



Preparation and MIR Luminescence Properties of Er³⁺ Doped Fluorochloride Glass

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Abstract: The Er³⁺ doped fluorochloride glass sample was prepared by incorporating Cl⁻ into the fluoride glass (ZBLAN) using a conventional melt quenching method. The chemical stability, thermal stability and fluorescent properties of the Er³⁺ doped fluorochloride glass were researched by increasing the Cl⁻ concentration. The effect of different Cl⁻ concentrations on the luminescent properties of the fluorochloride glass was compared. The results show that the luminescent intensity of infrared increases with the increase of Cl⁻ concentration. When the Cl⁻ concentration reaches 15 mol%, the luminescent intensity is the strongest. At the same time, the effects of different Er³⁺ concentrations on the luminescence properties of fluorochloride glass were compared. The optimum doping concentration of Er³⁺ was 1 mol%. Hence, it is represented here as ZBLAN:15Cl, 1Er. The X-ray diffraction (XRD), absorption spectrum, near-infrared spectrum (NIR) and mid-infrared spectrum (MIR) of Er³⁺ doped fluorochloride glass were analyzed by experiments. The energy level diagram of Er³⁺ and the infrared luminescence of the sample were analyzed. The infrared luminescence of Er³⁺ at the excitation of 980 nm was mainly studied. The Judd-Ofelt parameters were calculated. It was found that the value of Ω_2 increased first and then decreased to the Cl⁻ contents increasing in the glass matrix, while Ω_4 and Ω_6 did not change obviously in different glass composition. This is because the environment of the crystal field around the rare earth ions has changed. In the Er³⁺-doped fluoride glass, the introduction to Cl⁻ significantly enhances the mid-infrared luminescent intensity of the fluorochloride glass. The calculation of J-O theoretical parameters shows that the introduction to Cl⁻ enhances the covalency of the coordination bond with Er³⁺, reduces the local symmetry, and significantly enhances the luminescent intensity of fluoride glass. Rare earth ion doped fluorochloride glass provides a theoretical basis of improving luminescent properties. At the same time, it has important guiding significance of the research, development and application of similar MIR luminescent materials.

Keywords: Er³⁺ Doped, Fluorochloride Glass, MIR Luminescence

1. Introduction

Most mid-infrared (2~3 μ m) materials have a basic vibration absorption band that can produce a discontinuous half-width [1]. Mid-infrared lasers have great application prospects of medical [2], meteorological [3], laser radar [4], laser ranging and atmospheric communications. In addition, mid-infrared gains media has a large application in display and detection [5-7]. Therefore, the mid-infrared laser has attracted researchers' extensive attention and attention.

Various lasers can be achieved by different gain methods such as stimulated emission of gaseous, liquid and solid-state gain media [8, 9]. Compared with conventional lasers, rare earth doped fiber glass lasers have great advantages, such as high efficiency, small size, easy integration, good beam quality, strong anti-interference ability, and good heat dissipation [10]. Rare earth ions have different coordination fields in different glass matrices, such as fluorides, sulfates, phosphates and silicates. Therefore rare earth ions have different optical properties in different matrices.

After the matrix is doped with rare earth elements, the crystal field will have high symmetry and cannot effectively stimulate the light that people need [11-12]. Rare-earth ions have a large maximum absorption cross-sectional area and narrow bandwidth of sharp luminescence [13]. The selection of a suitable matrix material can provide higher energy transfer efficiency and conversion rate of rare earth ions [14-16], so several common matrix materials were analyzed.

The phonon energy of silicate glass is relatively high, reaching 1100 cm⁻¹. The probability of multi-phonon relaxation of rare earth ions increases, and the probability of mid-infrared emission decreases. At the same time quartz glass cannot achieve long-wavelength mid-infrared output is another of its drawbacks [17]. As₂S₃ glass as one of the chalcogenide glass has good thermal stability and glass forming ability, and has high transmittance in the infrared region. But it has a low glass transition temperature (200°C), high toxicity, and poor rare earth solubility. Ga-La-S (GLS) is non-toxic, high solubility of rare earth ions, high glass transition temperature, but low thermal stability of GLS glass, and the difference between the conversion and devitrification temperature is only 40°C, which poses a problem for fiber preparation [18].

