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Crystallization kinetics, optical and dielectric properties of $Li_2O \cdot CdO \cdot Bi_2O_3 \cdot SiO_2$ glasses

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ABSTRACT

Crystallization kinetics, optical absorption and electrical behavior of lithium cadmium silicate glasses with different amount of bismuth oxide were investigated using non-isothermal crystallization approach, UV–VIS–NIR spectroscopy and impedance spectroscopy, respectively. These glasses were synthesized by normal melt quenching technique. Variation in physical properties, viz. density, molar volume with Bi_2O_3:SiO_2 ratio were related to the structural changes occurring in the glasses. The glass transition temperature (T_g), crystalline peak temperature (T_p) and melting temperature (T_m) of these glasses were determined using differential scanning calorimeter at various heating rates. The dependence of T_g and T_p on heating rate has been used for the determination of the activation energy of glass transition and crystallization. Thermal stability parameters have revealed high stability of the glass prepared with 40 mol% of Bi_2O_3 content. The crystallization kinetics for the glasses was studied by using the Kissinger and modified Ozawa equations. Appearance of a sharp cut-off and a wide and reasonable transmission in VIS–NIR region makes these glasses suitable for IR transmission window. The cut-off wavelength, optical band gap and Urbach's energy have been analyzed and discussed in terms of changes in the glass structure. By analyzing the impedance spectra, the ac and dc conductivities, activation energy for dc conduction (E_{dc}) and for relaxation ($E_{M''}$) were calculated. The results obtained from dc conductivity confirm the network forming role of Cd^{2+} ion in the glasses. The scaling of the conductivity spectra has been used to interpret the temperature dependence of the relaxation dynamics. The observed conductivity spectra follows power law with exponent 's' which decreases with temperature and satisfies the correlated barrier hopping (CBH) model. The perfect overlying of normalized plots of electrical modulus on a single 'master curve' depicts temperature as well as composition independent dynamical process at several frequencies.

Introduction

The considerable interest of research workers in bismuth-silicate glasses is due to the possibility of their various applications in different fields of electronics based on the fact that these have superior physical, optical and electrical properties. Among other properties, Bi-doped silicate glasses have large refractive index, high transparency in the far infrared region, high density and also have high efficiency and absorption cross-section [1–3]. All these characteristics make these important for several applications such as advanced optical telecommunication, processing devices, infrared transmission components or as active medium for Raman-active optical fiber amplifiers and oscillators, radiation shield and as novel lasers [1–3]. Further, the doping of Bi ion in the host glass improves the chemical durability. However, bismuth oxide cannot form glass by itself like other conventional glass former due to its high polarizability and small field strength (of Bi^{3+} ion). In the presence of conventional glass forming cations; such as B^{3+}, Si^{4+} etc., Bi^{3+} ion can decrease its co-ordination number from VI to III and the glass network may consist of both [BiO_6] highly distorted octahedral and [BiO_3] pyramidal units [4,5]. In recent years, the glasses containing cadmium oxide (CdO) have been studied extensively by several authors because of their appealing electronic transport and optical properties. CdO, when added to the glass matrix, behaves as a good network modifier and thereby stabilized the glass structure and also enhanced the electrical properties by increasing the dielectric constant [6]. However, when the highly polarizable Cd^{2+} ions are added in large quantities in the glass

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matrix, it tend to occupy both network modifier and network former positions [7]. Furthermore, the glasses with high ionic conductivity attract a significant attention because of their potential applications as solid electrolytes in high energy density batteries and sensors etc. [8,9]. Thus, doping of these glasses by traces of other elements such as alkali metals (Li^+) modifies their structural network and consequently enhances the ionic conductivity [9], thereby rendering them valuable in solid state technology. During last few years, a number of studies have been done to interpret the crystallization kinetics of glasses using different techniques [10–13]. Differential thermal analysis (DTA) and differential scanning analysis (DSC) have been frequently used for such studies and allowed the possibility to determine valuable data with isothermal and non-isothermal methods [11,12]. In isothermal method, glass samples are heated and soaked at a temperature above the glass transition temperature, and hence crystallization occurs at a definite temperature. However, in non-isothermal method, glass samples are heated up at a definite heating rate and crystallized during the thermal analysis scan. The non-isothermal method is simpler and faster method [14]. In the present work, investigations on thermal properties and the crystallization kinetics of the lithium cadmium bismuth silicate glass system were carried out by the means of the non-isothermal DSC measurements. Thermal stability of glasses and characteristic temperatures such as glass transition temperature, crystalline peak temperature and melting temperature were measured using non-isothermal DSC curves. One of the most important parameter, i.e., activation energy for glass transition as well as crystallization of glasses was also measured using Kissinger [15] and Matusita–Ozawa methods [16]. Further, the physical, optical and electrical properties of the present glasses containing various amount of Bi_2O_3 have been analyzed to see that the effect of replacing SiO_2 with Bi_2O_3 on these properties. The present work also includes the conduction and relaxation mechanisms using impedance spectroscopy studied over a wide range of frequency and temperature.

