaternary glasses are often more stable than ternary glasses. The range of metal fluoride compositions that can readily form glasses when quenched from the molten state are often characterized by ternary (or pseudo-ternary) phase diagrams. For example, the pseudo-ternary phase diagram in Figure 1 illustrates the relatively narrow range of compositions that result in the stable vitrification of a particular fluoro-zirconate glass. The central point in this phase diagram corresponds to the one for which glass will form (as opposed to recrystallize) at a minimal cooling rate. The characteristics of a glass can be changed by adding components or by replacing one or more components. For example, AlF_3 is used as a stabilizer. Other components can alter the devitrification rates or cooling rates, mechanical strength or durability [4].

1.2.1 Properties of ZBLAN

The fluoride glass composition used in this study dubbed “ZBLAN” is widely viewed as the most stable one achieved. ZBLAN is composed of ZrF_4 , BaF_2 , LaF_3 , AlF_3 , and NaF [4]. The family of glasses in which ZrF_4 is the main component are known as fluoro-zirconates since ZrF_4 is assumed to be largely responsible for enabling the

Figure 1. Pseudo-ternary phase diagram for ZBLAN

vitrification process [4]. In the ZBLAN composition, ZrF_4 is considered the glass progenitor and BaF_2 the glass stabilizer. AlF_3 acts to stabilize the ZBLAN composition, but can act as a progenitor in other glass-forming recipes.

Like other fluoride glasses, ZBLAN is formed from molten salt mixtures and can be quench cast by a variety of methods. The ability to replace certain elements with others allows one to change the properties of the glass. Apropos to this study, a certain amount of the trivalent species LaF_3 can be replaced with EuF_3 in order to yield a doped ZBLAN sample because the ions are similar in size and chemistry. However, total lanthanide content will spoil glass formation if it exceeds 10 mol% [4]. Likewise, the EuF_3 can be chemically reduced in order to generate EuF_2 , which, in theory, could replace a certain amount of the divalent species BaF_2 [4].

1.3 Reduction of EuF_3

The partial reduction of EuF_3 to EuF_2 in the glass is of central importance to this thesis. Reduction of EuF_3 was necessary since efforts to make a mixed-valent glass by having both EuF_3 and EuF_2 present as starting materials proved unsuccessful since the EuF_2 would oxidize to EuF_3 . Both chemical and electrochemical methods used to reduce EuF_3 to EuF_2 in similar fluoride glasses were recently documented [5-6].

Electrochemical reduction, while in theory highly controllable, requires a specialized cell that can separate unavoidable anodic oxidation products from the working cathode so that the Eu^{2+} species are not re-oxidized in a cyclical reaction. This has not yet been achieved [5]. Similar to the work of MacFarlane, et al, these experiments demonstrated that the

addition of chemical reductants (e.g. CaH_2 , LiH , NaH , LiBH_4 , and $\text{ZrH}_{1.9}$) results in the formation of EuF_2 , however, these hydride reducing agents sometimes reduce ZrF_4 , which affects the glass quality and leaves gray or black deposits. The results in this work also agree with MacFarlane, et al, in that preparing the sample in a reducing atmosphere (4-25% H_2/Ar or H_2/N_2) is another method that will generate EuF_2 , however, only the surface of the sample will react unless the melt time is increased which unfortunately incurs a loss of ZrF_4 by sublimation [5].

1.4 Fluoride Ion Conduction

ZBLAN and closely related fluorozirconate glasses exhibit substantial F^- ion conductivity in the solid state. This conductivity is present as a background upon which the electron-transfer based conduction demonstrated in the thesis appears. With the exception of mixed Li^+/F^- conducting or exclusively Li^+ conducting systems (when $[\text{Li}^+] > 30\%$), F^- ions are believed to be the only mobile ions in the fluorozirconate glasses. In the alkali metal series $\text{Na} \rightarrow \text{Cs}$, F^- ion mobility clearly increases with the ionic radius of the alkali metal cation [7-12]. Fluorozirconate glass F^- conductivity ranges from 10^{-6} to $2 \times 10^{-5} \text{ S cm}^{-1}$ at 200°C [7, 12-15], where S is the conductance value, Siemen, with units of inverse ohms. Currently, the highest recorded fluoride glass conductivity reported is $10^{-4} \text{ S cm}^{-1}$ at 200°C for a glass comprised of In, Sn and Pb fluorides [9].

NMR data [7-11] indicate that fluoride ions occupy both bridging (e.g. Zr-F-Zr) and non-bridging sites (e.g. interstitial) in fluorozirconate systems. The bridging ions, since they are structurally linked to metal ions, are far less mobile than the non-bridging

species and thus do not contribute measurably to the glass conductivity [16].

1.5 Lanthanide Chemistry & Europium Properties

Europium is quite stable in the Eu^{3+} form and is one of only a few lanthanides to form a stable 2^+ oxidation state. Eu^{2+} is a strong reducing agent, with standard electrode potential $E^0 = -0.43 \text{ V}$ versus the standard hydrogen electrode potential [17] in aqueous solution. The electronic configuration of Eu^{3+} in the ground state is $4f^6$, with a term symbol of 7F_0 , with 6 unpaired electrons. This means the f shell is almost half-filled. The addition of one electron to Eu^{3+} results in the relatively favorable $4f^7$ configuration, hence Eu^{2+} is relatively accessible.

