Novel oxide-based glass nanocomposites for nonlinear optical applications

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Oxide based glasses containing ferroelectric phases were fabricated via a melt-quenching technique. The as-quenched glasses were found to contain nanocrystallites of non-centrisymmetric Bi_2TeO_5 phase. Heat-treatment procedures were adopted to get crystalline phases in the transparent glass matrix. These glass composites (both as-quenched and heat-treated glasses) were characterized for linear and nonlinear optical (NLO) properties and the suitability of the same for the device applications were explored. The influence of electrical poling at elevated temperatures on the second and third order nonlinear optical effects were also studied. The polar properties (pyroelectricity and ferroelectricity) in the nanoscale of the present materials were undertaken to corroborate the observed optical nonlinearity.

Introduction

The optical memory storage, switching and several other optical communication phenomena are based on the nonlinear optical (NLO) properties of materials [1,2]. Among variety of materials, glassy materials are considered to be very promising NLO materials, because of its interesting optical characteristics and easy fabrication. During the last ten years TeO_2- based glasses have attracted much attention due to their high refractive index, excellent infrared transmittance, good chemical durability and low melting temperatures [3,4]. The optical nonlinearity in these glasses are produced by breaking the macroscopic symmetry by poling or intentional additives in the glass or by crystallizing a phase within the glass matrix and thereby producing a glass composite without loosing the transparent nature of the sample. The size of the crystals, crystallized out of the glass, varies from nano to micrometer depending on the refractive index match between the crystal and glass phase.

Tellurite glasses with heavy metal oxides were found to show remarkable physical and optical properties [5]. It was also reported that the ternary tellurite glasses show excellent thermal resistance against crystallization when compared to the binary glasses [6]. With this background we prepared glasses of the composition (100-2x) TeO2 - x Bi2O3 - x ZnO.

Experimental

Transparent glasses in the system (100-2x) TeO_2 - x Bi_2O_3 - x ZnO (x=5, 10 and 15, in molar ratio) were prepared by conventional melt-quenching technique. The stoichiometric compositions of TeO_2, Bi_2O_3 and ZnO were melted in a covered platinum crucible at 800 - 850 °C. Transparent glasses were made by pouring the melts into brass moulds. These glasses were annealed at 265 - 275 °C (T_g - 40) depending upon the composition to release the thermal stress in the as-quenched glasses. Annealed glasses were polished to optical quality for various characterizations.

The glassy nature of the samples of different compositions was established by subjecting the as-quenched pieces (weighing ≈ 50 mg) to differential thermal analysis (DTA) (SSC/5200H Seiko Instruments) in the 25 - 550 °C temperature range. The heating rate used for this measurement was kept constant at 10 °C / min for all the samples. X-ray powder diffraction (XRD) was employed on the crushed powders of the as-quenched and heat-treated samples to analyze the amorphous and crystalline natures. The as-quenched and heat-treated samples were polished to optical quality and the optical transmission spectra of these samples were recorded at room temperature using a double beam spectrophotometer (CARY UV-VIS-NIR) in the wavelength range175 to 3300nm. The linear refractive indices were determined by the Brewster angle reflection method at 1064 and 532 nm.

Results and discussion

Fig.1 (a-c) show the DTA curves for the as-quenched samples corresponding to the compositions x = 5, 10 and 15 respectively. In all the Figs., we see an endotherm (307 - 317 °C) corresponding to the glass transition (T_g) and several exotherms corresponding to the crystallization (T_{cr}) of various phases. It was also observed that as the composition (x) increases the number of phases crystallizing were also increasing. It is interesting to note that the difference of temperature (ΔT) between the glass transition and final crystallization, which is supposed to be the crystallization of TeO_2, increases with increasing x. This implies that the thermal stability of the glass increases with x. The glasses of different compositions were heat-treated at various temperatures to confirm the phases that are crystallizing near the onset of the exotherms.

