

Study on Physical, Optical and Luminescence of Er³⁺ in K₂O-CaO-B₂O₃ Glasses for Photonic Application

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Abstract

In this work, potassium calcium borate glasses doped with of Er³⁺ ions (KCaB:Er) have been prepared by a melt quenching technique. The glass physical, optical and luminescence properties have been investigated as a function of Er₂O₃ concentration. Density was measured by Archimedes' principle and brought to calculate the molar volume. The optical absorption spectra were measured in the ultraviolet, visible light and near-infrared regions. The emission and excitation spectra represents the strong emission from glass sample. All results indicate the potential to use KCaB:Er glass in the photonic applications such as laser and optical amplification.

Keywords: Potassium; calcium; Borate glasses; Erbium; Photoluminescence; Photonic application

Introduction

The Erbium ion (Er³⁺) is one of the most popular and efficient ions for obtaining near infrared (NIR) to visible up conversion as well as 1.55 μm IR emission for lasers and optical amplification at the third telecommunication window.⁽¹⁾ Additional, the Er³⁺ ion has a number of strong absorption bands where the pumping sources are available. The laser at 1.55 μm wavelength attracted much attention since it is located in the "eye safe" spectral region and has attractive applications in atmospheric communication systems. Er³⁺-doped glasses with a broad 1.55 μm emission band have been extensively investigated in searching Er-doped fiber amplifiers with a wide and flat gain spectrum that is required for dense wavelength division multiplexing optical networks.⁽²⁾ Borate is one of the most important glass formers combined with various kinds of glass system as a flux material in order to attain materials having specific physical and chemical properties suitable for high technological applications.⁽³⁻⁴⁾

Some of the benefits in using modifiers (alkali/alkaline) in borate glass formulations

are increased thermal resistance and mechanical strength, enhanced aqueous, capacity to concentrate transition metal ions and chemical durability and also reduced of melting temperature.⁽⁵⁻⁶⁾

Taking potassium into glass network, it can improve chemical and electrical resistance of glass material.⁽⁷⁾ Adding calcium element can increase intensity of luminescence emission of glass.⁽⁸⁾ Therefore, The objective of work we have study potassium calcium borate glasses doped with of Er³⁺ ions (KCaB:Er³⁺).

Experimental

Glass preparation

Er³⁺ doped potassium calcium borate glasses (KCaB:Er³⁺) of composition (65-x) B₂O₃- 25K₂O- 10CaO- xEr₂O₃, where x = 0.05, 0.10, 0.50, 1.00 and 1.50 mol% were synthesized by melt quenching technique. Analytical reagent grade chemicals used H₃BO₃, K₂O, CaO and Er₂O₃. About 15 g of batch chemicals were thoroughly mixed in alumina crucible and then melted at 1,200°C by an electric

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furnace for 3 h after complete melting, the melts were then quickly poured into a stainless steel mould and annealed 500°C for 3 h before cooled down to room temperature. Finally, the as-prepared glasses were cut and polished.

Experimental methods

The densities (ρ) were measured by Archimedes's method using a 4-digit sensitive microbalance. Obtained densities were used to calculate by the relation,

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

where W_a is the weight in air, W_b is the weight in water and ρ_b is the density of water ($\rho_b = 1 \text{ g/cm}^3$). The corresponding molar volumes (V_M) were calculated using the relation,

$$V_M = \frac{M_T}{\rho} \quad (2)$$

Where M_T is the total molecular weight of glass system. The refractive indexes of glasses were measured on an Abbe refractometer, Model ATAGO, using the sodium wavelength 589.3 nm. The optical spectra of glass samples were measured with a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600) in the wavelength range 200-2,500 nm. The excitation, emission spectra were recorded by using a Quanta Master 3 luminescence spectrometer from Photon Technology International (PTI Inc.)