At present, fluoride has good performance in laser glass materials, and many researchers have carried out preparation and research. Mainly represented by fluoride glass, fluoride glass Er³⁺ doping material can generate mid-infrared emission at about 2700 nm, which is one of the most important materials in the 2-3μm region [19-22]. Fluoride glass has a high transmission rate of 0.3μm and 7μm, and its phonon energy is very low [23, 24] approximately 500 cm⁻¹. By doping Cl⁻ will improve infrared luminescence, which is caused by a decrease in the symmetry of the crystal field around Er³⁺[25]. It is speculated that the introduction to Cl⁻ enhances the covalency of the coordination bond with Er³⁺, reduces the local symmetry, and improves the luminescent intensity of fluoride glass. However, few researchers have studied the mid-infrared emission of fluorochloride glass.

In this work, a series of Er³⁺-doped fluorochloride glasses were prepared by the traditional melt-quenching method. The physical and chemical properties of these glasses were modified by introduction of Cl⁻. The luminescent properties of Er³⁺-doped fluorochloride glasses with different concentrations of Cl⁻ were investigated. The introduction of Cl⁻ has significantly improved the mid-infrared luminescent intensity. The effect of luminescent intensity was analyzed by Judd–Ofelt theory. At the same time, X-ray diffraction, absorption spectrum, near-infrared spectrum and mid-infrared spectrum were analyzed.

2. Experiment Section

Er³⁺ doped fluorochloride (ZBLAN: xCl, yEr) glasses were prepared in a reducing atmosphere using a conventional melt sintering method. The chemicals used in this work are spectrally pure ErF₃, others are analytically pure. A sample of 53ZrF₄-20BaF₂-4LaF₃-3AlF₃-(20-x) NaF-xNaCl-yErF₃

(mol%) was prepared. (x=0, 5, 10, 15, 20; y=1, 2, 3, 4) (Table 1). The raw materials were ground and mixed well and embedded in ammonium fluoride. Warm up to 800°C, then heat for 30 min. After the sample reaches a completely molten state, it is rapidly transferred to the muffle furnace and annealed at 200°C for 2 h to remove residual stress and internal defects. The basic fluorochloride glass samples were obtained by cooling naturally to room temperature. After the sample has been cut and polished, subsequent tests are continued. The crystal structure of the test samples used in this paper is a D/max-2500/PC diffractometer with Cu Ka as the radiation source, and the wavelength is 1.54184 Å. The absorption spectra were obtained by a Hitachi U-4100 absorption spectrometer. The mid-infrared luminescent spectra of the samples were measured by a Princeton Instruments Acton Advanced SP2500A spectrometer with a liquid nitrogen cooled detector. The excitation source uses a continuous laser with a wavelength of 980 nm. All tests were performed at room temperature.

Table 1. Chemical composition of samples

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

3. Results and Discussions

3.1. XRD Crystal Phase Analysis of Fluorochloride Glass

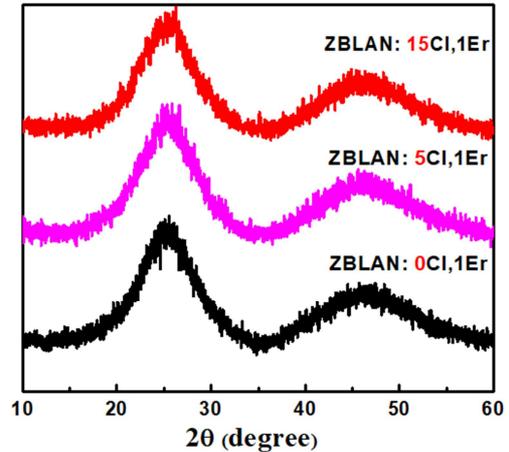


Figure 1. XRD patterns of Er³⁺ doped fluorochloride glass with 1.0 mol%.

Figure 1 is the XRD diffraction pattern of portion of a fluorochloride glass samples. By comparison, all samples exhibited typical broad diffraction peaks of vitreous at 26° and 47°. This indicates that the fluorochloride glass samples are all in an amorphous glass state, which is consistent with the results reported in most papers [26]. The fluorochloride glass is a network structure composed of a polyhedral ZrF_n, and the doping of Cl⁻ is to replace the F⁻ linked to the polyhedral ZrF_n. Therefore, the introduction to Cl⁻ does not change the polyhedral structure of the fluorochloride glass.

