



Influence of Eu_2O_3 on phase crystallization and nanocrystals formation in tellurite glasses

I.V. García-Amaya^a, Ma.E. Zayas^b, J. Alvarado-Rivera^{c,*}, M. Cortez-Valadez^d, M. Pérez-Tello^e, N. Cayetano-Castro^f, F. Martínez-Suárez^g, A. Mendoza-Córdova^h

^a Posgrado en Nanotecnología, Departamento de Física, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

^b Departamento de Investigación en Física, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

^c Conacyt-Departamento de Física, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

^d Conacyt-Departamento de Investigación en Física, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

^e Departamento de Ingeniería y Metalurgia, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

^f Centro de Nanociencias y Micro y Nanotecnologías, Instituto Politécnico Nacional, 07738 Cd. de México, Mexico

^g Centro Nacional de Metrología, Metrología de Materiales, 76246 El Marqués, QRO, Mexico

^h Departamento de Geología, Universidad de Sonora, 83000 Hermosillo, SON, Mexico

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ABSTRACT

Glasses of the $17\text{ZnO}\cdot 32\text{CdO}\cdot 51\text{TeO}_2$ system doped with Eu_2O_3 (0–0.75 mol per 100 mol of oxides) were obtained. Non-isothermal differential scanning calorimetry (DSC) tests showed that the glass transition temperature varied in the range of 354° to 371 °C with the addition of Eu_2O_3 . The samples were exposed to a thermal treatment in a laboratory oven at 420 °C. X-ray diffraction analysis of the treated samples showed crystalline phases of a variety of metallic oxides, the intensities of which decreased as the Eu doping amount in the samples increased. In all samples, the strongest peak corresponded to ZnTeO_3 with a crystallite size of about 36 nm. Fourier Transform Infrared Spectroscopy showed that CdO and ZnO change their role from modifier to a glass former. Raman spectra showed characteristic bands corresponding to $\gamma\text{-TeO}_2$. The observations suggest that Eu_2O_3 induced structural changes which in turn led to the formation of molecular oxygen in the interstitial network. Deconvolution analysis of Raman spectra and High-Resolution Transmission Electron Microscopy images confirmed the formation of Te_2O_5 , ZnTeO_3 and Te nanocrystals. Photoluminescence analysis showed that Eu ions are incorporated as Eu^{3+} and no reduction occurred after heat treatment.

1. Introduction

Tellurite glasses are of interest due to their capability to host rare earth ions, which show high intensity and narrow peak in photoluminescence emission spectra [1–5]. The low phonon energy of TeO_2 based glasses decreases the probability of occurrence of non-radiative energy transfer; this property makes these materials good candidates for laser applications [6–11]. Specifically, the properties of tellurites, as their wide transmission in the range of 0.4–5.0 μm , high refractive index, low melting temperature, good corrosion resistance, mechanical and chemical stability, make these materials of interest for optoelectronic applications [12,13].

Moreover, TeO_2 belongs to the intermediate class of glass-forming oxides. When this species is blended with a secondary component such as Na_2O , WO_3 , BaO , PbO , CdO , and ZnO , the capability of the resulting mixture to form a glass melt improves significantly. Several studies on

the use of TeO_2 as a glass-forming oxide have been reported in the literature. Sidek et al. [14] found that the $\text{ZnO}\text{--}\text{TeO}_2$ binary system presented good glass stability. In their experiments, the authors noted that the physical and optical properties of the glass were affected by the increment in ZnO concentration, causing the formation of non-bridging oxygens (NBOs) breaking the $\text{Te}\text{--}\text{O}\text{--}\text{Te}$ network. In general, modifier oxides lead to the formation of $\text{Te}\text{--}\text{O}\text{--}\text{M}$ (M = cation, like Na^+ , K^+ , Ca^{2+} , Fe^{3+} , Mg^{2+}) terminal bonds or NBOs leading to the depolymerization of the $\text{Te}\text{--}\text{O}\text{--}\text{Te}$ structure, changing the glass properties. In contrast with the conventional alkali or alkaline earth oxide modifiers, CdO is thermally stable, appreciably covalent, and shortens the time necessary for solidification of glasses during quenching [15]. In this laboratory, the glass-forming zone for the ternary system $\text{ZnO}\text{--}\text{CdO}\text{--}\text{TeO}_2$ was determined experimentally [16]. Further, the properties of the vitreous matrix were measured upon the incorporation of rare earth compounds (REC). During the experiments, the proportion of REC

* Corresponding author.