Results and discussion

The densities, molar volumes and refractive index of KCaB:Er³⁺ glasses are shown in Figure 1, 2 and 3 respectively. It can be seen in Figure 1, the densities increases with additional content of Er₂O₃ into the network. This indicates that replacing B₂O₃ by addition of a small amount of Er₂O₃ results in the increase of the total molecular weight in glass due to Er₂O₃ has a higher molecular mass than B₂O₃. As shown in Figure 2, the molar volume increases with increasing of Er₂O₃ concentration. Er³⁺ destroy the bridges that connect oxygen ions, generate non-bridging oxygen (NBOs), which decrease the concentration of borate units. Therefore, the resulting network gets loose and the connectivity of borate network decreases. The gradual increase in the molar volume can be attributed

to opening up of glass structure. The refractive index of KCaB:Er³⁺ glasses are shown the same trend with densities that increases with increasing of Er₂O₃ concentration (Figure 3). It indicates that light velocity was reduced when light move into more dense glass with increasing of Er₂O₃ concentration.⁽⁹⁾

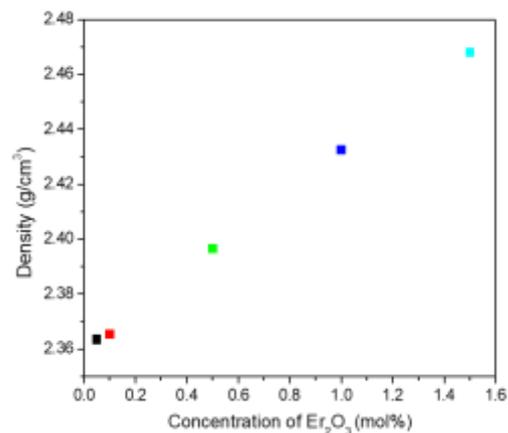


Figure 1. Densities of the KCaB:Er³⁺ glasses.

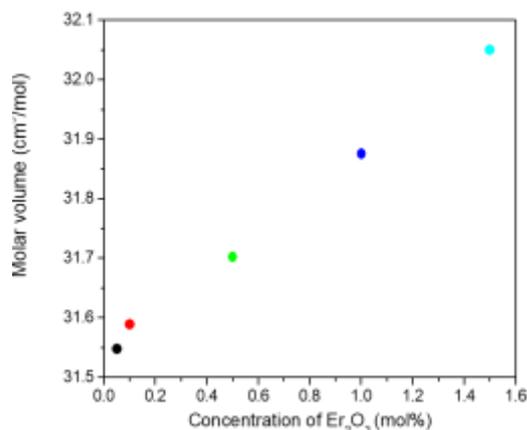


Figure 2. Molar volumes of the CaB:Er³⁺ glasses.

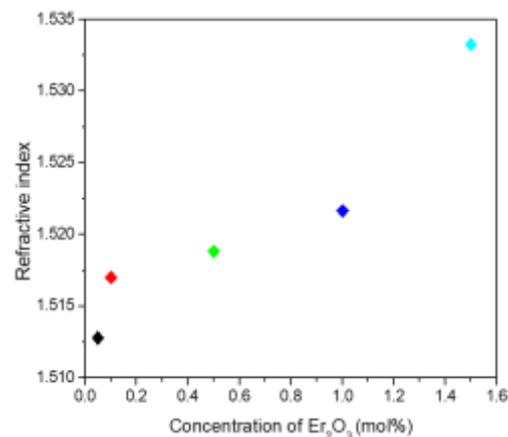


Figure 3. Refractive index of the KCaB:Er³⁺ glasses

Optical property

The absorption spectra of KCaB:Er^{3+} glasses was recorded with a UV-VIS-NIR region as shown in Figure 4. All transitions in the absorption spectrum of Er^{3+} start from the ground state $^4\text{I}_{15/2}$ to the higher excited states of Er^{3+} . Eight absorption transitions consist of $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$ (397 nm), $^4\text{I}_{15/2} \rightarrow ^2\text{G}_{9/2}$ (407 nm), $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{5/2}$ (452 nm), $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ (489 nm), $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ (522), $^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ (544), $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ (652 nm), $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ (801 nm), $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ (976 nm) and $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ (1533 nm) transitions^(1-2,10-11) It can be observed that the absorption intensity increases with the increase in concentration of Er^{3+} and the highest intensity of absorption peaks were observed in VIS and NIR region at 522 and 976 nm, respectively.

