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New tellurite glasses and crystalline phases in the Bi_2O_3–CaO–TeO_2 system: Synthesis and characterization

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ABSTRACT

Tellurite glasses containing calcium and bismuth oxides have been prepared at 800 °C and investigated by X-ray diffraction, DSC, IR and Raman spectroscopy. The crystalline phases of glasses in TeO_2–CaO revealed γTeO_2 phase which transforms into the stable αTeO_2 phase up to 500 °C. IR and Raman studies show the transition of TeO_4, TeO_{3+1} and TeO_3 units with increasing CaO content. The value of refractive index and density of glasses have been measured. The investigation in the system using XRD reveals new phases.

1. Introduction

Tellurite-based glasses are of technological interest because of their low melting temperature, high refractive index, good transmission in the infrared region and optical non-linearity. They are also not hygroscopic and have superior physical properties such as high dielectric constant and low melting point (800 °C) [1–4]. The origin of the extraordinary non-linear optical properties of TeO_2-based glasses is attributed to high hyperpolarizability of a lone electron pair related to the 5s orbital of tellurium atom [5,6]. TeO_2 dioxide is four-coordinate; although this oxide itself is only a conditional glass former; addition of heavy metal oxide (PbO, WO_3, Nb_2O_5, ZnO, BaO, etc.) rises to ranges of excellent glass formation and in fact enhanced stability against devitrification [7–12]. Tellurite glasses are also considered as one of the best hosts for doping with rare earth elements. They are good candidates for practical laser applications [13,14].

The present paper reports a preliminary investigation of new tellurite glasses and crystalline phases in Bi_2O_3–CaO–TeO_2 system. Elaboration process, thermal properties infrared (IR) and Raman studies in comparison to analogous crystalline phases will be described successively.

2. Experimental

The amorphous and crystalline samples were prepared using high purity commercial materials Bi_2O_3, TeO_2 and $CaCO_3$ of analytical grade (Aldrich 99.9%). The batches of suitable proportions of starting products were mixed in an agate mortar and then melted in air in porcelain crucible at 800 °C (30 min) for vitreous phases and at 750–850 °C (48 h) for crystalline phases. All of them are quenched to room temperature and identified by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Cu Kα radiation). T_g (glass temperature) and *Tc* (crystallization temperature) were determined by Differential Scanning Calorimetry (DSC) Netsch 2000 PC type from powder samples glasses for about 8 mg in aluminum pans. A heating rate of 10 °C/min was used in the 30–600 °C range. Infrared absorption measurements between 2000 and 400 cm^{-1} were made for powder specimens dispersed in a pressed KBr disk. The Raman spectra were recorded with an imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems) equipped with a holographic transmission grating and thermoelectrically cooled two-dimensional multichannel CCD detector (Newton, Andor Technology, 1600 × 400 pixels, −60 °C). An argon laser was used for the excitation and the 514.5 nm wavelength radiation was chosen.

The refractive index of some compositions was determined with an optical microscope NIKON model 104 by successive focusing on the two parallel faces of polished samples. The densities of samples were determined on blocks of glasses by Archimede's method using diethylorthophtalat as liquid.

3. Results and discussion

A wide range glass system based on the Bi_2O_3–TeO_2–CaO was successfully prepared at 800 °C. Glass formation region is obviously dependent on the temperature, so this temperature has been chosen to have a homogenous reagent on one hand, and to avoid volatization of TeO_2 at high temperature (T_{TeO_2} Melting = 732 °C)

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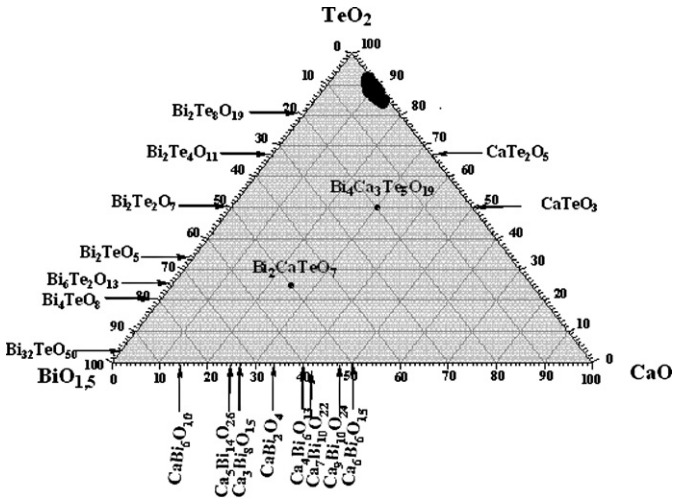

Fig. 1. Phase diagram of Bi_2O_3–CaO–TeO_2 system with new phases: Bi_2CaTeO_7 and $Bi_4Ca_3Te_5O_{19}$.

on the other hand (Fig. 1). The color of the glass changes slightly from dark yellow to yellow with increasing CaO and Bi_2O_3 concentrations.

In pseudo-binary CaO–TeO_2, the vitreous compositions are 5–15 mol% CaO content (Fig. 1). In comparison with pseudo-binary BaO–TeO_2 [15] and SrO–TeO_2 [16] studies previously this field is narrow. It seems that the vitreous field is closely related to the size of modifying oxide ($rBa^{2+} = 1.34\,Å > rSr^{2+} = 1.16\,Å > rCa^{2+} = 1.00\,Å$ [17]).