Theoretical background

Differential scanning calorimetry (DSC) is the most commonly used technique for studying the behavior of crystallization kinetics in glasses under non-isothermal methods. The crystallization kinetics of amorphous materials have been intensively studied using the classical Jonshson–Mehl–Avrami model [17] in which the crystallized fraction (χ) is depicted as function of time 't' according to:

$$\chi = 1 - \exp[-(Kt)^n] \tag{1}$$

where n is the Avrami exponent, which reflects the growth and dimensionality of the crystal. K is defined as the effective (overall) reaction rate constant and is represented as

$$K = K_0 \exp\left(-\frac{\Delta E_p}{RT}\right) \tag{2}$$

where K_0 is the frequency factor and ΔE_p is the activation energy for crystallization. To evaluate the activation energy for each crystalline peak, Kissinger [15] proposed a linear dependence between ln (b/T_p^2) and ($10^3/T_p$) and represented as

$$\ln\left(\frac{b}{T_p^2}\right) = \text{constant} - \frac{\Delta E_p}{RT_p} \tag{3}$$

where T_p is the crystalline peak temperature and b is the heating rate (in °C/min). According to Solimon [18], the Kissinger formula is also valid for non-isothermal glass transition peak and has the form

$$\ln\left(\frac{b}{T_g^2}\right) = \text{constant} - \frac{\Delta E_g}{RT_g} \tag{4}$$

where ΔE_g is the activation energy of glass transition temperature. Furthermore, the activation energy of crystallization can also be determined from the variation of the crystalline peak temperature T_p with heating rate by using the relation [16] as

$$\ln(b) = \text{constant} - \frac{\Delta E_p}{RT_p} \tag{5}$$

This relation is known as Matusita–Ozawa's equation.

Experimental details

Glasses having composition $30Li_2O{\cdot}20CdO{\cdot}xBi_2O_3{\cdot}(50-x)SiO_2$ ($x = 10$, 20, 30 and 40 mol%; abbreviated as LCBS 1, LCBS 2, LCBS 3 and LCBS 4, respectively) were synthesized using conventional melt quenching technique and high purity (≥99%) Li_2CO_3, CdO, Bi_2O_3 and SiO_2 chemicals were used. 20 g batches of these chemicals (well mixed) were taken in crucible and melted in air using an electric muffle furnace at 1100 °C for an hour. The melts were agitated by stirring frequently to ensure homogeneity of the melt. The homogeneous melts were then immediately quenched at room temperature (RT) by pouring it in between two stainless steel plates and brown colored glass samples were formed. All the samples were then annealed for about 24 h at 573 K (below glass transition temperature). The density of each glass sample (as prepared) was measured at room temperature using Archimedes's method with deionized water as the immersing liquid ($D_{deionizedwater} = 0.99766$ g cm^{-3}). All measurements were repeated two or three times per sample. The accuracy of the results in density measurement is ±0.001 g cm^{-3}. The molar volume, V_g, was calculated using the formula; $V_g = \sum(x_i M_i)/D_g$, where x_i is the molar fraction and M_i is the total molecular weight of the ith component. The thermal behavior was investigated by using differential scanning calorimeter (Model: Q600 SDT TA instruments). Each sample was heated at a constant heating rate of 5, 10 and 15 °C/min and the changes in heat flow as well as derivative of heat flow with respect to temperature were measured. During all the runs the sample chamber was purged with dry nitrogen. The glass transition temperature and crystalline temperature were determined with an accuracy of ±2 °. The thermal stability of glasses and the glass forming ability (qualitatively) were also determined by using these thermal parameters. The optical absorption of all the glasses was recorded at RT with a UV–VIS–NIR spectrometer (Cary 5000) in the wavelength range 200–3300 nm. The estimated error observed in wavelength is ±2 nm. The optical band gap (E_g) and the Urbach energy (ΔE) were evaluated from the observed absorption spectra. The temperature dependent electrical data for LCBS glasses were recorded by using an impedance gain/phase analyzer (Newton's 4th Ltd.) over a frequency range from 10 Hz to 1 MHz and in temperature range below the glass transition temperature. The obtained data was analyzed in the Nyquist representation form, a typical complex plane plot represented by imaginary part $Z''(\omega)$ vs. real part $Z'(\omega)$ for each temperature. The dc conductivity was calculated from the Nyquist plots. The experimental error in the complex impedance data is of order of ±1%.

Results and discussion

Physical properties

The compositional dependence of density (D_g) and molar volume (V_g) for all the glasses under study are shown in Fig. 1 and their