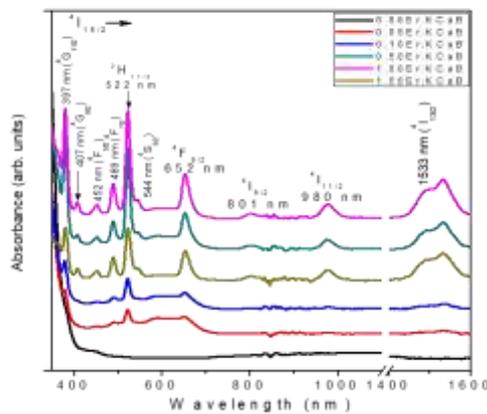


Figure 4. Absorption spectra of KCaB:Er^{3+} glasses.

Luminescence properties

As a results of the absorption spectra of glasses in the wavelength at 522 and 980 nm, these wavelength were used to study the NIR emission spectra of KCaB:Er^{3+} glasses in the range of 1,400 to 1,700 nm. Figure 5 and 7 showed the NIR emission spectra of Er^{3+} doped glasses, they were presented at 1,547 nm wavelength which corresponding from $^4\text{I}_{15/2}$ to excited state $^4\text{I}_{13/2}$ transitions⁽¹⁻²⁾. From the result, they found that excitation by 522 nm results in higher emission intensity than that of excitation by 980 nm due to the highest absorption intensity of 522 nm compared with other. Furthermore, the intensity of emission similar tended to increases with the increasing of Er^{3+} concentration up to 1.00 mol% and then decreases with the increase of Er^{3+} concentration as shown in Figure 6 and 8.

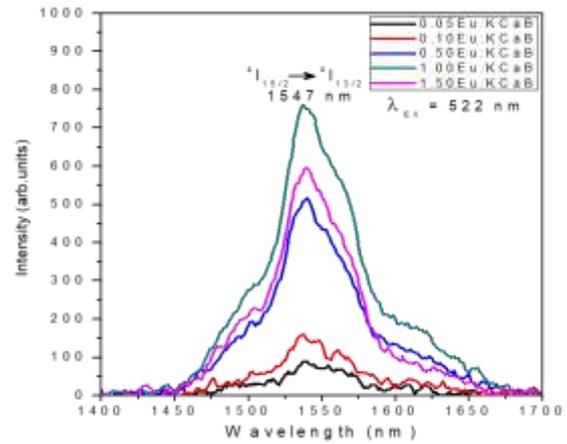


Figure 5. The emission spectra of KCaB:Er^{3+} glasses excited at 522 nm.

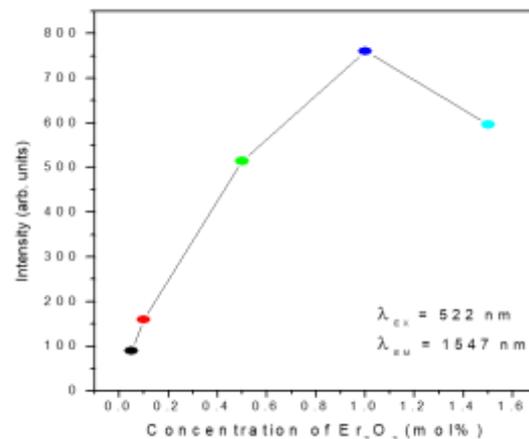


Figure 6. The NIR emission intensity of KCaB:Er^{3+} glasses excited at 522 nm.