In order for the long-term objective of electrogenerated chemiluminescence to work with fluoride glasses, Eu^{2+} or Eu^{3+} must fluoresce in inorganic settings, which it does [18]. The ligand based photoluminescence of the La^{3+} species is strong relative to the bare ion photoluminescence. Ligand-based photoluminescence occurs when a ligand is exposed to UV light. The UV light excites an atom and promotes the electron to an elevated energy level. After some period of time, relaxation can occur in one of several methods. Relaxation can lead to a thermal release of energy. Also, there can be a luminescent reaction when the ligand is excited by UV light where either the ligand fluoresces or the ligand transfers the energy to a metal ion and then the metal ion fluoresces.

The condensed phase, either solid or liquid, of ions and molecules generally exhibit broad absorption and emission peaks. In contrast, the lanthanide ions are quite

chemically inert and exhibit unusually sharp optical absorbances and emissions, attributable to electronic transitions. Both forbidden $f-f$ and allowed $d-f$ transitions are observed when excited states relax in radiative relaxations. This property (narrow bands) is due to the fact that the partially populated $4f$ shell is physically surrounded by and thereby heavily shielded within the filled $5s$ orbital [19]. Population of the f orbital is responsible for the unique Europium photo-physics.

Other noteworthy characteristics of Eu that are not centrally related to this thesis include the following. The shielding of $4f$ electrons by one another is imperfect and leads to lanthanide contraction in s and p orbitals due to poor shielding by d and f electrons, wherein atomic and ionic radii decrease as atomic number increases [19]. Eu^{3+} differs from other lanthanides because the very low-lying first, second and third electronic excited states are thermally populated at room temperature [19]. Eu^{2+} and Eu^{3+} , like other lanthanides, are paramagnetic because of the large number of unpaired electrons [19]. The principle absorption bands of Eu^{3+} are located at 375.5 nm and 394.1 nm [19].

1.6 Electrogenerated Chemiluminescence: Future Work

The application of this work is to create electroluminescent materials based on fluoride glasses. At this point, this is envisioned happening via a process known as electrogenerated chemiluminescence (ECL). In ECL, reactants generated at a cathode, an anode, or reactant pairs generated at cathode/anode pairs react to produce luminescent products. In ECL, the products of an electron transfer reaction are produced in electronically excited states, that may decay radiatively [20-21]. In lanthanides this was

observed by Richter et al. [20] when an electron was transferred from a ligand singlet state to the excited energy level of the rare earth metal center (4f level orbital) or when there was an energy transfer from a ligand to a metal ion and then the metal ion fluoresced.

This concept is illustrated recently in the solid state [22-23]. Light emitting diode-like behavior in solid polymeric films of a Ruthenium bipyridyl polymer was demonstrated. The following reaction accounts for light emission in that setting:

The basis for this reaction and the charge transport/electron-hopping mechanism can be illustrated with the diagram shown in Figure 2. This is the same scheme that is being pursued in the ZBLAN matrix.

Introducing Eu^{3+} and Eu^{2+} into ZBLAN could potentially result in electrogenerated chemiluminescence. The proposed mechanism for future work would not be centered on ligand-based luminescence. Rather, the introduction of a charge at the anode would lead to the oxidation of a second mixed-valent pair, eg. Ce^{3+} to Ce^{4+} , for example, and initiate a cyclic reaction analogous to that illustrated in Figure 2. This redox reaction serves as the 'donor' and provides the electron necessary to reduce Eu^{3+} to Eu^{2+} at the cathode. This redox cross-reaction between $\text{Ce}^{4+} + \text{Eu}^{2+} \rightarrow \text{Ce}^{3+} + \text{Eu}^{3+}$ may result in Ce^{4+} and Eu^{2+} and the formation of an excited electronic state. When this ion relaxes it will produce a photon.

Figure 2. Model for electrogenerated chemiluminescence

1.7 Outline of Research

Below is a brief outline of the various elements that comprised this research and the reasons for conducting each segment. Briefly, this thesis details the preparation, analysis and electrical characterization of ZBLAN samples that contain variable amounts of both Eu^{3+} and Eu^{2+} .

The ZBLAN composition used contained 53% ZrF_4 , 20% BaF_2 , 4% LaF_3 , 3% AlF_3 and 20% NaF . This composition is known to be quite stable. ZBLAN starting materials were measured out in a water-free dry box, transferred to a platinum crucible and then heated in a N_2 -purged box furnace. A dry environment is critical in order to prevent oxidation of the Eu^{2+} to Eu^{3+} . Differential scanning calorimetry (DSC) was used to characterize the ZBLAN.

Cyclic voltammetry was done on the molten ZBLAN to demonstrate the oxidation-reduction (redox) reactions that would take place in ZBLAN and that Eu^{2+} can survive in this ZBLAN system. It was critical to understand the limits of oxidation and reduction in ZBLAN and then how $\text{Eu}^{3+/2+}$ would affect those limits. If one of the elements of ZBLAN were to experience either oxidation or reduction before Eu^{3+} , it would be impossible to observe the redox of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$.

Several different experimental methods were tried in order to produce mixed-valent samples. The initial method was to add all components at once and heat the covered Pt crucible under a N_2 atmosphere. Adding the EuF_2 in the final minutes of the heating process, either in the powder form or in a shaped pellet was also tried. Next

chemical reduction with CaH_2 was tried in order to convert some or all of the EuF_3 to EuF_2 . All of the above methods were partially successful, however, the EuF_2 content was still not significant enough. Also, there needed to be a way to generate samples with variable amounts of EuF_3 and EuF_2 . The most successful method was the final method. This involved heating the ZBLAN and Eu^{3+} in an open Pt crucible held in a quartz cell and in a reducing atmosphere (forming gas, 4% H_2/N_2).