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

Figure 2 shows the absorption spectra of the fluorochloride glass of room temperature. There are eight sharp peaks at the 400-1800nm wavelength range. The central wavelengths are 1515, 972, 800, 650, 540, 519, 486, 448 nm, respectively. Corresponding to transitions to the energy levels of Er³⁺ from the ground states ⁴I_{15/2} 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}, ⁴F_{5/2}.

The J-O theory is a theory that discusses the influence of the matrix on luminescence and can be calculated from the absorption spectrum. The J-O intensity parameters for each glass sample can be calculated based on the reduced matrix element values of each radiative transition given by the J-O theory and literature (Table 2).

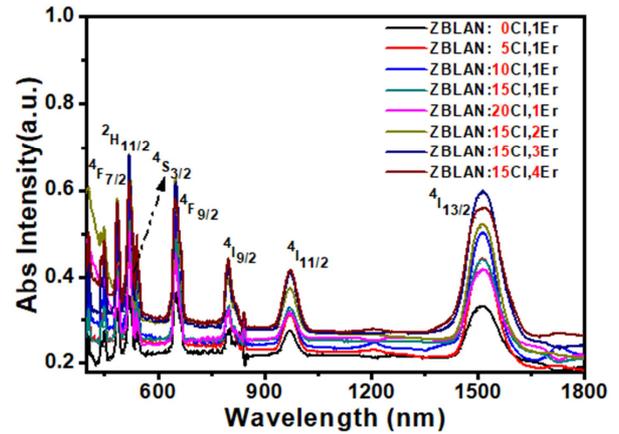


Figure 2. Absorption spectra of the fluorochloride glass.

Table 2. J-O parameter Ω_j of Er³⁺ doped fluorochloride glass.

	ZBLAN:0C l,1Er	ZBLAN:5C l,1Er	ZBLAN:10C l, 1Er	ZBLAN:15C l, 1Er	ZBLAN:20C l, 1Er	ZBLAN:15C l, 2Er	ZBLAN:15C l, 3Er	ZBLAN:15C l,4Er
$\Omega_2 (\times 10^{-20} \text{ cm}^{-2})$	3.22	3.82	4.10	4.56	4.21	3.75	3.41	3.12
$\Omega_4 (\times 10^{-20} \text{ cm}^{-2})$	1.60	1.65	1.71	1.83	1.69	1.53	1.41	1.38
$\Omega_6 (\times 10^{-20} \text{ cm}^{-2})$	1.03	1.18	1.25	1.32	1.21	1.19	1.15	1.08

Table 2 shows the calculated J-O theoretical strength of fluorochloride glass. The values of Ω_2 , Ω_4 , and Ω_6 show an increasing trend with the Cl⁻ content increasing. The Cl⁻ content reaches 15% and the Ω value reaches its maximum. Ω_2 represents the number of covalent bonds and is inseparably related to the structure of the matrix and the symmetry and ordering of coordination sites. As Ω_2 increases, the covalentness of the glass increases and the symmetry decreases. Ω_4 and Ω_6 indicate the hardness and pH of this material, respectively [27]. The Ω_2 of fluorochloride glass is larger than that of fluoride glass. This shows that Er³⁺-doped fluorochloride glasses have higher covalentness and symmetry. Ω_6 is related to the overlap of 4f and 5d shells, and the increase of Ω_6 is due to the decrease of alkalinity in the matrix glass. The Ω_6 value of fluorochloride glass is larger than that of fluoride glass, silicate glass, and phosphate glass, which proves that the basicity of fluorochloride glass matrix is smaller than other glasses [28].

3.3. Near-Infrared Analysis of Fluorochloride Glass

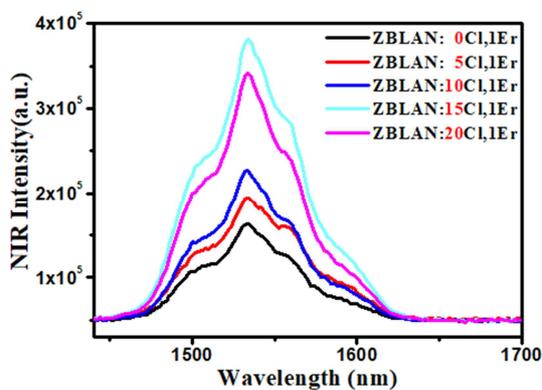


Figure 3. Near infrared spectra of Er³⁺ doped different Cl fluorochloride glasses under 980nm excitation.

