Journal of Non-Crystalline Solids 457 (2017) 116–125

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Synthesis, thermal and structural properties of pure TeO_2 glass and zinc-tellurite glasses

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ARTICLE INFO

Article history:
Received 1 September 2016
Received in revised form 14 October 2016
Accepted 28 November 2016
Available online xxxx

Keywords:
Pure TeO_2 glass
Zinc tellurite glasses
Alumino-tellurite glasses
Glass transition temperature
Density
Raman spectroscopy
Glass structure

ABSTRACT

We have synthesized pure TeO_2 glass and glasses in the systems $xZnO-(1-x)TeO_2$ ($0 \le x \le 0.50$) and $yAl_2O_3-(1-y)TeO_2$ ($0 \le y \le 0.03$) by melting in Pt crucibles, and measured their glass transition temperature (T_g), density (ρ) and Raman spectra to correlate glass properties with structure. For pure TeO_2 glass, synthesized using our newly developed intermittent quenching technique, we find onset- and midpoint-T_g at 301.1 and 306.7 °C and $\rho = 5.62$ g/cm^3, in clear disagreement with TeO_2 glass melted in alumina crucible for which we find $T_g \approx 380$ °C and $\rho = 4.86$ g/cm^3. This latter method, used frequently in the literature, was shown by Raman spectroscopy to introduce Al_2O_3 in the tellurite matrix which becomes cross-linked by Te-O-Al bridges, resulting in the increase of T_g and decrease of ρ. Raman spectroscopy showed also that doping TeO_2 with ZnO or Al_2O_3 causes the progressive conversion of TeO_4 trigonal bipyramids to TeO_{3+1} polyhedra with two terminal oxygens, and then to TeO_3 trigonal pyramids with three terminal oxygens. This structural transformation is reflected in the composition dependence of the volume per mole TeO_2 evaluated from density data. The ZnO-dependence of this parameter is described by two linear parts with an inflection point at $x = 0.25$, which indicates an increasing rate of forming terminal Te—O bonds at higher ZnO contents. The T_g was found to increase with ZnO and Al_2O_3 contents and this was attributed to the glass-forming ability of both oxides, while density was found to decrease due mainly to replacement of the heavier TeO_2 by the lighter ZnO and Al_2O_3. The results of this study are discussed with reference to previous works on TeO_2 and zinc-tellurite glasses.

1. Introduction

Glasses based on tellurium dioxide, TeO_2, have drawn considerable attention because of their unusual physical and chemical properties compared to typical oxide glasses like silicates and phosphates. In particular, tellurite glasses exhibit high refractive index, low phonon energy and good infrared transmittance, high dielectric constant, excellent third-order nonlinear optical properties, low melting temperature, better solubility of rare-earth ions and large thermo-optic coefficient [1–6]. Because of their exceptional properties tellurite glasses are promising materials for a broad range of applications including erasable optical recording media [7], optical switching devices [8], laser hosts [9], second harmonic generation [10,11] and Raman amplification [3,4,12]. In addition, scalable and tailor-shaped transparent tellurite-based ceramics can be fabricated to develop lenses and fibers for near infrared applications [13].

Vitrification of pure TeO_2 requires special quenching techniques, as this material is an intermediate glass-forming oxide [1]. Preparation of blobs of glassy TeO_2 (v-TeO_2) was reported using splat quenching [14], while quenching the bottom of the crucible containing the melt in a freezing mixture of ice, ethanol and NaCl at about −10 °C gave thin glass plates which were used to measure linear and nonlinear optical properties of v-TeO_2 [15]. Larger glass quantities in the form of flakes were produced using a twin-roller, and were employed in a neutron diffraction study of the structure of v-TeO_2 [16].