Ultraviolet-Visible absorption spectroscopy (UV-VIS) was used to characterize the samples in the range from 600 nm to 350 nm. These absorption spectra were the primary method of first determining whether or not Eu^{2+} and Eu^{3+} were present and then finally determining the Eu^{2+} and Eu^{3+} content. By measuring the Eu^{3+} still remaining in the sample, it was possible to determine how much Eu^{3+} had been converted to Eu^{2+} . Magnetic susceptibility was used to verify the spectroscopic results concerning the Eu^{2+} and Eu^{3+} content.

Solid-state measurements of the conductivity as a function of temperature and mixed-valent Europium species were the final portion of the analysis. A Fourier transform was used to measure conductivity based on frequency dependent impedance calculations. In this work there is a demonstrated correlation between Eu^{2+} content and elevated conductivity at low temperatures. Finally, the temperature dependence of the solid-state conductivity (σ) of both pure ZBLAN and doped ZBLAN/ $\text{Eu}^{3+/2+}$ was measured in order to evaluate the possible contribution of $\text{Eu}^{3+}/\text{Eu}^{2+}$ electron transfers to

charge transfers in the sample. In particular, the frequency dependence of the conductivity was measured using a Fourier transform method in order to better resolve the possible contributions of interfacial resistance to the experimental measurements.

2. Experimental

2.1 ZBLAN Components

The components for the glass were anhydrous and of uniformly high purity (99% - 99.99%) and were purchased from Alfa Aesar, with the exception of sodium fluoride (99.9%) which was purchased from Aldrich. The base fluorozirconate glass (ZBLAN) comprised 53% ZrF_4 , 20% BaF_2 , 4% LaF_3 , 3% AlF_3 , and 20% NaF . Europium containing samples were prepared by substituting EuF_3 for LaF_3 such that the total trivalent lanthanide species were at least 4%. EuF_2 was substituted for BaF_2 so that the divalent species did not exceed 20%.

2.2 Glass Preparation

Solid ZBLAN and EuF_2 / EuF_3 glass samples were made by placing the N_2 -purged dry-box ground and batched components into a small (5 cm^3) platinum crucible, and then heating the covered crucible to 825°C for 10 minutes in an N_2 -purged furnace. Chemical reduction was achieved by adding CaH_2 powder to the liquid ZBLAN in the furnace and stirring briefly with a Pt wire, allowing the ZBLAN to react briefly, and then casting solid ZBLAN by pouring the liquid into a 200°C brass mold. For experiments where H_2 reduction was desired, the open crucible was placed into the bottom of a closed quartz tube, heated as described above, and then cooled to 500°C during exposure to a very gentle flow of 4% H_2/N_2 for between 5 and 10 minutes. The crucible was then rapidly cooled (ca. $200^\circ\text{C}/\text{min}$) to 200°C by abruptly increasing the purge gas flow inside and outside the quartz vessel. This temperature was then held for 10 minutes in

order to anneal the glass before the final cooling to room temperature. Temperatures were controlled so that a K-type thermocouple inside the quartz tube and near the crucible achieved the desired temperature. After removing the glass from the crucible or the mold, it was polished to flatness with 2000 3M Imperial Wetordry 401Q paper wetted with ethanol or isopropanol.

2.3 Qualitative and Quantitative Analysis

Electrochemical analysis was performed with an EG&G/Princeton Applied Research Model 263A Potentiostat/Galvanostat using the standard model 273 software. Platinum working, quasi-reference and auxiliary electrodes were introduced into the Pt crucible containing the ZBLAN components and experiments were initiated in the liquid ZBLAN immediately after cooling to 500 °C from a standard 825 °C melting cycle. An N₂ environment was maintained in the quartz tube where the Pt crucible was housed.

ZBLAN was characterized by differential scanning calorimetry (DSC). The analysis was performed using an Al pan from 200-525 °C on an early model Perkin-Elmer DSC.

Infrared spectroscopic characterization was performed at room temperature using the ATI Mattson Infinity Series FTIR. Ultraviolet-Visible (UV-VIS) absorbance was measured at room temperature using a Cary 50 Bio UV-Visible Spectrophotometer. A three-point Eu³⁺ calibration curve was established by preparing ZBLAN standards with concentrations varying from 1 to 8 mol% EuF₃ and measuring the peak absorbance of the prominent Eu(III) band at 390 nm. Eu²⁺ concentrations had to be determined indirectly

because Eu^{2+} does not exhibit a clear and quantifiable absorption peak within the measurable spectral range of the equipment used in these experiments.

Eu^{2+} concentrations were thus estimated by assuming that the balance between the known total Eu concentration and the measured Eu^{3+} concentrations in the samples was exclusively Eu^{2+} . This $[\text{Eu}^{2+}]$ estimate was cross-checked with magnetic susceptibility measurements performed at room temperature using a Johnson Matthey magnetic susceptibility balance. In this experiment, a portion of the glass samples were ground into powder using a mortar and pestle, and then transferred to a height of 1.5 cm into a large-bore magnetic susceptibility tube to which the instrument had been previously zeroed. The filled tube was then re-weighed to determine the mass of the sample and three magnetic susceptibility readings were taken in order to obtain an average.

2.4 Solid-state Conductivity

Gold electrical contacts (ca. 100 nm in thickness) were thermally evaporated (10^{-6} to 10^{-5} Torr) onto the ZBLAN samples using a turbo-molecular pumped Denton Vacuum DV515. The temperature dependent (40-200 °C) conductivity measurements were performed with software, nanoammeter and other electronics of local construction. 2-contact Fourier transform based measurements of the frequency dependent impedance were made using a 1-10 KHz sampling 12 bit A-D converter (Datel PC412A) and locally written software. Details of these measurements are discussed below.

