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THERMAL ANALYSIS OF TeO_2-Nb_2O_5-Li_2O-Sm_2O_3 GLASS SYSTEM

Nuraffera Mohd Nasir, Md. Rahim Sahar and Md. Supar Rohani

Physic Dept., Faculty of Science, Universiti Teknologi Malaysia,
81310 Skudai, Johor Darul Takzim

ABSTRACT

A series of samarium-doped tellurite glass on the (70-x) TeO_2-20Nb_2O_5-10Li_2O-(x) Sm_2O_3 system, where x is 0 to 5mol.% has successfully been made by melt quenching technique. The density and the thermal parameters, such as T_g, T_c, T_m, and glass stability, have been determined by Differential Thermal Analysis (DTA). It is found that the variation in glass density with Sm_2O_3 content shows an increasing trend. It is also observed that the T_g and T_c were both compositionally dependent. Meanwhile, the glass stability (T_c-T_g) is highly dependent on the Sm_2O_3 content.

INTRODUCTION

Tellurite glasses are a relatively new non-crystalline material and are at present the subject of intensive investigations because of their technological and scientific importance. Tellurite glasses are candidates for new optical materials because of their superior properties, such as high refractive index, high dielectric constants, a wide band infrared transmittance and large third order non-linear optical susceptibility[1]. Furthermore, their low melting temperatures and non-hygroscopic nature, which limit applications of phosphate and borate glasses, make them of much current interest [2, 3].Therefore, tellurite glasses have been considered as promising materials for both fibre amplfiers and non-linear optical devices [4]. Because of this high technological importance, numerous studies on the properties of tellurite glasses have been carried out [1, 5-7]. An addition of oxides such as Nb_2O_5 to the glass has been reported to improve optical non-linearity, vitrification and stability of the glass [8].As reported by Shixun Dai et al. [9], the TeO_2–Nb_2O_5 glasses, particularly the glasses with 15 to 20 mol% Nb_2O_5 are thermally very stable.

Meanwhile, adding a little quantity of alkaline oxides as the network modifier gives a good quality optical glass system [10]. In addition, alkaline oxides give rise to ranges of excellent glass formation, and in fact enhanced stability against devitrification [11]. But among alkaline oxide (Li_2O, Na_2O, K_2O) network modifiers (NWM), only the Li_2O containing glass was seen as bubble free, highly stable and moisture resistant, suitable for a systematic optical analysis [10]. Keeping in view the desirable features of rare earth oxide, we have recently studied the properties of Samarium oxide doped TeO_2-20Nb_2O_5-10Li_2O. It is because, to our knowledge, very few results about the properties of Samarium oxide doped tellurite glasses have been reported in the literature. At present, our aim is to characterize the density and thermal property of Teo_2-Nb_2O-Li_2O-Sm_2O_3 glass system.

Corresponding Author: fera_nasir@yahoo.com

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EXPERIMENTAL DETAILS

The (70-x) TeO_2-20Nb_2O_5-10Li_2O-x Sm_2O_3, x = 0-6 mol % were prepared using a conventional melt quenching method. Reagent grade chemicals of TeO_2 (97% purity), Nb_2O_5 (99.9% purity), Li_2CO_3 (99.9% purity) and Sm_2O_3 (99.9% purity) were used as raw materials. Each batch (10 g) of prescribed compositions was mixed mechanically in milling machine for 1 hour. It was then melted in a Platinum crucible at 1000°C for 2 hours in an electric furnace. When the melting was completed, the melt was then poured onto steel plate and immediately quenched by pressing it with another steel plate before being annealed at 350°C for 5 hours, after which time the furnace was switched off and the glass allowed to cool to room temperature. The amorphous nature of the samples was checked by X-ray Diffraction (XRD) analysis. The densities, ρ of the glass samples were measured accurately to the fourth decimal by the Archimedes displacement method using toluene as an immersion liquid. The glass transition temperature (T_g), crystallization onset temperature (T_x) and melting temperature (T_m) were determined by differential thermal analysis (DTA) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Glass Forming Region

The nominal glass composition that has successfully been prepared is given in Table 1. The samples are found to be transparent with slight yellowish color. The XRD of this glass system showed a broad peak, which characterized an amorphous nature of the material. Table 1 shows that when the Sm_2O_3 content is low, the glass can easily be formed. However, as the Sm_2O_3 content is being increased up to 4-mol%, the glass seems to crystallize easily.

Table 1: Composition and appearance of TeO_2-Nb_2O_5-Li_2O- Sm_2O_3 glasses

Sample	Nominal Composition (mol %)				Color	XRD analysis
	TeO_2	Nb_2O_5	Li_2O	Sm_2O_3		
S1	70	20	10	0	Transparent yellow	Amorphous
S2	69	20	10	1	Transparent yellow	Amorphous
S3	68	20	10	2	Transparent yellow	Amorphous
S4	67	20	10	3	Transparent yellow	Amorphous
S5	66	20	10	4	Transparent yellow	Amorphous
S6	65	20	10	5	Opaque	Crystal
S7	64	20	10	6	Opaque	Crystal

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Density

Density of tellurite glass is (on average) high, which is more than 5.0 gcm^{-3} [3, 9] .Table 2, shows the typical density of the sample. From Table 2, the variation content may be made and is shown in Figure 1.

