



Spectroscopic and Thermal-Luminescence Behavior of Rare-Earth/Actinide-Doped Glasses for Advanced Optoelectronic Applications

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ABSTRACT:

A sample of Er³⁺ doped fluorochloride glass was prepared by incorporating chlorine (Cl⁻) into a fluoride glass (ZBLAN) using the conventional melt quenching technique. The research investigated the chemical stability, thermal stability, and fluorescent properties of the glass by varying the Cl⁻ concentration. It was observed that increasing the Cl⁻ concentration enhances the luminescent intensity in the infrared region. The strongest luminescent intensity was achieved at a Cl⁻ concentration of 15 mol%. Similarly, the study compared the effects of different Er³⁺ concentrations on the luminescent properties of the fluorochloride glass, identifying 1 mol% Er³⁺ as the optimal doping concentration. Consequently, the glass composition is denoted as ZBLAN:15Cl, 1Er. Experimental analyses including X-ray diffraction (XRD), absorption spectrum, near-infrared spectrum (NIR), and mid-infrared spectrum (MIR) were conducted to characterize the Er³⁺ doped fluorochloride glass. The energy level diagram of Er³⁺ and the infrared luminescence of the sample were thoroughly analyzed, focusing on the excitation at 980 nm. Judd-Ofelt parameters were computed to understand the luminescent behavior. It was observed that Ω_2 initially increased and then decreased with varying Cl⁻ content in the glass matrix, whereas Ω_4 and Ω_6 remained relatively stable across different compositions. This variability in Ω_2 suggests a change in the crystal field environment around the Er³⁺ ions due to the introduction of Cl⁻. In Er³⁺ doped fluoride glass, the addition of Cl⁻ significantly enhances the mid-infrared luminescence intensity. The calculated Judd-Ofelt theoretical parameters indicate that Cl⁻ introduction enhances the covalency of the coordination bond with Er³⁺, thereby reducing local symmetry and boosting the luminescent properties of the fluoride glass. This research on rare earth ion-doped fluorochloride glass provides a theoretical foundation for improving luminescent characteristics and offers valuable insights for the development and application of similar mid-infrared luminescent materials.

Introduction

Mid-infrared (2~3 μm) materials typically exhibit fundamental vibration absorption bands characterized by a distinct bandwidth [1]. Mid-infrared lasers hold significant promise for applications in medicine, meteorology, laser radar, laser ranging, and atmospheric communication. Furthermore, mid-infrared gain media find extensive use in displays and detection, underscoring their broad utility.

Different types of lasers can be realized using various gain media, including stimulated emission from gases, liquids, and solid-state materials. Rare earth-doped fiber glass lasers offer notable advantages over conventional lasers, including high efficiency, compact size, ease of integration, excellent beam quality, strong

resistance to interference, and efficient heat dissipation. The optical properties of rare earth ions vary depending on the coordination environments within different glass matrices, such as fluorides, sulfates, phosphates, and silicates. Thus, rare earth ions exhibit diverse optical behaviors across these matrices.

After doping with rare earth elements, the crystal field in the matrix often retains high symmetry, which can limit effective light stimulation. Rare earth ions are known for their large maximum absorption cross-sectional area and narrow luminescence bandwidth. Choosing an appropriate matrix material is crucial for achieving high energy transfer efficiency and conversion rates of rare earth ions, leading to analysis of several common matrix materials.



Silicate glass has a relatively high phonon energy of around 1200 cm^{-1} . This high energy promotes multi-phonon relaxation of rare earth ions, reducing the probability of mid-infrared emission. Additionally, quartz glass fails to achieve long-wavelength mid-infrared output, which is a significant limitation. As_2S_3 glass, a type of chalcogenide glass, offers good thermal stability and glass-forming ability, with high infrared transparency. However, it has drawbacks including a low glass transition temperature (210°C), high toxicity, and poor solubility for rare earth ions. Ga-La-S (GLS) glass is non-toxic, features high rare earth ion solubility, and boasts a high glass transition temperature. Nonetheless, GLS glass exhibits lower thermal stability, with a narrow temperature range (only 50°C) between conversion and devitrification temperatures, posing challenges for fiber production.