3. Results & Discussion

3.1 Cyclic Voltammetry

Cyclic voltammetry was performed in order to establish that Eu^{2+} is stable (oxidatively) in ZBLAN. Cyclic voltammetry was carried out at 550 °C immediately after the glass had been heated at 825 °C for 30 minutes. The cyclic voltammetry was done right in the platinum crucible, which was contained in the quartz column, with three platinum wires as the working, reference and auxiliary electrodes. It was possible to determine that liquid ZBLAN has a 2.5 V potential window (Figure 3) before it undergoes any reduction or oxidation. This was important to establish since it meant ZBLAN could host strongly reducing or oxidizing species. ZBLAN has a +0.3 V potential versus a platinum quasi reference before the platinum electrode would start to oxidize. There is also a -2.1 V potential before one of the ZBLAN components, probably Zr, starts to reduce.

Similar experiments on ZBLAN containing 1% Eu^{3+} demonstrated that Eu^{3+} reduction/re-oxidation is both chemically and kinetically reversible. The oxidation and reduction peaks are equal in size, which is theoretically expected for a system where both reactant and product are chemically stable. This was a critical result because both Eu^{3+} and Eu^{2+} had to be able to exist in this system. The peak separation distance shows kinetic reversibility. The theoretical value for the delta peak potential is 0.163 V (at 550 °C) and the observed value is 0.154 V. The Eu species is able to interconvert rapidly and so the peak separation is relatively small.

Figure 3. Cyclic voltammetry of ZBLAN and $\text{Eu}^{2+/3+}$ at 550 °C

3.2 Glass Preparation

The ZBLAN composition made for these experiments contained 53% ZrF_4 , 20% BaF_2 , 4% LaF_3 , 3% AlF_3 , and 20% NaF since this results in a very stable material. All of the components were weighed and placed in a platinum crucible. This batching took place in a N_2 or dry-air purged glove box to prevent H_2O contamination of the anhydrous metal fluorides. The ZBLAN glass samples were prepared by heating the covered platinum crucible containing all the components at 825 °C for 30 minutes with N_2 flowing, removing the covered platinum crucible from the oven and pouring into a polished brass mold.

Glasses weren't annealed and often cracked or shattered upon removal from the mold. Results improved when the brass mold was heated to 200 °C using a hot plate and heating tape. Using the above protocol, ZBLAN glass quality was often excellent (very transparent, free of particles or bubbles).

When attempting to make mixed-valent samples, the glass quality was best when the trivalent lanthanide species (EuF_3 and LaF_3) were around 4% and divalent species (BaF_2 and EuF_2) were between 16-20%. EuF_2 would be substituted for some portion of BaF_2 and EuF_3 for LaF_3 . With increasing amounts of EuF_2 added, the glass became more discolored, yellowish to light green/gray with flecks of black, and samples were no longer transparent. All of the conditions used to make the samples are listed in Table 1.

Sample	Atmosphere	% EuF₃	% EuF₂	Reductant
ZBLAN, blank	N ₂	0	0	None
4% Eu(III)	N ₂	4	0	None
4% Eu(II)	N ₂	0	4	None
Mixed-valent	N ₂	4	4	None
Late Add Eu(II)	N ₂	4	4	None
CaH ₂ reduction of Eu(III)	N ₂	8	0	CaH ₂
CaH ₂ no forming gas	N ₂	4	0	CaH ₂
5 min forming gas, 500 °C	4% H ₂ /N ₂	4	0	H ₂
10 min forming gas, 500 °C	4% H ₂ /N ₂	4	0	H ₂
Forming gas, 825 °C, 27min	4% H ₂ /N ₂	4	0	H ₂
Forming gas, 825 °C, 27min	4% H ₂ /N ₂	6	0	H ₂

Table 1. Glass making conditions for samples

3.3 Strategies for Eu Reduction

Qualitative analysis of $[\text{Eu}^{2+}]$ and $[\text{Eu}^{3+}]$ peaks found in the UV-VIS spectrum was based on previous work [24-25] (see Figures 4 & 5). The spectra in Figures 4 and 5 show the absorption peaks that are expected for EuF_3 and EuF_2 . The large peak at 390 nm detected the presence of EuF_3 . Similarly, the large shoulder starting around 320 nm indicated the presence of EuF_2 . The spectra collected in these experiments show that the early ZBLAN and EuF_3 / EuF_2 samples contained some EuF_2 , which is indicated by the presence of the shoulder that takes off immediately after the peak at 390 nm, however, it was not in appreciable amounts (Figure 6). The dashed vertical lines represent where the Eu^{3+} and Eu^{2+} peaks were expected based on the literature values reported. The data reported here agree well with the theoretical values since the dominant peaks of EuF_3 are within a few nanometers of the literature values and the EuF_2 demonstrates the large shoulder starting around 380 nm. The spectra are off-set for clarity. The relative differences in Eu^{3+} peak height can be seen between the various spectra as well as either the presence or absence of the Eu^{2+} edge. The samples were all of the same thickness since they were all prepared using the heated brass mold.

3.3.1 Late Addition and Chemical Reduction

In order to increase the amount of EuF_2 present in the ZBLAN glass, the EuF_2 was added in the final 10 minutes of heating time in the furnace instead of adding it along with all the other components during the normal batching process at the beginning. This approach was tried since exposing the EuF_2 to the atmosphere in the furnace for a shorter

Fig. 1. Absorption spectrum of Eu^{3+} in ZBL glass. $J-J'$ transitions are from the 7F_J ($J=0, 1$) levels to the higher-lying J' levels listed in fig. 2.