Figure 3 shows the near-infrared emission spectra of Er³⁺-doped fluorochloride glasses doped with different Cl⁻ ion concentrations excited at 980 nm. Er³⁺ has a strong emission at 1550 nm (transitions of ⁴I_{11/2}→⁴I_{15/2}, ⁴I_{13/2}→⁴I_{15/2}). The luminescent intensity increases and then decreases as the concentration of Cl⁻ increases from 0 to 20%. The luminescent intensity was the highest when the concentration of Cl⁻ was 15%. This has the same tendency as the intensity factor calculated by the J-O theory. ZBLAN:10Cl,1Er and ZBLAN:15Cl,1Er begin to be transformed from transparent glass to opaque glass ceramic.

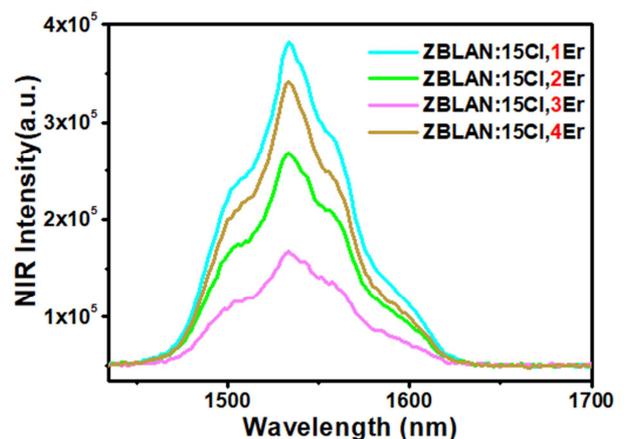


Figure 4. Near infrared spectra of Er³⁺ doped fluorochloride glass under 980 nm excitation.

Figure 4 shows the near-infrared fluorescence spectra of different concentrations of Er³⁺-doped fluorochloride glass excited at 980 nm. With different concentrations of Er³⁺ doped with fluorochloride glass, the fluorescence peak position did not shift as the concentration of Er³⁺ increased, but the luminescent intensity gradually decreased. This

means that excessive Er³⁺ doping will cause concentration quenching.

3.4. Mid-Infrared Analysis of Fluorochloride Glass

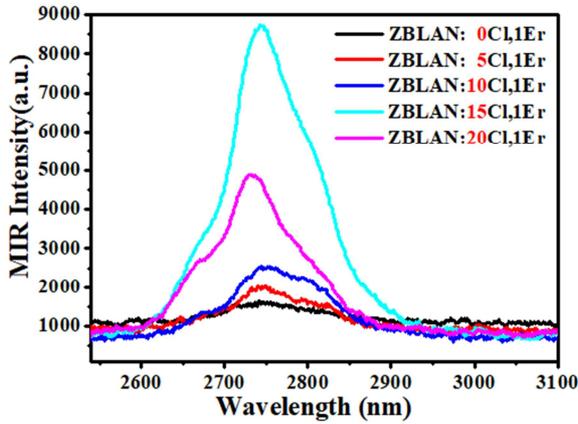


Figure 5. Mid infrared spectra of Er³⁺ doped fluorochloride glass with different concentration of Cl under 980 nm excitation.

Figure 5 shows the mid-infrared 2.7 μ m emission of fluorochloride glass of 980 nm excitations. In the figure, the luminescent intensity of 2.7 μ m (⁴I_{11/2}→⁴I_{13/2}) of Er³⁺ changes with the concentration of Cl. When the concentration of Cl reaches 15%, the luminescent intensity is maximum. At this point the sample has been fully ceramicized. A significant decrease in the luminescent intensity of the ZBLAN:20Cl,1Er samples can then be observed. In the near-infrared and mid-infrared fluorescence diagrams, the samples ZBLAN: xCl, yEr (x=0, 5, 10, 15, 20; y=1) have the same tendency. The Ω_2 value obtained by fitting with the J-O theory is consistent. The value of Ω_2 increases as the Cl content increases, resulting in a decrease in the symmetry of the Er ion.

