Study on Physical, Optical and Luminescence of Er\textsuperscript{3+} in K\textsubscript{2}O-CaO-B\textsubscript{2}O\textsubscript{3} Glasses for Photonic Application

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Abstract

In this work, potassium calcium borate glasses doped with of Er\textsuperscript{3+} ions (KCaBEr) have been prepared by a melt quenching technique. The glass physical, optical and luminescence properties have been investigated as a function of Er\textsubscript{2}O\textsubscript{3} 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 KCaBEr glass in the photonic applications such as laser and optical amplification.

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

Introduction

The Erbium ion (Er\textsuperscript{3+}) is one of the most popular and efficient ions for obtaining near infrared (NIR) to visible up conversion as well as 1.55 \( \mu \)m IR emission for lasers and optical amplification at the third telecommunication window.\textsuperscript{(1)} Additional, the Er\textsuperscript{3+} ion has a number of strong absorption bands where the pumping sources are available. The laser at 1.55 \( \mu \)m wavelength attracted much attention since it is located in the “eye safe” spectral region and has attractive applications in atmospheric communication systems. Er\textsuperscript{3+}-doped glasses with a broad 1.55 \( \mu \)m 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.\textsuperscript{(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.\textsuperscript{(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.\textsuperscript{(5-6)}

Taking potassium into glass network, it can improve chemical and electrical resistance of glass material.\textsuperscript{(7)} Adding calcium element can increase intensity of luminescence emission of glass.\textsuperscript{(8)} Therefore, The objective of work we have study potassium calcium borate glasses doped with of Er\textsuperscript{3+} ions (KCaB:Er\textsuperscript{3+}).

Experimental

Glass preparation

Er\textsuperscript{3+} doped potassium calcium borate glasses (KCaB:Er\textsuperscript{3+}) of composition (65-x) B\textsubscript{2}O\textsubscript{3} - 25K\textsubscript{2}O - 10CaO - xEr\textsubscript{2}O\textsubscript{3}, 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 H\textsubscript{3}BO\textsubscript{3}, K\textsubscript{2}O, CaO and Er\textsubscript{2}O\textsubscript{3}. About 15 g of batch chemicals were thoroughly mixed in alumina crucible and then melted at 1,200°C by an electric
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 ($\rho$) were measured by Archimedes’s method using a 4-digit sensitive microbalance. Obtained densities were used to calculate by the relation,

$$\rho = \frac{W_a}{W_a-W_b} \times \rho_b$$

(1)

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

$$V_M = \frac{M_T}{\rho}$$

(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:Er$^{3+}$ glasses are shown in Figure 1, 2 and 3 respectively. It can be seen in Figure 1, the densities increases with additional content of Er$_2$O$_3$ into the network. This indicates that replacing B$_2$O$_3$ by addition of a small amount of Er$_2$O$_3$ results in the increase of the total molecular weight in glass due to Er$_2$O$_3$ has a higher molecular mass than B$_2$O$_3$. As shown in Figure 2, the molar volume increases with increasing of Er$_2$O$_3$ concentration. Er$^{3+}$ 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:Er$^{3+}$ glasses are shown the same trend with densities that increases with increasing of Er$_2$O$_3$ concentration (Figure 3). It indicates that light velocity was reduced when light move into more dense glass with increasing of Er$_2$O$_3$ concentration.\(^9\)
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 $^4I_{15/2}$ to the higher excited states of Er$^{3+}$. Eight absorption transitions consist of $^4I_{15/2} \rightarrow ^4G_{11/2}$ (397 nm), $^4I_{15/2} \rightarrow ^4F_{5/2}$ (452 nm), $^4I_{15/2} \rightarrow ^4F_{7/2}$ (489 nm), $^4I_{15/2} \rightarrow ^2H_{11/2}$ (522), $^4I_{15/2} \rightarrow ^4S_{3/2}$ (544), $^4I_{15/2} \rightarrow ^4F_{9/2}$ (652 nm), $^4I_{15/2} \rightarrow ^4H_{11/2}$ (522), $^4I_{15/2} \rightarrow ^4I_{13/2}$ (1533 nm) transitions. 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.

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 $^4I_{15/2}$ to excited state $^4I_{13/2}$ transitions. 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 8. The NIR emission intensity of KCaB:Er$^{3+}$ glasses excited at 980 nm.

Figure 9 displays the excitation spectra in the wavelength range of 300-1,000 nm for the KCaB:Er$^{3+}$ glasses. The spectrum consists of seven bands due to the transitions from the ground $^4$I$_{15/2}$ state to various excited states that are $^5$G$_{11/2}$, $^4$G$_{9/2}$, $^4$F$_{5/2}$, $^4$F$_{7/2}$, $^2$H$_{11/2}$, $^4$F$_{9/2}$ and $^4$I$_{11/2}$ 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 Er$^{3+}$ ion in KCaB glasses is shown in Figure 10.

Figure 9. The excitation spectra of KCaB:Er$^{3+}$ glasses.

Figure 10. Energy level diagrams of Er$^{3+}$ doped KCaB glasses.

**Conclusion**

The Er$^{3+}$ 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 Er$_2$O$_3$ 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 $^4$I$_{13/2} \rightarrow ^4$I$_{15/2}$ transition of Er$^{3+}$ ions. The emission intensity at about 1547 nm can be highly enhanced with increasing of Er dopant till 1 mol%. The KCaB:Er$^{3+}$ glasses in this study could be a promising luminescence material in NIR region and 1.55 $\mu$m window telecommunication system.

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