Solid State Sciences 32 (2014) 48–55

Contents lists available at ScienceDirect

Solid State Sciences

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

Kinetic characterization of barium titanate–bismuth oxide–vanadium pentoxide glasses

Aref M. Al-Syadi [a,b], El Sayed Yousef [a,c,*], M.M. El-Desoky [a,d], M.S. Al-Assiri [a,e]

[a] Physics Department, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia
[b] Physics Department, Faculty of Education in AL-Nadirah, Ibb University, Yemen
[c] Physics Department, Faculty of Science, Al Azhar University, Assiut Branch, Assiut, Egypt
[d] Physics Department, Faculty of Science, Suez University, Suez, Egypt
[e] Physics Department, College of Science and Arts, Najran University, Najran, Saudi Arabia

ARTICLE INFO

Article history:
Received 15 January 2014
Received in revised form
27 February 2014
Accepted 24 March 2014
Available online 1 April 2014

Keywords:
Glasses
Annealing
Differential scanning calorimetry (DSC)
Glass transition

ABSTRACT

The glasses with the composition $(80 - x)V_2O_5 \cdot 20Bi_2O_3 \cdot xBaTiO_3$ with $x = 2.5$, 5, 7.5 and 10 mol % were prepared by a melting technique. The crystallization behavior and the microstructure of the glasses were investigated by using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mean value of the activation energy of structural relaxation ($\langle E_g \rangle$) decreased from 395 ± 3 to 369 ± 1.83 kJ/mol when $BaTiO_3$ increased from 2.5 to 10 mol %. The activation energies obtained by the methods Kissinger and Ozawa were in the range from 213 ± 0.65 to 256 ± 1.23 kJ/mol. Different analysis methods were used to estimate the Avrami exponents. Their values range from 4.26 ± 0.6 to 2.62 ± 0.11 for the exothermic peak of the prepared glasses. Moreover, synthesized glasses-ceramic containing $BaTi_4O_9$ and $Ba_3TiV_4O_{15}$ were estimated by using XRD.

1. Introduction

Glasses-ceramic nano/microcomposites are widely used for device applications, which include large area pyroelectric detectors, actuators, frequency doublers and electro-optic modulators [1–6]. The $BaTiO_3$ is one of the most widely used ferroelectric materials and its use of polycrystalline n-doped material in thermistors of thermal overload protection circuits, where the specific resistivity of $BaTiO_3$ increases with temperature by several orders of magnitude in the range of 110–140 °C. Depending on the temperature, $BaTiO_3$ have five kinds of crystal systems like hexagonal, cubic, tetragonal, orthorhombic and rhombohedral [7–11]. This indicates that the transition phase of $BaTiO_3$ may be a function of the temperature and the crystallite size. In particular, the quantitative structural information is important to control the ferroelectric properties for nanocrystalline $BaTiO_3$ ceramics. In order to investigate the properties of $BaTiO_3$ glassy ceramics, it is necessary to determine the crystal structure [12].

Although the main interest in vanadate glasses stems from their novel electrical properties [13,14], recent reports on the possibility of their application as oxygen gas sensors [15] and optical devices [16] have generated a keen interest in the thermal stability of these glasses. Non-isothermal properties, such as those obtained from a differential scanning calorimeter study, provide a lot of insight on the thermal stability of the glass, the chemical bonding in the glass and the nature of the glassy network structure [17].

According to Angell [18], the excess heat capacity at glass transition could be interpreted in terms of fragility of the glassy network. Several methods have been proposed to obtain the activation energy of glass transition and crystallization from differential scanning calorimetry (DSC) experiments [19]. These methods are based on the assumption that the reaction temperature of a kinetically driven transformation shifts when the sample is heated at different constant heating rates.

Moreover, transition metal oxide (TMO) glasses V_2O_5–PbO, V_2O_5–Bi_2O_3 and V_2O_5–P_2O_5 containing $BaTiO_3$, $SrTiO_3$, $NbTiO_3$, etc., are interesting because of their probable applications in non-volatile ferroelectric computer memories and cathode materials [20–22]. Little research work has been focused on studying the kinetic crystallization of these glasses with ferroelectric $BaTiO_3$, $SrTiO_3$, etc. Recently, Al-Assiri et al. [21] estimated only the glass

* Corresponding author. Physics Department, Faculty of Science, Al Azhar University, Assiut Branch, Assiut, Egypt.
E-mail address: omn_yousef2000@yahoo.com (E.S. Yousef).

http://dx.doi.org/10.1016/j.solidstatesciences.2014.03.015
1293-2558/

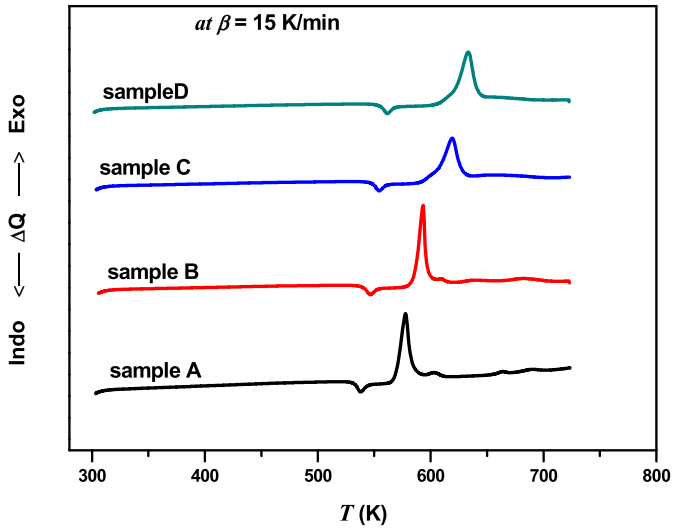

Fig. 1. DSC traces for prepared glasses at heating rate 15 K min^{-1}.