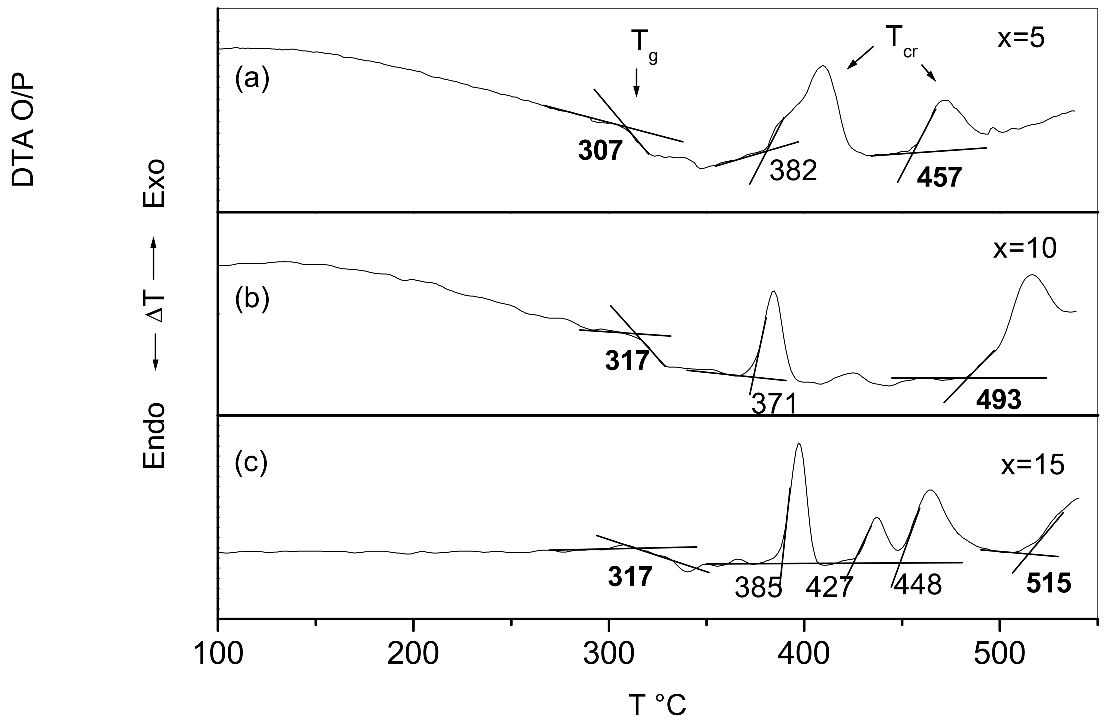

Fig. 1: DTA traces of the as-quenched samples corresponding to the compositions (a) x=5, (b) x=10 and (c) x=15.

The XRD patterns of the as-quenched glasses corresponding to the compositions x = 5, 10 and 15 are shown in Figs. 2 (a-c). Though the noisy patterns show partially the amorphous nature of the as-quenched samples, the presence of a broad peak around $2\theta=28°$ and few other small peaks suggest the presence of nanocrystallites in the glass matrix. The broad peak at $2\theta=28°$ was identified with the cent percent peak of Bi_2TeO_5, which is a good nonlinear optic and ferroelectric compound. The presence of nanocrystallites in the as-quenched glass is an interesting result and we believe that this will give rise to improved nonlinear optical properties when compared to the conventional tellurite glasses. It was also confirmed that the crystallites are dispersed through out the bulk of the as-quenched glass and it is not the surface phenomena. The XRD recorded on the plates and the crushed powders of these glasses show similar patterns.