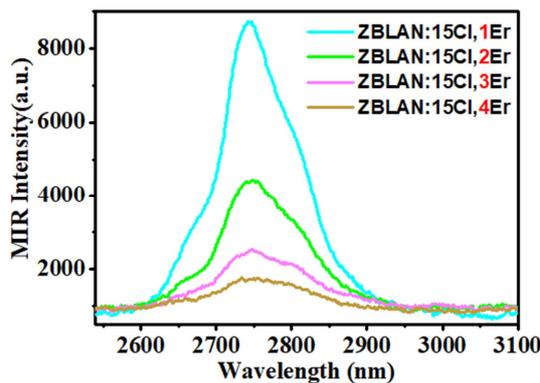


Figure 6. Mid infrared spectra of Er³⁺ doped fluorochloride glass under 980 nm excitation.

Figure 6 shows the mid-infrared fluorescence spectra of fluoride glasses with ZBLAN: xCl, yEr (x=15; y=1, 2, 3, 4) doped with different concentrations of Er³⁺ and Cl. Under the excitation of the 980 nm laser, for the ZBLAN: xCl, yEr (x=15; y=1, 2, 3, 4) sample, the emission peak appeared non-uniform broadening due to the site-to-site in the matrix, but the wavelength range of the emission peak did not change.

In the same concentration of Cl⁻, the luminescent intensity of ZBLAN: 15Cl, 1Er is the highest in the fluorochloride glasses doped with different Er³⁺. Increasing the concentration of Er³⁺, the luminescent intensity is significantly reduced, which is caused by concentration quenching. Therefore, the optimal doping concentration of Er³⁺ is 1 mol% in the optimal proportion of Cl⁻ doped fluorochloride glass.

3.5. Er³⁺ Energy Level Structure Diagram

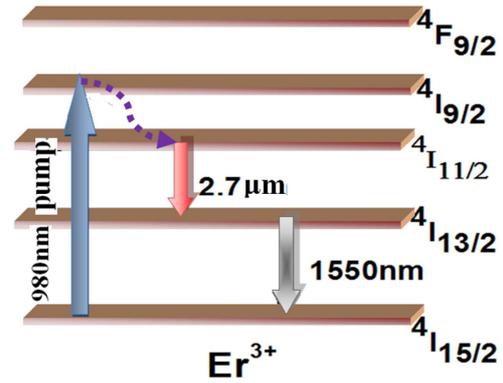


Figure 7. Er³⁺ energy level structure diagram.

The energy level transition diagrams of Er³⁺ [29] are shown in Figure 7. Er³⁺ is in the ground state (⁴I_{15/2}) at normal temperature, and is excited to the excited state of upper energy level (⁴I_{9/2}) under the action of laser pumping, and then transits to a non-irradiation state (⁴I_{13/2}) through a non-radiative state. Finally, after the radiation transition, 2.7 μ m of mid-infrared fluorescence (⁴I_{11/2}→⁴I_{13/2}) and 1550 nm of near-infrared fluorescence (⁴I_{13/2}→⁴I_{15/2}) were emitted.

4. Conclusion

In the work, fluorochloride glass was prepared for introducing Cl⁻ into an Er³⁺ doped fluoride glass by a conventional melt quenching method. To study the effect of Cl⁻ doping on the characteristic fluorescence spectra of Er³⁺-doped fluorochloride glass. In the near-infrared and mid-infrared spectra, the luminescent intensity gradually increases with to increase to Cl⁻. In addition, with the increase of Cl⁻ content, the sample gradually ceramicist, and the luminescent intensity of fluorochloride glass was also increased during the cremation process. Based on the calculations of the J-O theoretical parameters, the incorporation of Cl⁻ increases the covalency of the coordination bonds between Er³⁺ and reduces the local symmetry. The introduction to other elements in the fluoride glass enhances the chemical stability, thermal stability and fluorescent properties of the fluoride glass. The relationship between its structure and luminescence properties is clarified. The effect of fluorochloride glass of the glass properties after introduction to Cl⁻ was investigated. In order to improve the luminescence performance by using rare earth ion doped fluoride glass, it provides a certain theoretical basis. At the same time, it has

important guiding significance of the research, development and application of similar luminescent materials.

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