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Structural and optical study of tellurite–barium glasses

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ABSTRACT

The goal of this work was to determine the effect of barium oxide on the structural, thermal and optical properties of the TeO_2–BaO–Na_2O (TBN) and TeO_2–BaO–WO_3 (TBW) glass systems. Raman spectra allow relating the glass structure and vibration properties (i.e. vibrational frequencies and Raman intensities) with the glass composition. Raman spectra show the presence of TeO_4 and TeO_{3+1}/TeO_3 units that conform with the glass matrix. Differential thermal analysis DTA, XRD measurements have been considered in term of BaO addition. The spectral dependence of ellipsometric angles of the tellurite–barium glass has been studied. The optical measurements were conducted on Woollam M2000 spectroscopic ellipsometer in spectral range of 190–1700 nm. The reflectance and transmittance measurements have been done on spectrophotometer Perkin Elmer, Lambda 900 in the range of 200–2500 nm (UV–VIS–NIR). From the transmittance spectrum, the energy gap was determined.

1. Introduction

The development of new materials, which combine desirable thermal and optical properties with sufficient mechanical strength, is necessary for a high performance laser and optical waveguides [1]. Since many years various tellurite glass composition are considered to be promising materials for many applications in optics [2]. They have attracted much attention because of excellent physico-optical properties, e.g. low glass transition temperature T_g, high refractive index, high dielectric constant, high thermal expansion coefficient and high optical transmission in the infrared (IR) region, low phonon energy (640–790 cm^{-1}) which is attractive for designing near-IR and mid-IR lasers and amplifiers [3–7]. TeO_2 based glasses are unique amongst oxide glasses, in their structure the large Te cation in oxygen polyhedra (pyramid, bipyramid and distorted pyramid) is responsible for extended multiphonon absorption edge beyond 4 μm in combination with the UV–visible cutoff edge in the region of 0.32–0.38 μm [8]. The coordination geometry of Te atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the glassy network modifier [9]. The addition of transition metal oxides to the TeO_2 matrix, changes the coordination of Te from a TeO_4 trigonal bipyramid (tbp) group to a TeO_3 trigonal pyramid (tp) through intermediate polyhedra TeO_{3+1}. The TeO_4 tbp group has two axial and two equatorial oxygen atoms, in which an electron pair occupies the third equatorial position of the sp^3d hybrid orbital. This electron pair plays a key role in the glass network and manifestation of non-linear optical properties of tellurite glasses [9,10]. In our previous studies, we tested the thermal and optical properties of tellurite glasses from TeO_2–PbO–WO_3–La_2O_3 or TeO_2–PbO–WO_3–Lu_2O_3 system [11–13]. Besides high thermal stability of mentioned glasses, we achieved a very high refractive index. In this study, the ternary TeO_2–BaO–Na_2O and TeO_2–BaO–WO_3 family of glasses were selected due to their large spectral bandwidth as compared to fused silica and good thermal stability. These glass compositions were selected also because barium seems to be good candidate for development of Ba – based radiation shielding glass owing to strong absorption of x-rays, gamma rays and non-toxicity compared with lead [14]. Compared to other tellurite glasses, WO_3 containing tellurite glasses have slightly higher phonon energy and higher glass transition temperature, therefore they can be used at high optical intensities without exposure to thermal damage. The presence of sodium is to increase the glass forming stability of the mixtures and the rare

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Table 1
Chemical composition of glasses.

Glass ID	Glass composition [%mol]			
	TeO_2	BaO	Na_2O	WO_3
TBN1	85	5	10	–
TBN2	80	10	10	–
TBN3	85	10	5	–
TBN4	85	13	2	–
TBW1	60	10	–	30
TBW2	60	15	–	25

earth solubility. However, the high alkali concentration usually presents poor chemical durability [15]. Thus, the right selection of glass composition with desirable optical properties and high performance depends on the application and often is a compromise among many factors. The purpose of this research was to identify those glasses that will have good thermal stability and high refractive index. Moreover, we focused to identify structural, thermal and optical–property relationships to advance the understanding of the tellurite glass components influence on their properties.

2. Experimental

Host glass compositions were selected as the TeO_2–BaO–Na_2O (TBN) and TeO_2–BaO–WO_3 (TBW). The following raw materials were used to prepare the batches: tellurium oxide (TeO_2), barium oxide (BaO), sodium oxide (Na_2O) and tungsten trioxide (WO_3). All the chemicals were mixed properly to ensure the homogeneity. Tellurite–barium glass was obtained by melting 25 g batch in gold crucible in an electric furnace at the temperature 850 °C in air atmosphere. The crucible was covered with a platinum plate to avoid vaporization losses. The melt was poured onto a steel plate, which was preheated to 340 °C, forming a layer thickness of 2–5 mm, then annealed in the temperature range 310–350 °C.