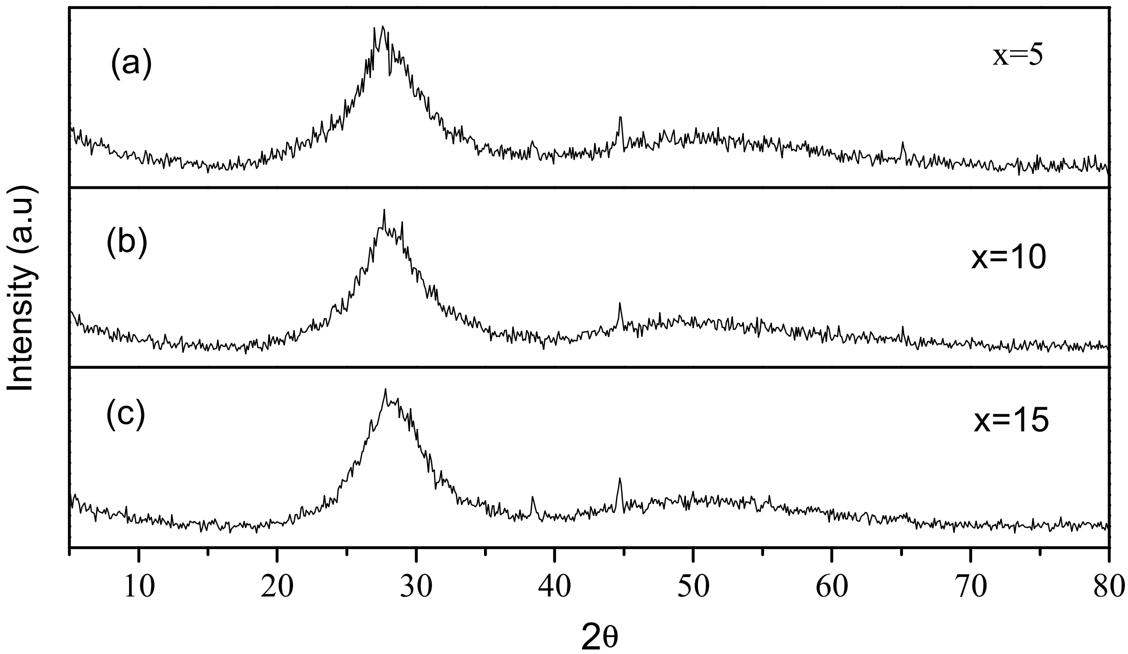

Fig. 2: XRD patterns for the as-quenched glasses

Fig. 3 show the XRD patterns of the samples heat-treated at a temperature where we get large crystallites in the glass matrix without loosing the transparency of the samples. These temperatures were found to be 350°C for x=5 and 10 and 375°C for x=15, beyond which abnormal grain growth occurs and the sample becomes opaque. In addition to that beyond these temperatures, there are several phases started crystallizing as it was seen in DTA studies (Fig. 1) including the TeO_2 glass matrix. All the diffraction peaks in Fig. 3 were indexed to Bi_4TeO_8 , which is a centro-symmetric phase in the Bi_2O_3 - TeO_2 phase diagram. The FWHM (full width at half maximum) studies suggest that the crystallites are of micron size. Attempts are made to retain the non centro-symmetric nature of the nanocrystallites present in the as-quenched glasses during the heat-treatment.

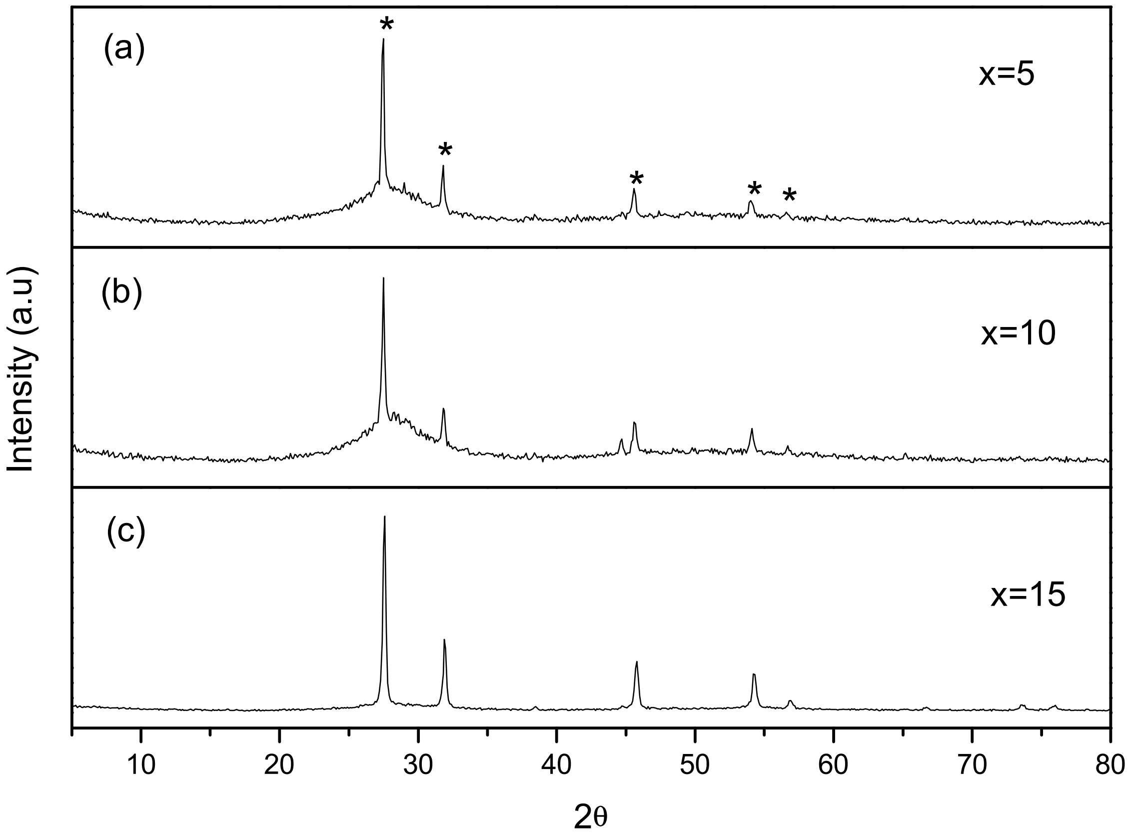

Fig. 3: XRD patterns for (a) x=5, heat-treated at 350 °C, (b) x=10, heat-treated at 350 °C and (c) x=15, at 375 °C. (* - Bi_4TeO_8)

