Journal of Alloys and Compounds 508 (2010) 266–272

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Effect of rare-earth dopants on the thermal behavior of tungsten–tellurite glasses

A.E. Ersundu*, G. Karaduman, M. Çelikbilek, N. Solak, S. Aydın

Istanbul Technical University, Department of Metallurgical and Materials Engineering, Istanbul, 34469, Turkey

ARTICLE INFO

Article history:
Received 18 June 2010
Received in revised form 25 August 2010
Accepted 25 August 2010

Keywords:
Amorphous materials
Rare-earth alloys and compounds
Rapid-solidification
Quenching
Thermodynamic properties
Thermal analysis

ABSTRACT

In the present study, the effect of rare-earth element addition on the thermal behavior of tungsten–tellurite glasses was investigated by running detailed differential thermal analyses. The glasses were prepared with the compositions of $(1-x)TeO_2$–xWO_3, where $x = 0.10$, 0.15 and 0.20 in molar ratio and all three samples were doped with 0.5 and 1.0 mol% of Nd_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3. By applying different glass preparing methods, the effect of melt-quenching techniques on the thermal behavior of tellurite glasses was also investigated and almost the same thermal behavior was observed for all attempts. Therefore, the glass samples were obtained by heating high purity powder mixtures to 800 °C in a platinum crucible with a closed lid, holding for 30 min and quenching in water bath. In general, the addition of rare-earth elements to undoped samples affected the thermal behavior of tungsten–tellurite glasses by shifting the glass transition and exothermic reaction temperatures to higher values and increasing the thermal stability. Moreover, the introduction of rare-earth dopants significantly decreased the temperature values of the first endothermic peaks corresponding to the eutectic reaction; whereas a slight decrease was observed in the second endothermic peak temperatures representing the liquidus reaction. Addition of rare-earth elements with higher atomic number (Er_2O_3, Tm_2O_3 and Yb_2O_3) resulted in peak splitting of the eutectic reaction.

1. Introduction

Tellurite glasses have received considerable attention for their potential use in fiber optics, laser hosts and non-linear optical materials. Tellurium oxide, as a pure oxide, does not have glass forming ability under normal cooling conditions, therefore addition of a network modifier such as heavy metal oxides (PbO, Bi_2O_3 and WO_3 etc.) increase the glass forming ability. Among heavy metal oxide containing tellurite glasses, tungsten–tellurite glasses exhibit various excellent properties such as doping in a wide range, modifying the composition by a third, fourth, and even fifth component which allows controlling the optical properties, enhancing the chemical stability and devitrification resistance [1–4]. It is known that the main drawbacks of tellurite glasses are their low glass transition temperature and relatively low-phonon energy. However, since tungsten–tellurite glasses have slightly higher phonon energy and higher glass transition temperature compared to other tellurite glasses, they can be used at high optical intensities without exposure to thermal damage [5].

Glasses doped with rare-earth ions have been investigated intensively for fabricating lasers and amplifiers since the last quarter of the twentieth century. Tellurite glasses doped with rare-earth ions have attracted a great deal of interest due to their advantageous properties over silicate, borate and phosphate glasses such as a wide transmission range from ultraviolet to mid-infrared, low-phonon energy, high refractive index, high dielectric constant and chemical stability [1–3,6–10]. The optical properties of different rare-earth element ions in tellurite based systems have been extensively studied for several years. Nd^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} are the most commonly used rare-earth ions in tungsten–tellurite glasses. Er^{3+} and Tm^{3+} doped tellurite glasses find wide applications which involve Er^{3+} doped fiber amplifiers (EDFA) for C and L bands and Tm^{3+} doped fiber amplifiers (TDFA) for the S band [5,11]. Moreover, Nd^{3+} doped tellurite glasses show efficient laser emission closer to Q-switched operation under pulsed excitation and Yb^{3+} doped tellurite glasses are advantageous for Q-switched lasers, high power ultra short pulse amplification and also for sensitizers of energy transfer [12,13].