Currently, fluoride materials exhibit excellent performance in laser glass applications, and extensive research has been conducted in this area, primarily focusing on fluoride glasses. When doped with Er^{3+} , fluoride glass materials can emit mid-infrared light around 2800 nm , making them crucial for the $3\text{-}4\text{ }\mu\text{m}$ wavelength range. Fluoride glass boasts high transparency from $0.5\text{ }\mu\text{m}$ to $7.2\text{ }\mu\text{m}$ and features a low phonon energy of approximately 5050 cm^{-1} .

The introduction of Cl^- into fluoride glass has been observed to enhance its infrared luminescence by disrupting the crystal field symmetry around Er^{3+} ions. This modification is speculated to increase the covalent nature of the coordination bond with Er^{3+} , thereby reducing local symmetry and boosting the luminescent intensity of the fluoride glass. Despite these advancements, research on mid-infrared emission from fluorochloride glass remains limited.

In this study, a series of Er^{3+} -doped fluorochloride glasses were synthesized using the conventional melt-quenching technique. The physical

and chemical characteristics of these glasses were modified by incorporating Cl^- . The luminescent properties of Er^{3+} -doped fluorochloride glasses at various Cl^- concentrations were systematically investigated. Notably, the introduction of Cl^- led to a significant enhancement in mid-infrared luminescence intensity. The influence on luminescent intensity was further analyzed using Judd–Ofelt theory. Additionally, X-ray diffraction, absorption spectrum, near-infrared spectrum, and mid-infrared spectrum analyses were conducted to comprehensively characterize these glasses.

Experiment Section

Er^{3+} -doped fluorochloride glasses (ZBLAN: $x\text{Cl}$, $y\text{Er}$) were fabricated under reducing conditions using a conventional melt quenching method. The chemical constituents included spectrally pure ErF_3 and analytically pure materials. A composition of $53\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}4\text{LaF}_3\text{-}3\text{AlF}_3\text{-}(20\text{-}x)\text{NaF-xNaCl-yErF}_3$ (mol%) was utilized, varying x from 0 to 20 and y from 1 to 4.

The process involved grinding and thorough mixing of raw materials, followed by embedding in ammonium fluoride. The mixture was heated to 800°C , held for 30 minutes until completely molten, and quickly transferred to a muffle furnace. Annealing at 200°C for 2 hours relieved residual stresses and internal defects, yielding basic fluorochloride glass samples that were cooled naturally to room temperature. Subsequent steps included cutting, polishing, and conducting further tests.

The crystal structure analysis utilized a D/max-2600/PC diffract meter with Cu K α radiation. Absorption spectra were obtained using a Hitachi U-4200 absorption spectrometer. Mid-infrared luminescent spectra were measured with a Princeton Instruments Acton Advanced SP2500A spectrometer equipped with a liquid nitrogen-cooled detector. Excitation was provided by a continuous laser emitting at 980 nm . All experiments were conducted at room temperature.

Table 1.1. Composition of Chemicals

ZBLAN: Xcl, yEr							
x=0	x=5	x=10	x=15	x=20	x=15	x=15	x=15
y=1	y=1	y=1	y=1	y=1	y=2	y=3	y=4



Results and Discussions

XRD Crystal Phase Analysis of Fluorochloride Glass

Figure 1.1 XRD patterns of Er³⁺ doped fluorochloride glass with 1.0 mol%.