The optical transmission spectra recorded for the as-quenched glasses of the composition x= 5, 10 and 15 are shown in Fig. 4. All the glasses have good transparency (≈80%) in the 500 – 2500 nm wavelength range. Below 400 nm the percentage transmission becomes zero at characteristic wavelength called λ_{cutoff} (lower wavelength cutoff). The λ_{cutoff} lies around 375 nm for the sample corresponding to the composition x=5. However, the λ_{cutoff} shifts towards the higher wavelength side as the composition (x) increases. The refractive indices (n) of the as-quenched and heat-treated glasses were measured at room temperature by Brewster angle method and are shown in Table 1, at two different wavelengths (1064 and 532 nm). There was no appreciable change in n as x varies from 5 to 15 for both the as-quenched and heat-treated glasses. However, the heat-treated glasses have got higher refractive index than the as-quenched glasses. Although there is no detectable dispersion in n with respect to wavelength for the as-quenched glasses, it is observed from Table 1 that there is a remarkable dispersion in n for the heat-treated glasses. This dispersion is mainly due to the presence of micron sized crystallites in the glass matrix. Studies are in progress to investigate the structural and nonlinear optical properties of these glasses.

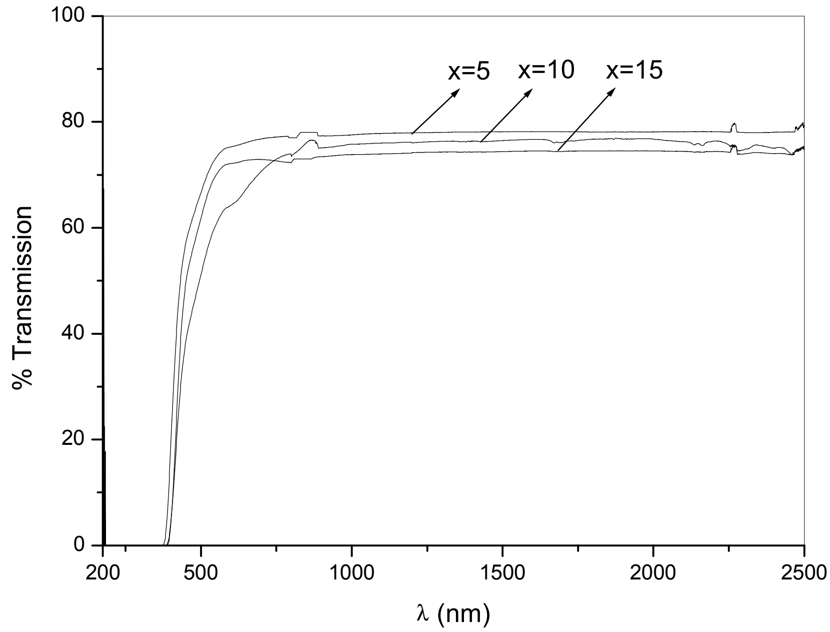

Fig. 4: Transmission spectra for the as-quenched glasses.

Table 1: Refractive indices (n) of the as-quenched and heat-treated glass samples at 1064 and 532 nm.

Sample	x	n (1064 nm)	n (532 nm)
As-Quenched	5	2.14	2.14
	10	2.10	2.10
	15	2.09	2.08
Heat-treated	5	2.19	2.28
	10	2.15	2.20
	15	2.16	2.23

Conclusions

Optical glass composites containing nanocrystallits were fabricated by conventional melt-quenching technique in the system (100-2x) TeO_2 - x Bi_2O_3 - x ZnO (x=5, 10 and 15). The nanocrystallits in the as-quenched glasses were found to belong to the non centro-symmetric Bi_2TeO_5 phase. Unfortunately, the further heat-treatment produced crystallites (micron sized) of a centro-symmetric phase. Efforts are in progress to characterize these glass composites for efficient nonlinear optical properties. These glass composites have got higher refractive indices, which are suitable for NLO applications.

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