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Spectral studies on Cu^{2+} doped sodium leadbismuthate glasses

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Abstract

Copper doped sodium leadbismuthate glasses were prepared in the chemical composition (wt.%) $35Bi_2O_3 + 35PbO + (30 - x)Na_2O + xCuO$ (where $x = 1$, 2, 3 and 4). The optical spectra of the glasses have been investigated. The optical absorption spectra of Cu^{2+} doped glasses show a broad absorption band between 560 and 880 nm, which is attributed to the $^2E_g \rightarrow {}^2T_{2g}$ transition of Cu^{2+} ion. FTIR spectral studies confirm the Bi–O bonds and the presence of $[BiO_3]$ pyramidal units.

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Keywords: Glass; Optical materials; FTIR; Optical absorption

1. Introduction

Developments in telecommunication industry require the new materials suitable for optical wave guides, optical switching devices, and magneto optic devices. Inorganic glasses are the most suitable materials for these devices because they can be easily prepared, and changing the dopant will change the properties of the glasses. Doping rare-earth ions in the glasses makes them suitable as lasing materials [1] and fiber amplifiers [2]. Doping semiconductors like CdS [3], and PbS [4] in the glasses find applications in all-optical switching devices.

Heavy metal oxide glasses are gaining much attention because of their higher linear and nonlinear refractive index. But, a heavy metal oxide like Bi_2O_3 does not form glass by itself because bismuth ions are highly polarizable and the co-ordination number of the Bi^{3+} ions may decrease and the cations may exist in the glass network in $[BiO_3]$ pyramids in the presence of conventional glass forming cations such as P^{5+}, Si^{4+}, B^{3+}, and the presence of other metal ions [5,6]. Hazra et al [5] reported that in multicomponent bismuth cuprate glasses are built-up of both $[BiO_6]$ octahedral and $[BiO_3]$ pyramidal units. Bismuth based glasses are also used in the fabrication of switching and memory devices because of their higher order hyper polarizability. In addition, several authors have reported many glass systems based on Bi_2O_3 [7–9].

In recent years considerable interest has arisen in the chemistry of heavy metal oxide glasses doped with various transition metal ions [8] and rare-earth ions [10–12] but there are only limited studies that use Cu^{2+} ion as doping agent. In view of the limited studies on the Cu^{2+} doped glasses, we were motivated to prepare and analyse the Cu^{2+} doped glasses. Thus the purpose of the present study is to prepare and to evaluate the thermal and spectral characteristics of the Cu^{2+} doped sodium leadbismuthate glasses.

2. Experimental

The glass samples were prepared by using high purity Bi_2O_3, PbO, Na_2CO_3 and CuO in the composition range of (in wt.%) $35Bi_2O_3 + 35PbO + (30 - x)Na_2O + xCuO$, where $x = 1$, 2, 3 and 4. Appropriate amounts of weighed chemicals were ground well in a mortar to produce 25 g of each glass mixture. The mixture was heated and maintained at 450 °C for about 2 h for decarbonization and then the temperature was raised up to 1050 °C and maintained for an hour. The molten liquid was stirred frequently to make mixture as homogenous mixture. The melt was quenched at room temperature in air by pouring the melt on a stainless steel plate and pressing with another stainless

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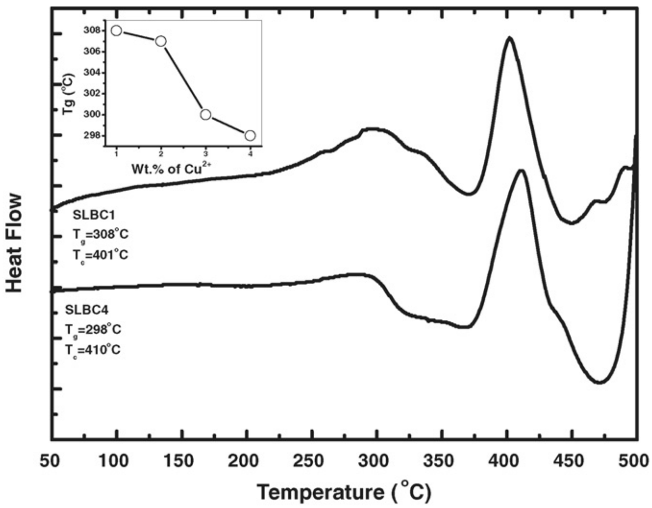

Fig. 1. DSC thermograms of SLBC1 and SLBC4 glasses.