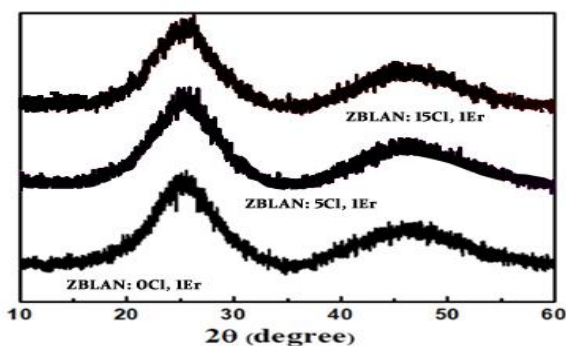


Figure 1.1 depicts the XRD diffraction patterns of a selection of fluorochloride glass samples. Upon comparison, all samples exhibited characteristic broad diffraction peaks typical of vitreous materials at 28° and 49°. This confirms that the fluorochloride glass samples are uniformly in an amorphous glass state, consistent with findings reported in numerous studies. The fluorochloride glass is structured as a network composed of polyhedral ZrF_n units, where the introduction of Cl⁻ ions involves replacing the F⁻ ions linked to these polyhedral ZrF_n units. Therefore, the incorporation of Cl⁻ does not alter the fundamental polyhedral structure of the fluorochloride glass.

Table 2. J-O parameter Ω_t of Er³⁺ doped fluochloride glass.

	ZBLAN: 0Cl,1Er	ZBLAN: 5Cl,1Er	ZBLAN: 10Cl,1Er	ZBLAN: 15Cl,1Er	ZBLAN: 20Cl,1Er	ZBLAN: 15Cl,2Er	ZBLAN: 15Cl,3Er	ZBLAN: 15Cl,4Er
Ω_2 ($\times 10^{-20}$ cm ⁻²)	3.26	3.85	4.15	4.62	4.23	3.79	3.46	3.18
Ω_4 ($\times 10^{-20}$ cm ⁻²)	1.64	1.69	1.74	1.85	1.73	1.56	1.45	1.42
Ω_6 ($\times 10^{-20}$ cm ⁻²)	1.06	1.21	1.28	1.35	1.24	1.23	1.18	1.09

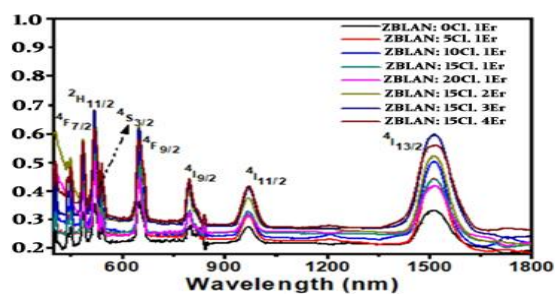
Table 2 presents the calculated Judd-Ofelt (J-O) theoretical parameters for fluorochloride glass. The values of Ω_2 , Ω_4 , and Ω_6 exhibit an increasing trend with higher Cl⁻ content. Specifically, when the Cl⁻ content reaches 20%, the Ω values peak. Ω_2 reflects the number of covalent bonds and is closely tied to the matrix structure, symmetry, and arrangement of coordination

Er³⁺ Absorption Spectra and J-O Theory in Fluoride Glass

Figure 2 displays the absorption spectra of the fluorochloride glass at room temperature, revealing eight distinct peaks spanning the 450-1850 nm wavelength range. These peaks correspond to transitions from the ground state ⁴I_{15/2} of Er³⁺ to the excited states ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2}, ⁴F_{9/2}, ⁴S_{3/2}, ²H_{11/2}, ⁴F_{7/2}, and ⁴F_{5/2}, with central wavelengths at 1525, 982, 810, 660, 550, 529, 496, and 448 nm, respectively.

The Judd-Ofelt (J-O) theory is employed to analyze the influence of the glass matrix on luminescence, leveraging data derived from the absorption spectrum. J-O intensity parameters for each glass sample are computed using reduced matrix elements for each radiative transition, as described in literature and summarized in Table 2.