Adam, J.L., Poncon, V., Lucas, J., Boulon, G., *J. Non-Crystalline Solids*, **1987**, 91, 191-202.

Figure 4. Eu(III) transitions seen in ZBL

Figure 1. Absorption spectra of a $\text{KMgF}_3:\text{Eu}^{2+}$ (1.1 mol% in the melt) crystal at 296 K. The crystal thickness is 1.98 mm. The absorption band due to the $4f^7 \rightarrow 4f^6d$ transition (curve a) is shown in a reduced scale.

Figure 2. Absorption bands due to the $8S_{7/2} \rightarrow 6P_{7/2}$ and $6P_{5/2}$ transitions in $4f^7 \rightarrow 4f^7$ parity-forbidden transitions of Eu^{2+} ions in KMgF_3 crystal at 16 K. Inset shows the $8S_{7/2} \rightarrow 6P_{7/2}$ band at 16 and 296 K. ABS. COEFF. means absorption coefficient.

Tsuboi, T., Scacco, A., *J. Phys. Condens. Matter*, **1998**, *10*, 7259-7266.

Figure 5. Eu(II) transitions in KMgF_3

Figure 6. UV-VIS of Eu(II) and Eu(III) in ZBLAN

amount of time should reduce the amount of EuF_2 that oxidizes to EuF_3 and yet still allows the sample to become a homogeneous melt. The shorter exposure time in the furnace was expected to lessen the amount of EuF_2 that oxidizes to EuF_3 since it would be in the oxidizing atmosphere for less time. The composition started out with 4% EuF_3 and then 4% EuF_2 was added. This resulted in a higher concentration of EuF_2 , but it was still less than 3% according to the calculations, however, this amount of EuF_2 is suspect. The reason the 2.76% EuF_2 seems unlikely is due to the fact that although the absorption spectra does show the presence of EuF_2 , the shoulder is not larger than the one present in other samples that do have larger amounts of EuF_2 present.

Chemical reduction with CaH_2 was also tried based on the following equations.

This composition started with 8% EuF_3 and enough CaH_2 was added in order to reduce all of the EuF_3 to EuF_2 , since it was anticipated that some of the EuF_2 would oxidize back to EuF_3 . The CaH_2 was added along with the other batched components in the glove box before entering the furnace. This approach resulted in greater amounts of EuF_2 present in the ZBLAN, but still in small quantities, ca. 2.5% (Figure 7). Again, the spectra are offset in order to view the relative difference in peak heights associated with the Eu^{3+} peaks at 390 nm. The dashed vertical lines represent the expected Eu^{2+} peaks as reported in the literature. Therefore, due to the fact that this spectrum has the largest shoulder present immediately after the peak at 390 nm these samples contained the most EuF_2 .

Figure 7. UV-VIS of Eu(II) using different methods of glass preparation

3.3.2 Reducing Atmosphere

Finally, the MacFarlane method of making the glass in a reducing atmosphere was tried [6] based on the following equation.

It was imperative that a clean and dry environment was maintained so there was minimal loss of EuF_2 . The components were batched as usual and placed in a platinum crucible but this time without a lid because the components, specifically the EuF_3 , needed to be in contact with the H_2 atmosphere. The crucible was placed in a quartz tube in the furnace so that the forming gas could flow directly into the sample, further controlling the atmosphere for the sample and preventing the EuF_2 from oxidizing back to EuF_3 . Some samples were allowed to remain at 825 °C with forming gas (4% H_2/N_2) flowing the entire time and other samples were heated to 825 °C for 10 minutes and then cooled to 500 °C before the introduction of forming gas. The forming gas was present for various amounts of time in order to determine which method produced the most EuF_2 without reducing too much of the ZrF_4 . In the latter cases, forming gas was present for either 5 or 10 minutes. All of these samples were quenched in the crucible by turning off the forming gas, opening the furnace and abruptly increasing the flow of N_2 .

This preparation method resulted in glasses with a wide range of EuF_2 present, anywhere from 0.5% to 2.7%. However, the sample with the most EuF_2 present produced in this manner (Forming Gas 27 min #2) also had formed a black cap, which could be the result of reduced Zr. The glasses that only had forming gas present for 5 or

10 minutes did not produce a black cap, however, they did have black specks throughout the samples. All of the latter samples were much more brittle than previously had been experienced. This could be due to the different quenching method being used. Also, the samples were not of as high a quality glass as produced earlier. Regions of the samples were glass and other portions were quite cloudy, probably due to other reduced species in the glass.

3.4 Eu Quantitation

Inorganic Eu^{2+} is known to exhibit a broad and intense ultraviolet absorbance band observably tailing out to 400 nm at concentrations above ca. 1% Eu^{2+} . Very weak, narrow bands centered on 359.3 nm and 353.9 nm were reported for Eu^{2+} in $\text{KMgF}_3/\text{EuF}_2$ crystals, (see Figure 5), but these peaks were too weak to observe in the samples. Accordingly, Eu^{3+} and Eu^{2+} were quantified by constructing a 1-8% Eu^{3+} calibration curve, and, for partially reduced samples, assuming that the difference between the total [Eu] and $[\text{Eu}^{3+}]$ was due to conversion to $[\text{Eu}^{2+}]$ according to the following equation.

$$[\text{Eu}^{2+}\text{F}] = [\text{Eu}^{3+/2+}]_{\text{TOTAL}} - [\text{Eu}^{3+}\text{F}]_{\text{OBSERVED}} \quad (6)$$

By using the linear calibration curve, it was possible to quantitatively analyze how much EuF_2 was present by calculating how much EuF_3 remained (Figure 8). The resulting concentrations of Eu^{3+} and Eu^{2+} remaining in the glasses are listed in Table 2.