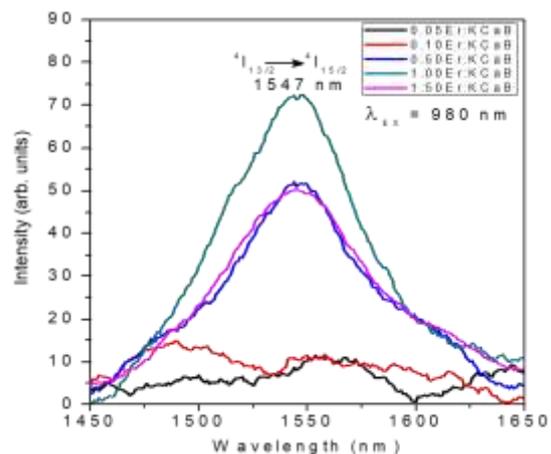


Figure 7. The emission spectra of KCaB:Er^{3+} glasses excited at 980 nm.

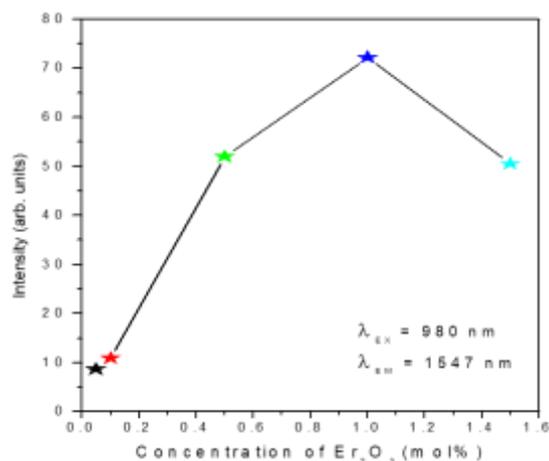


Figure 8. The NIR emission intensity of KCaB:Er³⁺ glasses excited at 980 nm.

Figure 9 displays the excitation spectra in the wavelength range of 300-1,000 nm for the KCaB:Er³⁺ glasses. The spectrum consists of seven bands due to the transitions from the ground ⁴I_{15/2} state to various excited states that are ⁴G_{11/2}, ⁴G_{9/2}, ⁴F_{5/2}, ⁴F_{7/2}, ²H_{11/2}, ⁴F_{9/2} and ⁴I_{11/2} transitions with the corresponding band positions centered at 379, 405, 451, 485, 522, 653 and 980 nm respectively⁽¹⁻²⁾. The energy level diagram for excitation and emission spectra of Er³⁺ ion in KCaB glasses is shown in Figure 10.

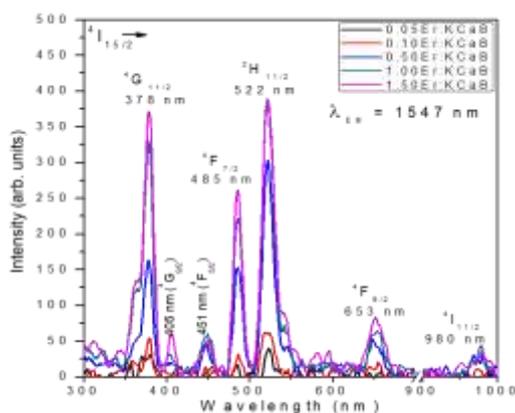


Figure 9. The excitation spectra of KCaB:Er³⁺ glasses.

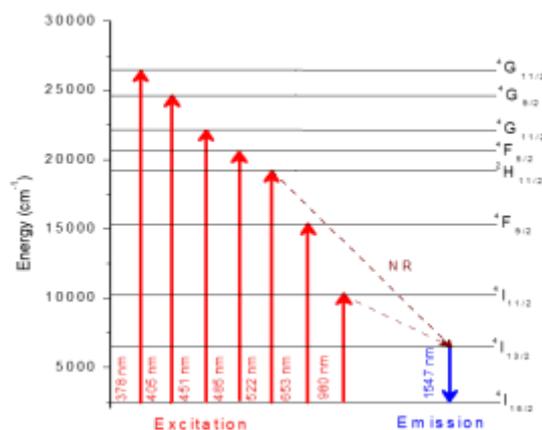


Figure 10. Energy level diagrams of Er³⁺ doped KCaB glasses.