The curves (DSC) exhibit endothermic effect due to glass transition (T_g); the value of T_g is evaluated from the point of reflection of this change. At still higher temperatures three exothermic peaks *Tc* are observed corresponding to crystalline phases. Figs. 2 and 3 show the dependence of characteristic temperature, glass transition, the first crystallization (Tc_1), the second (Tc_2) and the third crystallization (Tc_3) on CaO content. The values of T_g, Tc_1, Tc_2 and Tc_3 are presented (Fig. 2 and Table 1). The appearance of single peak (all glasses) due to the glass transition temperature indicates the homogeneity of the glasses prepared. With the increase in the concentration of CaO in the glass matrix, the T_g increases and the difference ($Tc - T_g$) (about 20–50 °C) implies a thermal stability of glasses. In a study of alkali tellurite glasses, Inoue and Nukui [18] showed that the temperature of the glass transition decreases with increasing amount of Li, Na or K compounds. The dependence of CaO content shows a different tendency, especially of glass transition compared with the alkali tellurite glasses. The alkali atoms easily move in the glass structure. However, Ca ions move with greater difficulty in the glass, because the Ca atom is restrained by relatively strong bands to every coordinate oxygen. The light change of the temperature of crystallization of a vitreous composition to another is due to the kinetic phenomenon. Based on XRD and DSC analysis for glassy samples 5–15 mol% CaO (see Fig. 4) a first peak of crystallization corresponds to the αTeO_2 and the γTeO_2 polymorphic at 380–390 °C range.

Table 1
Characteristics (T_g, *Tc*) and difference ($Tc_1 - T_g$) of some glasses in the CaO–TeO_2–Bi_2O_3 system.

mol% $BiO_{1.5}$	mol% TeO_2	mol% CaO	T_g (°C)	Tc_1 (°C)	Tc_2 (°C)	Tc_3 (°C)	$Tc_1 - T_g$
0	95	5	340	390	430	515	50
0	90	10	359	384	475	515	25
0	85	15	365	385	451	525	20

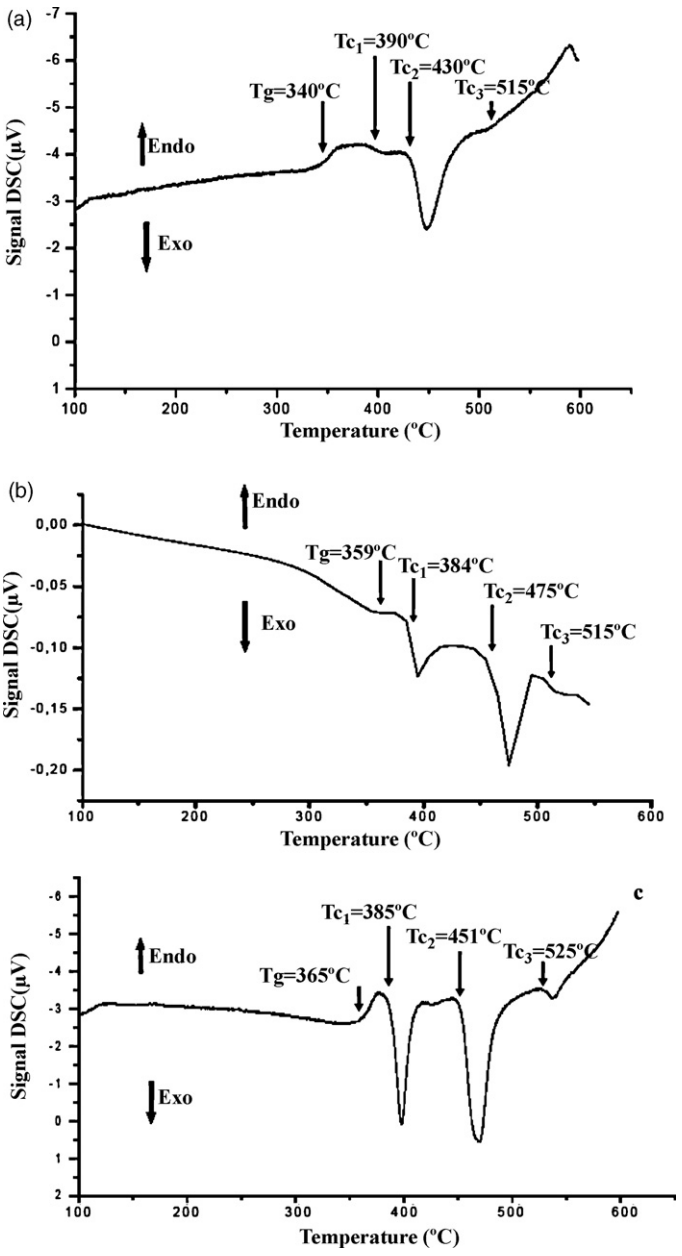

Fig. 2. DSC curves of glassy samples (5 mol% CaO (a), 10 mol% CaO (b), 15 mol% CaO (c)) obtained in CaO–TeO_2 pseudo-binary.

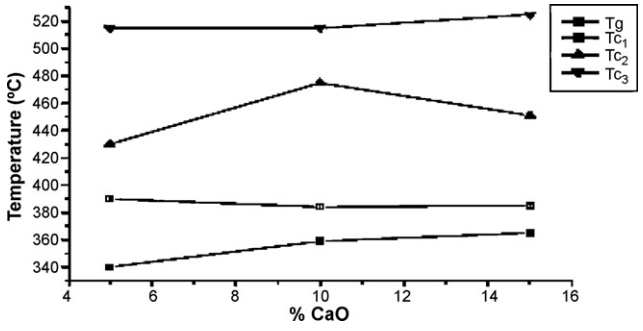

Fig. 3. Evolution of glass transitions (T_g) and crystallizations (*Tc*) with composition.