3.4.1 Qualitative Aspects of Eu Ultraviolet-Visible Spectra

Clearly, the strongest Eu^{3+} peak in the UV-VIS data occurs at 390 nm. This peak is due to the electronic transition from $^7\text{F}_0$ ground state to $^5\text{L}_6$. The other Eu^{3+} peaks that

Figure 8. Eu^{3+} calibration curve

Sample	Eu conc (start)	Eu3 conc (end)	Eu2 (end)
4% Eu3	4	3.29	0.71
4% Eu2	4	2.39	1.61
4% Eu3 + 4% Eu2	8	2.59	5.41
Late Add Eu2	8	5.24	2.76
8% Eu3 + CaH2	8	5.42	2.58
CaH2 no F.G.	4	3.54	0.46
5 min FG 500 °C	4	1.93	2.07
10 min FG 500 °C	4	1.83	2.17
FG 27 min	4	3.42	0.58
FG 27 min	6	3.28	2.72

Table 2. Initial and final Eu concentrations

are noticeable in the absence of Eu^{2+} are at 375 nm, the ${}^7\text{F}_0$ to ${}^5\text{G}_4$ transition, and at 360 nm, the ${}^7\text{F}_0$ to ${}^5\text{D}_4$ transition. The UV edge signifies where a material starts to absorb in the UV spectrum. Eu^{2+} has a UV edge starting around 400 nm. Eu^{3+} also absorbs as a UV edge at about 320 nm. With the Eu^{2+} samples, the fine peaks found at 359 nm and 353 nm were not observed (Figure 5) due to the large shoulder that is present. This is the reason why the Eu^{2+} spectrum could not be used to calculate the amount of EuF_2 present.

3.5 Other Analytical Techniques

3.5.1 Differential Scanning Calorimetry

The ZBLAN was characterized with differential scanning calorimetry (DSC). In this analytical method, a small amount of sample is placed in an Al pan and the heat flow is measured as the sample is heated and goes through various phase transitions. ZBLAN has characteristic phase transitions. These transitions occur at T_g , which is the glass transition temperature, T_x , which is the crystallization temperature and T_l , which is the liquidus temperature. T_x and T_l are irreversible because once the sample is heated beyond T_x and especially T_l , it loses its optical clarity since the sample recrystallizes. The literature values for these three points are: $T_g = 262\text{ }^\circ\text{C}$, $T_x = 352\text{ }^\circ\text{C}$ and $T_l = 455\text{ }^\circ\text{C}$ [4]. The ZBLAN (no Eu present) sample that was measured matched the literature values very well, within $\pm 5\text{ }^\circ\text{C}$ (see Figure 9).

3.5.2 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) analysis was done to ensure that there wasn't a large hydroxide present in the samples (Figure 10). This technique was

Figure 9. Thermal properties of ZBLAN by Differential Scanning Calorimetry

Figure 10. IR analysis of ZBLAN with Eu

used for routine monitoring of the samples to ensure hydroxides, either from the processing steps or from exposure to the atmosphere after casting, were not present which would affect future analysis. It was important to know what was being made, in terms of glass quality. The hydroxide peak, at 3400 cm^{-1} , is quite small. The peak found at 2900 cm^{-1} is due to a low energy electronic transition for Eu^{3+} . The other peak, found at 2400 cm^{-1} is due to CO_2 , which is found in atmosphere and for this experiment is believed to be a measurement artifact. The concern about hydroxide stems from the following reactions [4]:

These reactions are possible at various temperatures. Reaction (7) primarily occurs at low temperatures such as T_g , and Reaction (8) mostly occurs at high temperatures. The reason this is important is that extensive hydroxide content could compromise the optical quality and structure of the glass.

3.5.3 Magnetic Susceptibility

Magnetic susceptibility measurements were used to substantiate the UV-VIS data. Magnetic susceptibility is based on the concept that closed shell atoms have all paired electrons and therefore are diamagnetic, whereas atoms with unpaired electrons are paramagnetic. Diamagnetic atoms are weakly repelled by a magnetic field, so there is a correction factor that is taken into account when calculating the overall magnetic contributions. Paramagnetic ions, on the other hand, are attracted to magnetic sources

with a strength that corresponds to the number of unpaired electrons. Eu^{3+} , with the electronic configuration $4f^6$, has 6 unpaired electrons and Eu^{2+} , with electronic configuration of $4f^7$, has 7 unpaired electrons [26].

The following calculations were used to determine the magnetic susceptibility [26-27].

$$X_g = \frac{(R - R_0) (L) (C_m)}{(\alpha) (m)} = \text{magnetic susceptibility in weight} \quad (9)$$

where R_0 = tube with sample; R = empty tube; L = length of sample;

C_m = machine correction factor; $\alpha = 1 \times 10^{-9}$, factory setting;

and m = mass of sample.

$$X_m = X_g (\text{FW}) = \text{molar susceptibility} \quad (10)$$

where FW = formula weight of sample

$$X_a = X_m + \text{CF} \times 10^{-6} \quad (11)$$

where CF = diamagnetic correction factor for elements

$$\mu_{\text{eff}} = 2.828 [(X_a) (T)]^{1/2} = \text{magnetic susceptibility} \quad (12)$$

where T = temperature of sample (297 K)

Theoretical values for the magnetic susceptibility (μ_{eff}) of Eu^{3+} and Eu^{2+} are 3.4-3.6 and 7.8-8.0 respectively [26]. Table 3 lists the experimental values calculated. Figure 11 shows the relationship between μ_{eff} values and the Eu^{2+} concentrations expected based on the UV-VIS absorption spectra.