Conclusion

The Er³⁺ doped potassium calcium borate glasses were prepared and investigated for their characteristics related to dopant concentrations. The density, molar volume and refractive index of glass increased with increasing of Er₂O₃ concentration. Glass samples absorbed photon in visible light and near infrared region. Absorption bands at 522 and 980 nm are highest absorption spectra in VIS and NIR region, respectively. The NIR emission located at about 1,547 nm (under 980 nm excitation) is observed in these glasses, which should be ascribed to the ⁴I_{13/2}→⁴I_{15/2} transition of Er³⁺ ions. The emission intensity at about 1547 nm can be highly enhanced with increasing of Er dopant till 1 mol%. The KCaB:Er³⁺ glasses in this study could be a promising luminescence material in NIR region and 1.55 μm window telecommunication system.

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References

1. Babu P., Hyo Jin Seo, Kyoung Hyuk Jang, Upendra Kumar K., Jayasankar C.K. (2007). 1.55 μ m emission and upconversion properties of Er^{3+} -doped oxyfluorotellurite glasses” *Chemical Physics Letters*. **445**: 162-166.
2. Kumar, U., Linganna, K., Surendra Babu K. S., Piccinelli F., Speghini A., Giarola M., and Mariotto, Jayasankar G. C. K. (2012). Synthesis, Structural Properties and Upconversion Emission of Er^{3+} and Er^{3+}/Yb^{3+} Doped Nanocrystalline $NaNbO_3$. *Science of Advanced Materials*. **4**: 584-590.
3. Becker P. (1998). Borate materials in nonlinear optics. *Advanced Materials*. **10**: 979-992.
4. Furetta C. (2003). Handbook of thermoluminescence. *New York: World Scientific Publisher*.
5. Kayhan M. and Yilmaz A. (2011). Effects of synthesis, doping methods and metal content on thermoluminescence glow curves of lithium tetraborate” *Journal of Alloys and Compounds*. **509**: 7819–7824.
6. Madzlan A., Saad S.A., Wan R.W.B. and Wan Z.W.M. (2012). Structure of SnO_2 nanoparticles by sol-gel method. *Materials Letters*. **74**: 62-64.
7. Hugo R. Fernandes, Dilshat U. Tulyaganov, Maria J. Pascual, Vladislav V. Kharton, Aleksey A. Yaremchenko, José M.F. Ferreira. (2012). The role of K_2O on sintering and crystallization of glass powder compacts in the $Li_2O-K_2O-Al_2O_3-SiO_2$ system. *Journal of the European Ceramic Society*. **32**: 2283-2292.
8. Kaewkhao, J., Wantana, N., Kaewjang, S., Kothan S. and Kim H.J. (2016). Luminescence Characteristics of Dy^{3+} Doped $Gd_2O_3-CaO-SiO_2-B_2O_3$ Scintillating Glasses. *Journal of Rare Earths*. **34**: 583-589.
9. Sangwal, K. and Kucharczyk, W. (1987). Relationship between density and refractive index of inorganic solids. *Journal of Physics D: Applied Physics*. **20(4)**: 522-525.
10. Ratnakaram, Y.C., Lakshmi, J. and Chakradhar, R.P.S. (2005). Optical absorption and fluorescence properties of Er^{3+} in sodium borate glass. *Bulletin of Materials Science*. **28(50)**: 461-465.
11. Liu, S., Zhao, G., Li, Y., Ying, H., Wang, J., and Han, G. (2008). Optical absorption and emission properties of Er^{3+} doped mixed alkali borosilicate glasses. *Optical Materials* **30**: 1393-1398.