Table 2: The density of TeO_2-Nb_2O_5-Li_2O- Sm_2O_3 glasses

Sample	Sm_2O_3 (mol %)	Density, ρ (gcm^{-3}) (±0.0001)
S1	0	5.0127
S2	1	5.0631
S3	2	5.0868
S4	3	5.1235
S5	4	5.1519

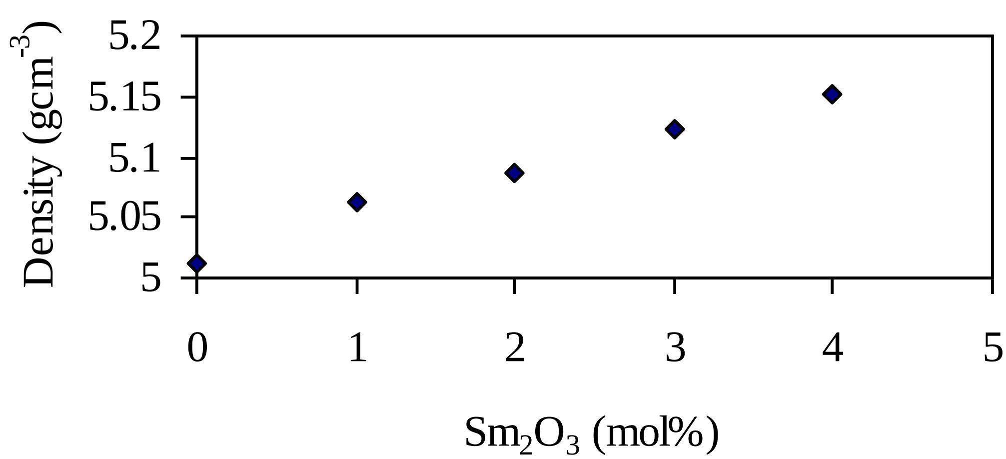

Figure.1 Density vs. Sm_2O_3 contents of TeO_2-Nb_2O_5-Li_2O-Sm_2O_3 glasses.

As seen from Figure 1, the variation of the glasses densities with Sm_2O_3 mol% concentration shows an increasing trend and in the range of 5.0127 to 5.1519 g cm^{-3}. This is due to the change in the atomic mass and atomic radii of the constituent elements (Te and Sm).The atomic mass of Te and Sm is 127.6g and 150.36g respectively, and their atomic radii are 1.42Å and 2.59Å respectively. The replacement of Te by Sm atoms explains the observed increase in density with increasing Sm_2O_3 content [3].

Thermal Stability

Thermal analysis was employed to determine the effect of glass composition on glass stability. The glass transition temperature (T_g) and crystallization temperature (T_c) are important information in the thermal analysis. Table 3 shows a nominal glass composition containing different concentration of Sm_2O_3 and their respective thermal

Corresponding Author: fera_nasir@yahoo.com

parameter. With increase in the Sm_2O_3 content, some general observations may be noted.

Table 3: Glass composition and thermal characteristics

TeO_2	Nb_2O_5	Li_2O	Sm_2O_3	T_c (°C)	T_g (°C)	T_c-T_g (°C)	T_m (°C)
70	20	10	0	545.83	409.77	136.06	136.06
69	20	10	1	576.43	412.41	164.02	164.02
68	20	10	2	572.7	426.07	146.63	146.63
67	20	10	3	561.04	436.65	124.99	124.99
66	20	10	4	560.71	437.32	123.39	123.39

The glass transition temperature, T_g of these glasses were observed to increase with the increase of Sm_2O_3 content. These may attributed to an increase in rigidity formed by the TeO_3 tp units and the increase of non bridging oxygen (NBO) atoms in the glass [12]. This result is in agreement with the fact that the rare earth ions promote the formation of a high number of NBO atoms [13]. The quantity of (T_c-T_g) has been frequently used to measure the glass stability against crystallization, which was usually determined by DTA or DSC [9]. From Table 3, it can be seen that the values of (T_c-T_g) shows an increasing trend with increasing Sm_2O_3 but up to about 1 mol% only, before start to decrease with further increase of Sm_2O_3. These again would reflect that a small amount of rare earth ions such as Sm_2O_3 is capable of stabilizing the glass but as the content is being increased, this factor is no longer effective. The (T_c-T_g) is exceeding 100^0C, indicating that these samples are stable against devitrification [14].

CONCLUSION

The TeO_2-Nb_2O_5-Li_2O-Sm_2O_3 glass with different concentration of Sm_2O_3 from 0 up to 4 mol% has successfully been prepared using conventional melt quenching technique. The density was found to be slightly increased from 5.0127 to 5.1519gcm^{-3} with the increasing of Sm_2O_3 content. An increasing of Sm_2O_3 content to more than 1 mol% to this glass system seems to decrease the glass thermal stability.

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Corresponding Author: fera_nasir@yahoo.com

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Corresponding Author: fera_nasir@yahoo.com