3.6 Solid-state Conductivity

The central hypothesis that is being attempted to test is this: a contribution to the conductivity of ZBLAN should appear in proportion to the concentration product $[\text{Eu}^{2+}][\text{Eu}^{3+}]$. Accordingly, solid-state conductivity measurements were made on both blank ZBLAN and homologous preparations including a variable $[\text{Eu}^{2+}][\text{Eu}^{3+}]$ product. To measure conductivity, pairs of gold contacts were deposited onto the samples separated by a narrow (ca 300 μ) gap. Temperature dependent conductivity was then measured beginning at 40 °C and on 10 °C increments up to 200 °C.

Because the current-voltage property of Au-contacted ZBLAN is not steady state (i.e., the materials are not ohmic conductors), and because there may exist elements such as interfacial resistance or blocking capacitances at the Au contacts, the electrical conductivity of the samples was measured as a function of frequency. The resulting frequency dependent impedances were fit to an equivalent circuit intended to both quantitatively match the frequency dependence impedance and correspond element-for-element with physical aspects of the ZBLAN sample. For example, the equivalent circuit used in this work included serial pairs of impedances intended to match the physically serial ZBLAN interface and bulk. Within the serial impedance that corresponds to the

Sample	U_{eff}	% Eu₂
4% EuF ₃	3.30	0
#7 (5 min FG @ 500C)	4.07	2.07
#7b (10 min FG @ 500C)	4.20	2.17

Table 3. Experimental values of μ_{eff}

Figure 11. μ_{eff} values for Eu^{2+}

interface, there is a capacitance that corresponds to the ionic double layer at the metal | ZBLAN interface, and a resistance that corresponds to the interfacial charge transfer process. Within the impedance element that models the bulk, a capacitor is included to account for the bulk dielectric, and this is in parallel with a resistance corresponding to the movement of charge within the bulk of the ZBLAN. Comparing the magnitudes of the circuit elements with physically believable ones could check the validity of the model.

Models were developed by beginning very simply (i.e., with a simple series R and C), which did not fit the data well at all, and progressing methodically to find the simplest reasonable models, ones that accurately predicted the data. At this point, the heuristic connection between model elements and physical parts of the sample are established. Notably, the electronic conduction (i.e., that due to electron hopping) is expected to appear in parallel with ionic conduction – and therefore is not readily distinguishable in the frequency domain. However, the distinction between ion and electron based conduction is evidently revealed in the form of an elevated conductivity observed in a mixed-valent sample at low temperatures (relative to native ZBLAN).

It must be disclosed however that the geometry of these contacts obfuscates the assignments somewhat. Both of the contacts lie on the same face of the ZBLAN sample, i.e., contact-gap-contact, in what is termed “open-face” geometry. A more ideal geometry would be one where the Au contacts sandwich the sample – i.e., parallel plate geometry. Because of the open-face geometry, there must be an approximation when

converting the data from conductance to conductivity. For parallel plates, conductance is related to conductivity by the following equation:

$$\sigma = Sd/a \quad (13)$$

where σ = conductivity ($\Omega^{-1}\text{cm}^{-1}$); S = conductance (Ω^{-1});

d = plate separation; and a = plate area

The value of σ is approximated by assuming that fictitious parallel plates lie in the gap between the open-face contacts. The dimension of the parallel plates is assumed to be equal in depth to the size of the gap (d). Accordingly, these fictitious plates will have areas dl , where l is the length of the gap. So, conductivity is approximated as follows:

$$\sigma \approx sd/a = sd/dl = s/l \quad (14)$$

where l = the length of the gap

Interestingly, this model implies that for ‘open-face’ contacts, the observed conductance should be independent of the gap dimension. In fact, it has been observed that conductance is independent of gap dimension in the range of 400-1000 microns.

The data collection and analysis was accomplished with a Fourier transform method wherein a set of frequencies was simultaneously applied to the cell (in the form of a square wave), and the resulting current collected with a fast (10 KHz, 12-bit) A-D converter. Repetitive 5 V square waveforms were applied and the resulting current transients digitized and averaged together until the desired signal to noise ratio was achieved – typically ca. 5 minutes. The resulting $E(t)$ (see Figure 12) and $i(t)$ data were Fourier transformed into $E(\omega)$ and $i(\omega)$, ($10,000 \geq \omega \geq 0.1$) and the complex impedance

Figure 12. Fourier analysis of conductance

calculated as $Z(\omega)_{\text{EXP}} = E(\omega)_{\text{EXP}} / i(\omega)_{\text{EXP}}$. $Z(\omega)_{\text{EXP}}$ could then be compared directly to equivalent circuit models (see Figures 13 and 14).

Typical current-time transients, normalized to peak current, are illustrated in Figure 15. Clearly, the higher temperature data appears to be more nearly steady-state in character. A transient element begins to appear within the measurable frequency range at about 120 °C. This transition from quasi steady state is reasonable since resistances increase exponentially with decreasing temperature, and so the corresponding time constants ($\tau = RC$) become long enough to ‘see’ or measure as this happens. Accordingly, the low temperature data require a more complex equivalent circuit to model the responses; presumably these ‘new’ elements are interfacial resistance and capacitance.