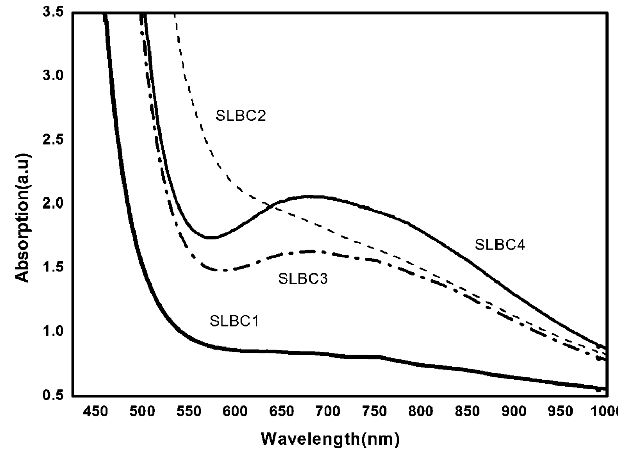

Fig. 2. Optical absorption spectra of SLBC glasses.

steel plate. The quenched dark green coloured glasses were cut into proper shape for further studies and the glasses were semi transparent in nature. The samples were marked as SLBC1 to SLBC4 with respect to 'x' values in the composition of the glasses. The XRD studies carried out using a Rigaku Miniflex table top spectrometer confirmed the amorphous nature of the samples. The thermal studies were carried out in a mettler differential scanning calorimeter (DSC) in the range of 50–500 °C at a heating rate of 10 °C/min. The optical absorption spectra were recorded in a Shimadzu UV Spectrometer. The FTIR spectra were recorded on a Shimadzu FTIR-8700 spectrometer in the wave number range of 400–4000 cm^{-1} by the KBr pellet technique.

3. Results and discussion

3.1. XRD and thermal analysis

The diffractograms show no sharp peaks, which confirm the amorphous nature of the glasses under investigation. The DSC curve for SLBC1 and SLBC4 are presented in Fig. 1. The inset of Fig. 1 shows that the glass transition decreases gradually when the Cu^{2+} concentration increases, while T_c increases with increasing dopant concentration. This implies that the glass