Difficulties associated with glass formation from pure TeO_2 could be at the origin of controversial results on physical properties of v-TeO_2, and in particular its glass transition temperature (T_g) and density (ρ). These fundamental properties are known to be related to the atomic arrangements in glass and, thus, they are sensitive to factors influencing glass structure like chemical composition, preparation conditions and thermal history [17]. In any case, a correct density value is needed in analyzing the data of experimental techniques such as neutron diffraction and X-ray scattering, and density is also an essential property in molecular dynamics simulations [17]. Concerning v-TeO_2, reported T_g values include 320 °C [18], 325 °C [19] and 385 °C [20], as well as 317 °C [21]

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.11.033
0022-3093/

and 325 °C [22]; these literature values span a range of nearly 70 °C wide. Measured density of v-TeO_2 shows also a large diversity as it covers the range of values 4.80 g/cm^3 [20], 4.97 g/cm^3 [19], 5.105 g/cm^3 [18], 5.57 g/cm^3 [23] and 5.61 g/cm^3 [21].

Formation of tellurite glasses by conventional melt-quenching can be improved drastically by adding to TeO_2 glass-forming oxides like P_2O_5 and B_2O_3 [1,2], and/or metal oxide modifiers e.g. alkali, alkaline earth, transition metal and post-transition metal oxides [1,2,24,25]. ZnO-containing tellurite glasses, $xZnO - (1 - x)TeO_2$, which can be prepared in a continuous glass forming range with up to ca. 45 mol% ZnO [24,25], are of interest as host matrices for applications such as second harmonic generation after electro-thermal poling [10] and fiber amplification [12]. Despite the relative easiness to form glasses in the ZnO-TeO_2 system, there are basic disagreements in the literature regarding the dependence of T_g and ρ on the ZnO content. There are reports showing a steady decrease of T_g with increasing ZnO content [20,26], or a decrease of T_g followed by an increase with ZnO content [27], and other works demonstrating a monotonic increase of T_g with incorporation of ZnO in the tellurite glass matrix [21,24,25,28]. Similarly, the density of ZnO-TeO_2 glasses was found to increase [20,29] or decrease [21,24,25,28,30–33] with increasing the ZnO content.

The reports cited above reveal open questions in the relevant literature regarding some previously synthesized 'pure' TeO_2 glasses, as well as the role of ZnO on transition temperature, density and structure of ZnO-TeO_2 glasses. Central aims of this work were to search for a synthesis route that would permit the production of sizable quantities of pure TeO_2 glass, and to understand the dependence of glass transition temperature and density of v-TeO_2 on the synthesis conditions. To this aim, we synthesized TeO_2 glasses in Pt and alumina crucibles, measured their properties and Raman spectra and compared them with those of glasses $yAl_2O_3 - (1 - y)TeO_2$ (y = 0.01, 0.02, 0.03) prepared in Pt crucibles. We introduced in this work a synthesis method for pure TeO_2 glass which involves melting in Pt crucible, and quenching the bottom of the crucible containing the viscous melt into room temperature water. With this method, we managed to synthesize monolithic pieces of pure TeO_2 glass with approximate dimensions 2.5cm × 1.5cm × 2mm, and to measure reliable T_g and ρ values on pure TeO_2 glass. The properties and Raman spectra of TeO_2 glasses prepared by melting in alumina crucibles were found to deviate strongly from those of the glass melted in Pt crucible, as a result of doping the TeO_2 network with Al_2O_3 leached from the crucible. We prepared also glasses $xZnO - (1 - x)TeO_2$ ($0 \le x \le 0.5$) by quenching melts in Pt crucibles, and measured their transition temperature, density and Raman spectra to probe the evolution of properties and structure with ZnO content. Particular attention was paid to ZnO-TeO_2 glasses approaching the TeO_2 composition by preparing and studying glasses with x = 0.01, 0.02, 0.03, and 0.04, while glasses with larger ZnO contents were prepared and investigated in composition intervals of x = 0.05. Key findings in the ZnO-TeO_2 glass series include the monotonic increase of T_g and decrease of ρ with ZnO content, with the parallel transformation of the tellurite structure from TeO_4 trigonal bipyramids to TeO_{3+1} units and to TeO_3^{2-} trigonal pyramids with terminal oxygen atoms. The results of this work are discussed in relation to those of previous studies on TeO_2 and zinc-tellurite glasses.