E-mail address: jalvaradori@conacyt.mx (J. Alvarado-Rivera).

in the ternary system was maintained constant while the proportions of CdO and TeO₂ were varied. The formation of CdTeO₃ and CdTe₂O₅ crystalline phases were found when the glass was doped with Tb₄O₇ and EuCl₃ [17,18]. However, when the system was doped with YbBr₃ and Nd₂O₃ no presence of crystalline phases were detected [17,19]. Also, it has been reported that for ZnO–TeO₂ glasses, ZnTeO₃ and Zn₂Te₃O₈ are the crystalline phases that appear around 428° and 458 °C respectively, according to DTA analysis [20]. Thus, there are several crystalline phases that can be expected to appear in the ZnO–CdO–TeO₂ system.

Glasses with embedded nanocrystals are of interest because of the optical properties of such materials like photoluminescence, refractive index, and non-linear optics [21–24]. However, the information regarding some crystalline phases like ZnTeO₃, Zn₂Te₃O₈ or CdTeO₃ embedded in TeO₂ glasses is scarce [25–29]. The goal of this investigation was to test the effects of europium concentration and thermal treatment on the development of crystalline phases in a glass of 17ZnO:32CdO:51TeO₂. For that purpose, an experimental program was followed as described below.

2. Experimental procedure

A glass matrix consisting of 17ZnO:32CdO:51TeO₂ was doped with varying concentrations of europium nitrate. Reagent grade of zinc oxide (ZnO, Fluka Analytical), cadmium oxide (CdO, 99.5%), tellurium dioxide (TeO₂ ≥ 99%), and europium nitrate hexahydrate (Eu(NO₃)₃·6H₂O, 99.99%) from Sigma Aldrich were used to prepare the glass batches. The content of the metallic oxides in the glass matrix was maintained constant as indicated in the chemical formula: 17ZnO:32CdO:51TeO₂ as mol%, whereas Eu₂O₃ was introduced as Eu(NO₃)₃·6H₂O and the amount was varied according to Table 1.

The batch mixtures were processed by the melt-quenching method in high alumina crucibles at 1000 °C for 30 min in a Thermolyne 46100 furnace. Further, the glasses were quickly transferred into an annealing Thermolyne 48000 furnace at 350 °C for 20 min and then cooled down slowly to room temperature. Thermal characterization of the glasses thus obtained was conducted in a Thermal Analysis SDT 2960 Simultaneous DCS-TGA unit at a heating rate of 20 °C/min in the temperature range of ambient temperature up to 1000 °C in an alumina crucible and air atmosphere. Based on the DSC results and ZnO–TeO₂ and CdO–TeO₂ phase diagrams [27,30], a temperature of 420 °C was selected to carry out the heat treatment of as-cast glasses. The samples were maintained at the selected temperature for 5 h in a Thermolyne 48000 furnace. A small amount of the glassy material was crushed and milled down to a particle size under 30 μm in an agate mortar to conduct X-ray diffraction (XRD) analyses in a Bruker D8 advanced diffractometer. For that purpose, the Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 15–65° was used. The final composition of the samples was analyzed by SEM/EDS in a JEOL JSM-7800F field-emission scanning electron microscope (FE-SEM) using a Bruker EDS Analyzer. Fourier Transform Infrared (FT-IR) spectra of the glasses were obtained using a Perkin Elmer 1600 Series FTIR spectrophotometer in the range of 1000–400 cm⁻¹. The samples were analyzed in a KBr tablet. Micro-Raman Spectroscopy analysis was performed at ambient temperature in

Table 1

Sample ID and nominal composition of the 17ZnO:32CdO:51TeO₂ samples.