Figure 1.2. Absorption spectra of the fluochloride glass.



sites. As Ω_2 increases, the glass tends to exhibit higher covalent character and reduced symmetry. Ω_4 and Ω_6 are indicators of the hardness and pH of the material, respectively. Comparing with fluoride glass, the Ω_2 of fluorochloride glass is notably higher, indicating enhanced covalency and reduced symmetry. Ω_6 , associated with the overlap of 4f and 5d electron shells,



increases due to decreased alkalinity in the glass matrix. Notably, the Ω_6 value of fluorochloride glass surpasses that of fluoride, silicate, and phosphate glasses, underscoring its lower basicity compared to these materials.

Near-Infrared Analysis of Fluorochloride Glass

Figure 1.3 Near infrared spectra of Er³⁺ doped different Cl⁻fluorochloride glasses under 990nm excitation.

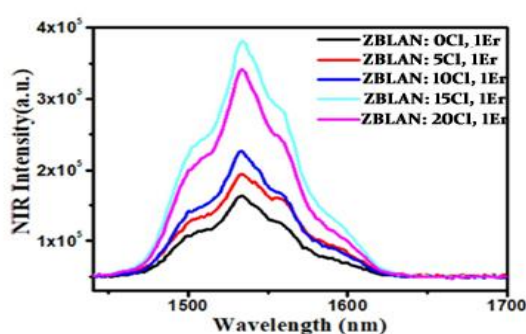


Figure 3 illustrates the near-infrared emission spectra of Er³⁺ doped fluorochloride glasses with varying concentrations of Cl⁻ ions, excited at 980 nm. Er³⁺ exhibits strong emission at 1600 nm corresponding to transitions from $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$. The luminescent intensity initially increases and then decreases with increasing Cl⁻ concentration, reaching its peak at 20%. This trend mirrors the intensity factor calculated by the Judd-Ofelt (J-O) theory. Notably, at Cl⁻ concentrations of 10% (ZBLAN:10Cl,1Er) and 20% (ZBLAN:15Cl,1Er), the glasses begin to transition from transparent to opaque glass ceramics.

Figure 1.4. Near infrared spectra of Er³⁺ doped fluochloride glass under 980nm excitation.

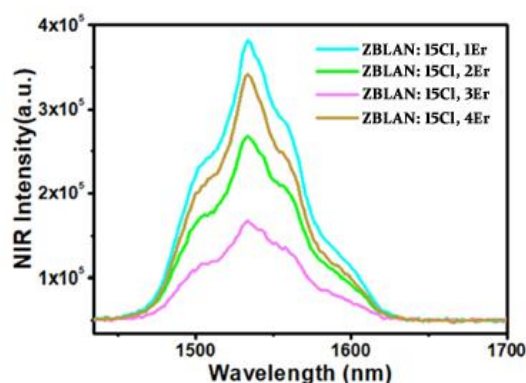


Figure 1.4 depicts the near-infrared fluorescence spectra of fluozirconate glass doped with various concentrations of Er³⁺, excited at 980 nm. As the concentration of Er³⁺ increases, the fluorescence peak position remains unchanged, indicating no shift in emission wavelength. However, the luminescent intensity gradually decreases with higher concentrations of Er³⁺. This phenomenon suggests that excessive doping of Er³⁺ leads to concentration quenching, where the luminescent efficiency diminishes despite the increased dopant concentration.

Mid-Infrared Analysis of Fluorochloride Glass

Figure 1.5. Mid infrared spectra of Er³⁺ doped fluochloride glass with different concentration of Cl⁻ under 980 nm excitation.