Raman studies were carried out using Horriba Yvon Jobin Lab-RAM HR micro-Raman spectrometer equipped with a CCD detector. Excitation wavelength of 532 nm was used and beam intensity was about 10 mW. The ability of the obtained glasses to crystallize was determined by DTA measurements conducted on the Perkin Elmer operating in heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate 10 °C•min^{-1} in dry nitrogen atmosphere to the temperature 1100 °C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve; the jump-like changes of the specific heat ΔC_p accompanying the glass transition, enthalpy ($\Delta H_{cryst.}$) of crystallization of glasses were calculated using the Perkin Elmer Thermal Analysis Software Library [16]. The ability of glasses for crystallization was measured by the values of the temperature of exothermal events ($T_{cryst.}$), the enthalpy of crystallization ($\Delta H_{cryst.}$) and the values of the thermal stability parameter of glasses ($\Delta T = T_{cryst.} - T_g$) [17]. Glasses revealing the effect of crystallization were selected for further thermal treatment. For spectroscopic measurements, the annealed glass samples were sliced and polished to dimensions of about 10 × 10 × 2 mm^3. The compositions of melted glasses are shown in Table 1.

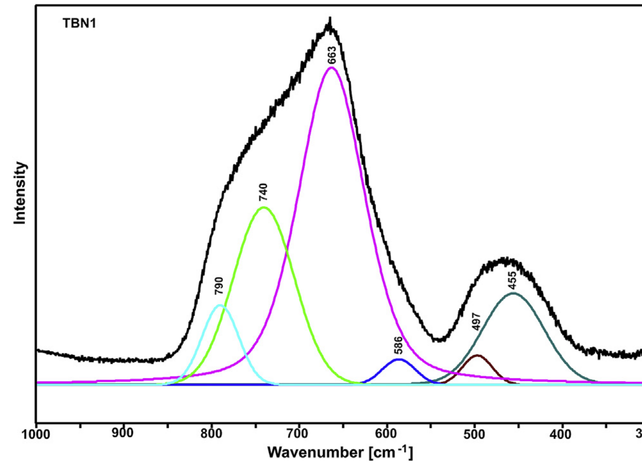

Fig. 2. Deconvolved Raman spectrum of TBN1 glass.

The ellipsometric data were collected with a M-2000 Woollam ellipsometer in the spectral range 190–1700 nm. Knowledge of Ψ and Δ allows one to determine not only the dispersion of the optical constants but also roughness σ of a glass [18]. The samples have been measured for three angles of incidence, namely 60°, 65° and 70°. To analyze the data, we have combined all the angular spectra and we have fitted all the data simultaneously. The data have been analyzed using CompleteEASE 4.1 software. The transmittance and reflectance spectra were recorded with a Perkin Elmer, Lambda 900 spectrophotometers.

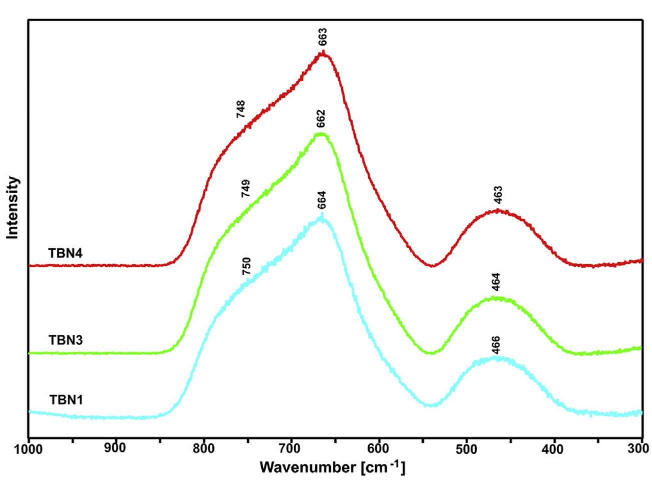

Fig. 1. Raman spectra of TBN glass series.

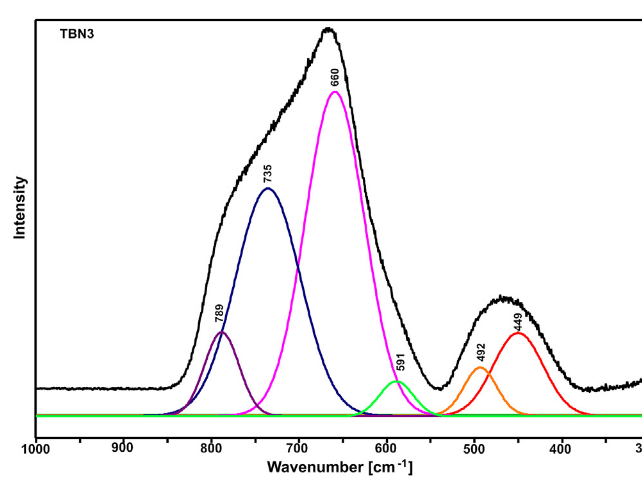

Fig. 3. Deconvolved Raman spectrum of TBN3 glass.

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