The simplest successful equivalent circuits that predicted the data are illustrated in Figure 16. The resistance and capacitance of the interface (ZBLAN | gold) and the resistance and capacitance of the bulk (ZBLAN) are modeled by a series combination of parallel elements – (R_1C_1 and R_2C_2) corresponding reasonably to the 2-probe experiment when R_1C_1 represents bulk impedance and R_2C_2 the interfaces. The serial combination of R_1C_1 and R_2C_2 fit the low temperature (<100 °C) data adequately, but above 100 °C the R_2C_2 elements were no longer needed. At high temperatures the magnitude of the resistance and capacitance of the bulk and interface may be very similar and so difficult to distinguish or degenerate. More likely however, the magnitude of R_2 simply does not rise as fast as that of R_1 , so its importance in the circuit diminishes.

Figure 13. Experimental data vs the model in the frequency domain

Frequency domain impedance of two parallel RC elements in series

$$Z_T(\omega) = \frac{1}{\left[\frac{1}{-j} + \frac{1}{R_I} \right] + \left[\frac{1}{-j} + \frac{1}{R_B} \right] \omega C_B}$$

Frequency domain Ohm's law-calculation of current followed by inverse FT to restore current to time domain.

$$I(\omega) = \frac{E(\omega)}{Z_T(\omega)} \quad I(t) = \text{Inverse Fourier transform}(I(\omega))$$

Figure 14. The model: frequency domain calculation of complex impedance

Figure 15. Transients at different temperatures using Potential Step methods

Figure 16. Equivalent circuit for our ZBLAN system

The theoretical capacitance of the interface can be calculated by the concentration of mobile ions ($[F_{\text{MOBILE}}] \approx 10 \text{ M}$) using the following formula from the Gouy-Chapman theory [28]:

$$C_I = 228zC^{1/2} \cosh(19.5z\Phi_0) \quad (15)$$

where z = charge of ion; C = concentration of ions, $\approx 10 \text{ M (F}^-)$;

and Φ_0 = potential drop across the interface, $\approx 0 \text{ V}$

The capacitance of the ZBLAN bulk can also be calculated using the following formula:

$$C_B = \frac{\epsilon_0 \epsilon A}{d} \quad (16)$$

where ϵ_0 = permittivity of free space; ϵ = dielectric constant of the

material, ≈ 10 ; A = area; and d = distance between the parallel plates

Using the above formulae $C_{I(\text{theory})} = 1 \times 10^3 \mu\text{F}$ and $C_{B(\text{theory})} = 6 \times 10^{-13} \text{ F}$.

Experimental data revealed C values of the order $10^{-14} - 10^{-10} \text{ F}$. Capacitances as large as $10^3 \mu\text{F}$ would not be observable on these experimental timescales ($\sim / \text{s}$). Accordingly the likely origin of transient behavior in these samples is due to bulk capacitance. The data also matched the model quite well in the time domain as shown in Figure 17.

The mixed-valent samples had higher conductivity than ZBLAN at lower temperatures (Figure 18). The conductivity of ZBLAN can be explained by the fluoride ion conductivity. The samples with mixed-valent concentrations of Eu have elevated conductivity at lower temperatures, compared to the fluoride ion conductivity of undoped ZBLAN. This is due to electron transfers, or electron hopping, that is taking place.

Table 4 shows the conductivity due to electron hops for the CaH_2 sample.

Figure 17. Experimental data vs the model in the time domain

Figure 18. Temperature dependence of total conductance

Temp	Conductance
40 °C	1.66E-10
50 °C	1.51E-10
60 °C	1.55E-10

Table 4. CaH₂ conductivity contribution due to e⁻ hops

The e^- transfer-based conductivity may be translated into an electron self exchange rate constant using the following formula:

$$K_{ex(\sigma)} = \frac{6RT\sigma}{n^2 F^2 \delta^2 C_o C_r} \quad (17)$$

where C_o = concentration of oxidizing species; and C_r = concentration of reducing species

The 40 °C K_{ex} experimental value is $\sim 20 \text{ M}^{-1}\text{s}^{-1}$, a value on the lower end of the spectrum when compared to most polymeric (10^5) or fluid solution values ($10^3 - 10^7$) [1].

A few points should be clarified concerning these methods and calculations.

Several samples seem to have variable concentrations of Eu^{2+} present, according to the UV-VIS spectra, however, there does not seem to be a corresponding increase in conductivity for these samples. This could be due to several reasons. First, there could be an error in the absorption measurements caused by samples that are too thick, inhomogeneous samples or the incorrect starting concentration of Eu^{3+} recorded. Also, the large increase in conductivity for the sample with CaH_2 might be due to the Ca^+ ion and not directly related to the presence of Eu^{2+} .

4. Conclusion

Fluorozirconate glasses with mixed-valent $\text{Eu}^{3+}/\text{Eu}^{2+}$ species can be generated using techniques described in this thesis. Maintaining the original EuF_3 concentration was very straightforward since the EuF_3 is quite stable. The EuF_2 concentration, however, proved to be more challenging to maintain since it easily oxidizes to EuF_3 . The greatest amount of success resulted by preparing the samples in a reducing atmosphere (4% N_2/H_2), which resulted in EuF_2 concentrations of 2.7 mol%. Chemical reduction with CaH_2 also proved successful, with concentrations of EuF_2 in the range of 2.58 mol%.

The conductivity of the fluorozirconate glass, ZBLAN, can be attributed to the F^- ion conductivity. This conductivity increases with increasing temperature in a linear fashion. By adding rare-earth mixed-valent species, such as EuF_3 and EuF_2 , it was possible to slightly increase the conductivity at near-room temperatures compared to the F^- ion conductivity alone. The samples with the highest concentration of EuF_2 also had the highest conductivity.

Future work in this area could involve several different aspects. First, it would be important to understand at what concentration of EuF_2 does the electron-transfer based portion of the conductivity level off or peak. Secondly, electrogenerated chemiluminescence could be investigated by the addition of another rare-earth redox ion.

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