Sample ID	Dopant concentration, mol% Eu (NO ₃) ₃ ·6H ₂ O/100 mol of oxides	Eu ₂ O ₃ concentration mol %/100 mol of oxides
ZCT	0	0
ZCT-0.15	0.3	0.15
ZCT-0.3	0.6	0.30
ZCT-0.45	0.9	0.45
ZCT-0.6	1.2	0.60
ZCT-0.75	1.5	0.75

Table 2

SEM/EDS elemental analysis of glasses.

Element	Composition (wt%)					
	ZCT	ZCT-0.15	ZCT-0.3	ZCT-0.45	ZCT-0.6	ZCT-0.75
O	15.08	10.97	9.48	10.31	10.78	10.25
Zn	12.02	10.67	10.38	10.80	11.15	10.28
Cd	25.97	28.57	29.01	28.62	28.45	28.75
Te	46.66	49.38	50.62	49.68	48.73	49.67
Al	0.18	0.21	0.08	0.12	0.09	0.13
Eu	–	0.12	0.27	0.41	0.73	0.81

a HORIBA LabRam HR spectrometer, using a He–Ne laser with a wavelength of 632.8 nm, a 600 g/mm grating coupled with a Synapse CCD Horiba detector thermoelectrically cooled at –58 °C and a spectral width of 4.546 cm⁻¹ (resolution). Prior to the High-Resolution Transmission Electron Microscopy (HRTEM) observations, the powder samples were suspended in distilled water. A drop of this suspension was placed on a copper microgrid coated with carbon, and the sample was vacuum-dried at room temperature for 4 h. The images were obtained in a JEOL Transmission Electron Microscopy (TEM) unit, model JEM-2010F with an acceleration voltage of 200 keV. Finally, Photoluminescence (PL) was acquired in a spectrofluorometer using either a 450 W ozone free Xe lamp, or a 325 nm He–Cd laser, coupled with a Horiba Triax 320 excitation and an emission iHR320 monochromator.

3. Results and discussion

3.1. Composition

The final composition of the as-cast glasses was determined by SEM/EDS analysis, and the results are presented in Table 2. Upon addition of europium nitrate, the concentration of Cd and Te slightly increased while O and Zn content decreased as compared with the undoped glass. Among the glasses with Eu₂O₃, there is no significant variation in Cd, Zn and Te concentration, and Eu content increased as expected. For all glasses, a low quantity of aluminum was detected, which possibly originated from the corrosion of the high-alumina crucible during fusion.

3.2. Thermal properties

DSC thermograms of as-cast glasses in the temperature range of 300° to 700 °C are shown in Fig. 1. They exhibit several features; namely, the glass transition temperature (see inset in Fig. 1), exothermic peaks associated with crystallization and phase transformations, as well as endothermic peaks resulting from decomposition and melting of the phases crystallized at low temperature [31]. The numerical values of the glass transition temperature (T_g), crystallization temperature (T_c), melt temperature (T_m), and thermal stability ($\Delta T = T_c - T_g$) of the as-cast glasses are summarized in Table 3. Crystallization temperatures were determined over temperature onset. It is noted that the endothermic change associated with the T_g increased from 354° to 371 °C as the europium doping amount increased. The glass transition temperature is an important property of glasses which is affected by the thermal history and the nature of the glass matrix and its structural changes [32]. Nukui's [33,34] previous study was the basis for Reza Dousti et al. [35] and Kaur et al. [13] analysis where they reported on the appearance of two exothermic peaks around 420° and 470 °C (T_{c1} and T_{c2} , respectively) in the 20ZnO:80TeO₂ system. The first peak was attributed to the crystallization of TeO₂ and ZnTeO₃ which are close to each other and formed a broad peak. This was followed by the crystallization of Zn₂Te₃O₈. As was reported by El Azhari et al. [36], the crystallization of CdTeO₃ is also favored at 420 °C. The values shown in Table 3 indicate that T_{c1} varied in the range of 406°–424 °C. Those T_c

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