There exists a substantial amount of literature on the optical properties of Nd^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} doped tungsten–tellurite glasses [14–20]. However, apart from the study realized by El-Mallawany and Abbas Ahmed [21] which reported the effect of Nd^{3+} and Er^{3+} on the glass transition temperature of tellurite based quaternary glasses, no studies exist about the effect of rare-earth elements on the thermal behavior of tellurite glasses in a wide temperature range. Therefore, in the present study, we report, for the first time to our knowledge, the effect of rare-earth oxides (Nd_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3) on the thermal behavior of tellurite glasses by running detailed differential thermal analyses. Since different glass preparing methods are used in the literature to obtain

* Corresponding author. Tel.: +90 212 285 7203; fax: +90 212 285 3427.
E-mail address: ersundu@itu.edu.tr (A.E. Ersundu).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.08.120

Table 1
Labels of the doped samples and change in glass composition with respect to subtraction of rare-earth oxide addition from different components in the glass system.

$(1-x)TeO_2–xWO_3$	Rare-earth dopant content (mol%)	Label	Subtraction from TeO_2		Subtraction from WO_3		Subtraction from both TeO_2 and WO_3	
			TeO_2 (%)	WO_3 (%)	TeO_2 (%)	WO_3 (%)	TeO_2 (%)	WO_3 (%)
x = 0.10	0.5	TW10–RE0.5	89.5	10	90	9.5	89.55	9.95
(TW10)	1.0	TW10–RE1.0	89	10	90	9	89.1	9.9
x = 0.15	0.5	TW15–RE0.5	84.5	15	85	14.5	84.575	14,925
(TW15)	1.0	TW15–RE1.0	84	15	85	14	84.15	14.85
x = 0.20	0.5	TW20–RE0.5	79.5	20	80	19.5	79.6	19.9
(TW20)	1.0	TW20–RE1.0	79	20	80	19	79.2	19.8

RE (Nd_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3).

tellurite glasses with better optical properties, in the present study the effect of different melt-quenching techniques on the thermal behavior of tellurite glasses was also investigated.

2. Experimental procedure

From the glass forming region of $TeO_2–WO_3$ system, three compositions were selected for the present investigation on the basis of the knowledge obtained from our earlier studies on tungsten–tellurite binary system due to their high glass forming ability and chemical stability [2,4,7,8,22–25]. Therefore, different glass samples were prepared with the compositions of $(1-x)TeO_2–xWO_3$, where x = 0.10, 0.15 and 0.20 in molar ratio, and the samples were named as TW10, TW15 and TW20, respectively. According to these compositions, all three samples were doped with 0.5 and 1.0 mol% of Nd_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3 to investigate the effect of rare-earth dopants on the thermal behavior of tungsten–tellurite glasses. Table 1 presents the labels of the doped samples and the compositional change in tungsten–tellurite glasses with respect to subtraction of rare-earth oxide addition from different components.

There exist different approaches for rare-earth doping in tungsten–tellurite glasses such as, subtraction of rare-earth dopant addition from the glass former (TeO_2), from the network modifier (WO_3) or both from the glass former and network modifier. Although, the changes in the glass composition are very small as a result of different subtraction approaches, the stoichiometry of the glasses change by subtracting rare-earth dopant addition only from one component in the glass system. Therefore, in the present study rare-earth doping was realized by subtracting rare-earth oxide addition from both TeO_2 and WO_3 in order to keep the stoichiometry of the glasses constant.

To investigate the effect of rare-earth dopants on the thermal behavior, the glass samples were prepared by applying a conventional melt-quenching technique using reagent-grade powders of TeO_2 (99.99% purity, Alfa Aesar Company), WO_3 (99.8% purity, Alfa Aesar Company), Nd_2O_3 (99.9% purity, Alfa Aesar Company), Er_2O_3 (99.9% purity, Sigma–Aldrich Company), Tm_2O_3 (99.99% purity, Sigma–Aldrich Company) and Yb_2O_3 (99.9% purity, Alfa Aesar Company). The powder batches of 2 g size were thoroughly mixed in an agate mortar and melted in a platinum crucible with a closed lid at 800 °C for 30 min to provide complete homogeneity of the melts and then the molten samples were removed from the furnace and quenched in water bath.