2. Materials and experimental methods

2.1. Synthesis of glasses

Starting materials for glass synthesis were polycrystalline TeO_2 (Alfa Aesar, 99.99%) and ZnO (Alfa Aesar, 99.9%). For the preparation of TeO_2 glass, 2 g of TeO_2 powder were placed in a platinum crucible (ca. 20 cm^3) and preheated in an electric furnace at 200 °C for 2 h. The temperature of the furnace was then increased at a rate 50 °C/min until it reached 900 °C, and the melt was kept at this temperature for 30 min. Several melt-quenching techniques were tried to vitrify the pure TeO_2 melt. The most successful method involved removing the crucible from the furnace, stirring carefully the melt for few seconds to become viscous and then quenching by dipping quickly part of the bottom of crucible in-and-out of water at room temperature. This intermittent quenching technique (IQ-technique) was found suitable for producing fairly large samples of pure TeO_2 glass which are yellow and transparent; such as the sample with approximate dimensions 2.5 cm × 1.5 cm × 2 mm shown in the inset of Fig. 1. X-ray diffraction (XRD) revealed the amorphous nature of the synthesized TeO_2 glass (Fig. 1, x = 0). Attempts to melt larger quantities and produce larger samples of TeO_2 glass using the technique described here lead to partially or totally crystallized materials based on visual inspection. This was confirmed by XRD, as shown by the sharp-line pattern in Fig. 1 for a totally crystallized TeO_2 sample.

To search for a possible origin of the broad range of values reported for glass transition temperature and density of TeO_2 glass, we prepared a TeO_2 glass sample by melting in alumina crucible as employed frequently in literature [18–20,26,27,29]. We used the same amount of starting material, the same temperature and melting time as presented above. It was found that a glass can be easily formed by simply pouring the melt from the alumina crucible on a metal block. Additionally, we prepared glasses of composition $yAl_2O_3 - (1 - y)TeO_2$, y = 0.01, 0.02 and 0.03, using appropriate amounts of Al_2O_3 (Alfa Aesar, 99.99%) and TeO_2 raw materials and melting in Pt crucibles as described below for glasses in the ZnO-TeO_2 system.

Besides pure TeO_2 glass, we prepared fourteen additional glasses in the system $xZnO - (1 - x)TeO_2$ with x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50. Stoichiometric mixtures of TeO_2 and ZnO were first preheated in Pt crucibles in an electric furnace at 400 °C for 2 h, and then melted for 1 h at 800–950 °C depending on composition. The melts were carefully stirred several times during heating. Glasses were obtained by quenching the melts between

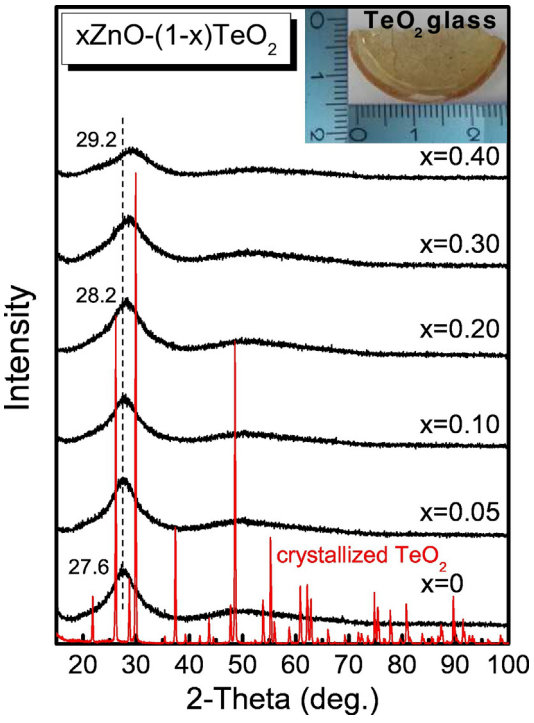

Fig. 1. XRD patterns of glasses $xZnO - (1 - x)TeO_2$ melted in Pt crucible (black lines), including the pattern for pure TeO_2 glass (x = 0). The XRD pattern presented by sharp (red) lines corresponds to an unsuccessful attempt to produce larger samples of pure TeO_2 glass using the intermittent quenching technique of this work and a platinum crucible of the same size (ca. 20 cm^3). The resulted crystalline phase corresponds to paratellurite, α-TeO_2.The inset shows the optical image of a monolithic sample of pure TeO_2 glass (dimensions in cm).(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)