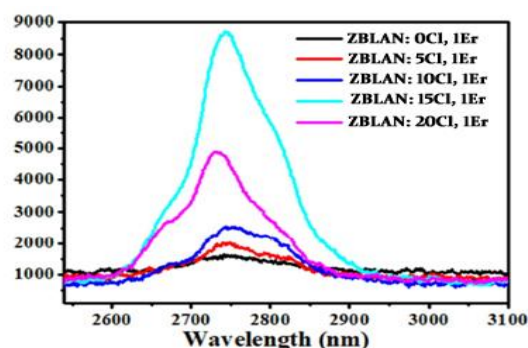


Figure 5 illustrates the mid-infrared emission at 2.9 μm from fluorochloride glass under excitation at 980 nm. The luminescent intensity of Er³⁺ at 2.9 μm (transition from $^4I_{11/2}$ to $^4I_{13/2}$) varies with the concentration of Cl⁻. Maximum luminescent intensity is achieved when the Cl⁻ concentration reaches 15%, coinciding with the point where the sample undergoes full ceramization. Subsequently, a significant decrease in luminescent intensity is observed in ZBLAN:20Cl,1Er samples. This trend is consistent across both near-infrared and mid-infrared fluorescence spectra for samples labeled ZBLAN: xCl, yEr (where x = 0, 5, 10, 15, 20 and y = 1). The value of Ω_2 , obtained from Judd-Ofelt (J-O) theory fitting, increases with higher Cl⁻ content. This increase indicates a reduction in the symmetry of the Er ion environment within the glass matrix.



Figure 1.6. Mid infrared spectra of Er³⁺doped fluochloride glass under 980 nm excitation.

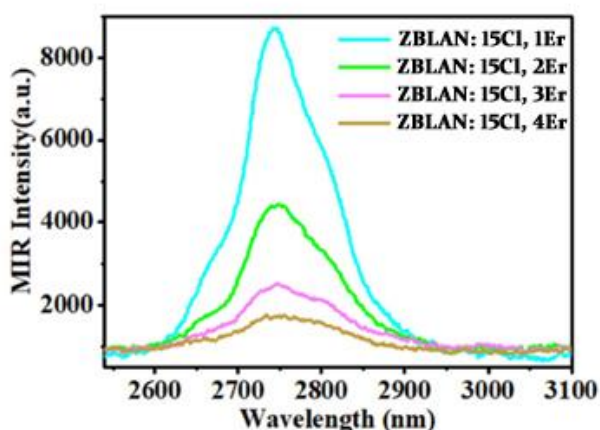


Figure 1.6 displays the mid-infrared fluorescence spectra of fluoride glasses labeled ZBLAN: xCl, yEr (x=15; y=1, 2, 3, 4), doped with varying concentrations of Er³⁺ and Cl⁻. When excited by a 980 nm laser, the spectra for these samples exhibit emission peaks characterized by non-uniform broadening, indicative of site-to-site variations within the matrix. However, the wavelength range of the emission peaks remains consistent across different concentrations of Er³⁺ and Cl⁻.

Among fluorochloride glasses doped with different concentrations of Er³⁺, ZBLAN:15Cl,1Er exhibits the highest luminescent intensity when Cl⁻ concentration is held constant. However, as the concentration of Er³⁺ increases, the luminescent intensity diminishes significantly due to concentration quenching. Thus, the optimal doping concentration of Er³⁺ in fluorochloride glass doped with Cl⁻ is determined to be 1 mol%.

Conclusion

In this study, fluorochloride glass was prepared by incorporating Cl⁻ into Er³⁺ doped fluoride glass using a conventional melt quenching method. The focus was on investigating how Cl⁻ doping affects the characteristic fluorescence spectra of Er³⁺ doped fluorochloride glass. Both near-infrared and mid-infrared spectra showed a gradual increase in luminescent intensity with increasing Cl⁻ content. Moreover, as Cl⁻ content increased, the samples transitioned towards a more ceramic-like state,

coinciding with enhanced luminescent intensity during the ceramization process.

The Judd-Ofelt (J-O) theoretical parameters were calculated to understand the impact of Cl⁻ incorporation on the glass matrix. It was found that Cl⁻ enhances the covalency of coordination bonds with Er³⁺, leading to reduced local symmetry. The introduction of Cl⁻ and other elements into the fluoride glass also improved its chemical stability, thermal stability, and fluorescent properties, elucidating the relationship between glass structure and luminescence characteristics.

This research underscores the potential for enhancing luminescence performance through rare earth ion doping in fluoride glass, providing a foundational basis for further advancements in the development and application of similar luminescent materials.

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