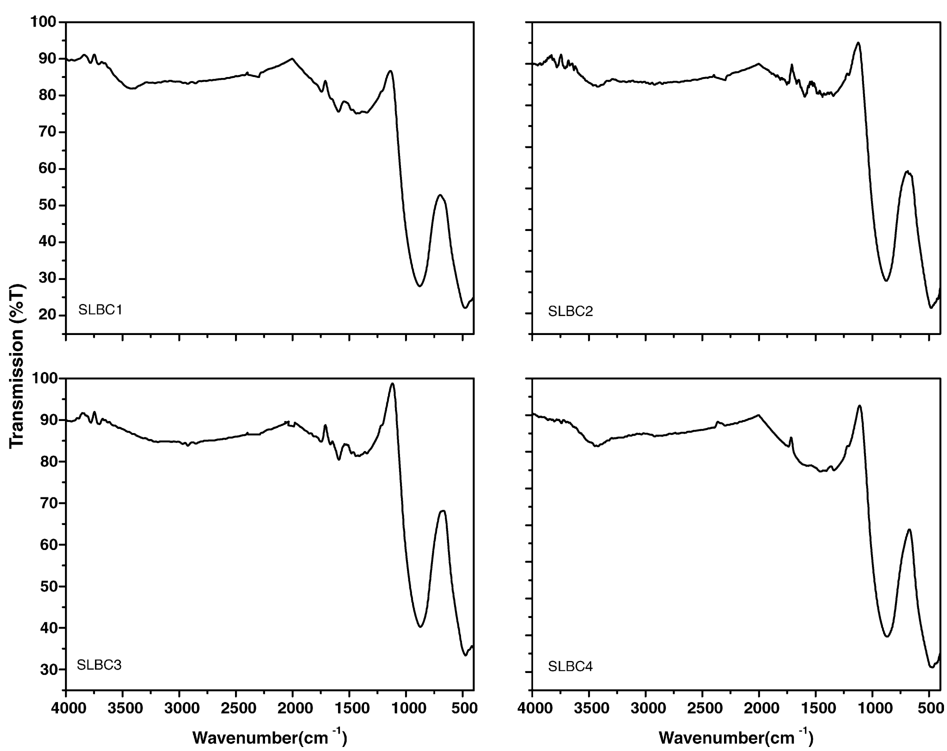

Fig. 3. FTIR spectra of SLBC glasses.

thermal stability ($T_c - T_g$) increases with the concentration of Cu.

3.2. Optical absorption studies

The optical absorption spectrum is an important tool for analyzing the effect of doping of transition metal ions in the glasses. The optical absorption spectra of all glass samples are shown in Fig. 2. In optical absorption the observed broad peak in between 560 and 880 nm can be attributed to the d–d transition band of Cu^{2+} ion corresponding to $^2E_g \rightarrow {}^2T_{2g}$ [13]. The optical absorption studies confirm the presence of Cu^{2+} ions in the sodium leadbismuthate glasses used in the present investigation.

3.3. FTIR spectral studies

The room temperature FTIR spectra of the sodium leadbismuthate glasses are shown in Fig. 3. The spectra indicate that the glasses have good transparency in the IR region up to 11 μm. Bi_2O_3 alone is not a glass former but in the presence of other metal oxides it will also form the glass. In the infrared spectral region, the vibrational modes of the bismuthate network have three fundamental vibrational bands which are observed at 820, 618 and 543 cm^{-1}. Bishay and Maghrabi [14] have reported that in the presence of strong polarizing cations, Bi^{3+}can reduce their coordination number (6) from the $[BiO_6]$ octahedral units and form a glass network into $[BiO_3]$ pyramidal units which belong to the C_{3V} point group. The band at 3450 cm^{-1} is observed in all the glass samples and is assigned to the hydroxyl or water groups present in the glasses. The band seen around 480 cm^{-1} is ascribed to Bi−O symmetric stretching vibrations and also assigned to the degenerate stretching vibrations of $[BiO_3]$ pyramidal unit. The vibrational band at 883 cm^{-1} is attributed to Bi–O stretching vibrations of the pyramidal $[BiO_3]$ unit. The broad band between the wavenumber range 1340 and 1560 cm^{-1} is assigned to the ${CO_3}^{2-}$ ions dissolved in the glasses, which arises from the Na_2CO_3 used as the starting material. The vibrational assignments agree well with the literature values [5,15,16].

4. Conclusion

In the present investigation, a complete spectral and thermal analysis of Cu^{2+} doped sodium leadbismuthate glasses has been carried out using XRD, DSC, optical absorption spectra and Fourier-transform infrared spectral techniques. From the entire analysis, the following observations are made:

(i) The glasses exhibit a good IR transmitting window up to 11 μm.
(ii) The doping of Cu^{2+} in the glasses much improves their stability significantly.
(iii) The optical absorption measurements show that Cu is in the Cu^{2+} state and the intensity of the peak also increases with the concentration of Cu^{2+} ion.
(iv) The FTIR studies clearly confirm that the Bi_2O_3 will work as a glass modifier and is present in the $[BiO_3]$ pyramidal form.

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