Different glass preparing methods were applied in the literature to acquire tellurite glasses with better optical properties, therefore the effect of different glass preparing techniques on the thermal behavior was investigated and for this purpose 1.0 mol% Tm_2O_3 doped TW20 sample was prepared via three different melt-quenching techniques. As the first glass preparing method, the powder batches were melted in a platinum crucible with a closed lid at 800 °C for 30 min, removed from the furnace and quenched in water bath which was also used for the investigation of the effect of rare-earth dopants on the thermal behavior. As the second glass preparing method, the powder batches were melted at the same temperature for 30 min and quenched in water bath and then crushed and powdered to achieve homogenization. Afterwards, the powdered sample was re-melted and quenched in water bath. Lastly, as the third glass preparing method, the same melting procedure was applied and the glass melts were casted into a pre-heated stainless steel mold.

The thermal characterization experiments were realized by using differential thermal analysis (DTA) technique. DTA scans of the samples were carried out in a PerkinElmer™ Diamond TG/DTA to determine the glass transition onset (T_g), crystallization onset and peak (T_c/T_p), melting onset and peak (T_{mo}/T_{mp}) temperatures. The temperature difference between the T_g and the first exothermic peak onset (T_{c1}), $\Delta T = T_{c1} - T_g$, indicating the thermal stability against crystallization was calculated. The glass transition onset temperatures (T_g) were determined as the inflection point of the endothermic change of the calorimetric signal. Onset temperatures were specified as the beginning of the reaction where the crystallization or melting first starts and peak temperatures represent the maximum value of the exotherm or endotherm. The DTA scans were recorded by using 25 mg powdered samples. All thermal analyses were realized in a platinum crucible with a heating rate of 10 K/min from room temperature to 750 °C in a flowing (100 ml/min) argon gas.

3. Results and discussion

3.1. Effect of glass preparing methods on the thermal behavior

The DTA curves of 1.0 mol% Tm_2O_3 doped TW20 samples prepared via three different methods are given in Fig. 1.

As can be seen from Fig. 1, almost the same thermal behavior was observed for all three samples prepared via different melt-quenching techniques. However, the prepared glasses with different methods showed different colors representing a change in their optical properties. Therefore, it can be concluded that although different glass preparing techniques affect the optical properties, they do not have a significant effect on the thermal behavior. Since the thermal behavior of the glasses are not affected due to different glass preparing methods, in the experimental studies all the samples were prepared by applying the first glass preparing method (melting and quenching in water bath).

3.2. Effect of rare-earth dopants on the thermal behavior

The DTA curves of undoped and 0.5–1.0 mol% rare-earth oxide (Nd_2O_3, Er_2O_3, Tm_2O_3 and Yb_2O_3) doped TW10, TW15 and TW20 glasses are shown in Fig. 2, Fig. 3 and Fig. 4, respectively. In general, the DTA curves showed a glass transition, several exothermic peaks

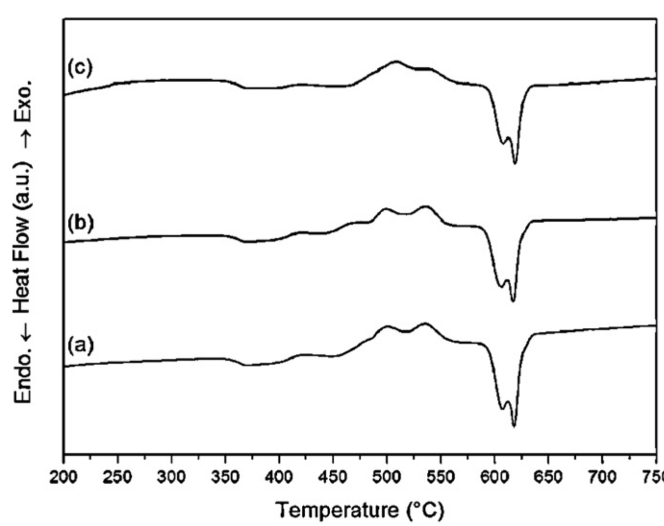

Fig. 1. Effect of different glass preparing methods on the thermal behavior of 1.0 mol% Tm_2O_3 doped TW20 sample, (a) melted and quenched in water bath, (b) melted and quenched in water bath, to achieve homogenization crushed and powdered, re-melted and quenched in water bath, (c) melted and casted into a pre-heated stainless steel mold.