transition temperature of $BaTiO_3 \cdot Bi_2O_3 \cdot V_2O_5$. In the present study, the formation of kinetics crystallization behavior at different heating rates, the activation energy of grain size and kinetic exponent of the $BaTiO_3 \cdot Bi_2O_3 \cdot V_2O_5$ glass–ceramics were obtained by three analysis methods and using DSC, XRD and SEM techniques.

2. Experimental details

The glass systems with the composition $(80 - x)V_2O_5 \cdot 20Bi_2O_3 \cdot xBaTiO_3$ with $x = 2.5$, 5, 7.5 and 10 mol %, were prepared by mixing specified weights of Barium Titanium oxide ($BaTiO_3$, purity 99%, Alfa Aesar), Bismuth oxide (Bi_2O_3, purity 99.9%, Sigma–Aldrich), Vanadium oxide (V_2O_5, purity 99%, Sigma–Aldrich). The powder mixture was heated in a silica crucible at 1323 K for 30 min. The material at melting point which had a high viscosity was cast in a brass mold. Subsequently, the sample was transferred to an annealing furnace and kept for 2 h at 503 K. Then, the furnace was switched off, and the glass sample was allowed to cool.

The thermal behavior was investigated using differential scanning calorimetry (Shimadzu DSC 50). The powdered samples ($\approx$15 mg) were placed into covered aluminum crucibles and the DSC curves were recorded between 300 and 800 K using an increased uniform rate β ranging from 5 to 25 K min^{-1}. The particle size of studied glasses $\approx$25–50 μm in DSC measurement was used. The glass transition temperature (T_g), onset crystallization temperature (T_c) and the temperature of the crystallization peak (T_p) were determined.

The samples were examined by X-ray diffraction (Siemens D 6000) using CuK_α radiation at 40 kV in the 2θ range from 5 to 90°. Scanning electron microscopy (SEM) a JEOL ™ Model JSM-T330 operating at 25 kV was performed of tempered sample coated by gold (Au). Solver Next AFM was used to investigate present glass ceramic.

Table 1
Crystallization rate β, glass transition T_g, onset crystallization temperature T_c and exothermic peak of crystallization T_p.

Sample name	System composition in mol %	B in K/min	$T_g \pm 3$ in K	$T_c \pm 3$ in K	$T_p \pm 3$ in K
Sample A	$2.5BaTiO_3 \cdot 20Bi_2O_3 \cdot 77.5V_2O_5$	5	526	559	567
		10	529	563	573
		15	532	566	578
		20	534	568	583
		25	535	570	585
Sample B	$5BaTiO_3 \cdot 20Bi_2O_3 \cdot 75V_2O_5$	5	534	576	582
		10	538	582	589
		15	540	585	593
		20	542	588	597
		25	544	590	600
Sample C	$7.5BaTiO_3 \cdot 20Bi_2O_3 \cdot 72.5V_2O_5$	5	541	593	604
		10	546	600	613
		15	548	604	619
		20	550	607	624
		25	552	610	627
Sample D	$10BaTiO_3 \cdot 20Bi_2O_3 \cdot 70V_2O_5$	5	548	604	620
		10	552	611	628
		15	555	616	633
		20	557	620	638
		25	559	622	642

Table 2
Crystallization kinetic parameters of prepared glasses.

Sample name	System composition in mol %	ΔT in K	H'	F
Sample A	$2.5BaTiO_3 \cdot 20Bi_2O_3 \cdot 77.5V_2O_5$	34	0.064	32.98
Sample B	$5BaTiO_3 \cdot 20Bi_2O_3 \cdot 75V_2O_5$	45	0.083	32.32
Sample C	$7.5BaTiO_3 \cdot 20Bi_2O_3 \cdot 72.5V_2O_5$	56	0.102	29.85
Sample D	$10BaTiO_3 \cdot 20Bi_2O_3 \cdot 70V_2O_5$	61	0.11	29.50

3. Result and discussion

3.1. Thermal characterization

Fig. 1 shows the differential scanning calorimetric traces of samples with the composition $(80 - x)V_2O_5 \cdot 20Bi_2O_3 \cdot xBaTiO_3$ with $x = 2.5$, 5, 7.5 and 10 mol % glasses at 15 K min^{-1}. The data of T_g, T_c and T_p are summarized in Table 1. Hruby's developed $H' = \Delta T/T_g$ where $\Delta T = T_c - T_g$, and glasses compositional dependencies of the Hruby coefficient were estimated by Sestak [23,24]. The thermal stability value, ΔT, of prepared glasses increases from 34 to 61 °C with increasing $BaTiO_3$ content. This can be attributed to the glass network that was getting closely packed by increasing of $BaTiO_3$ content and it leads to increase the rigidity of the glass matrix. The sample A within composition $2.5BaTiO_3$–$20Bi_2O_3$–$77.5V_2O_5$ in mol % has the lowest value of the $\Delta T = 34$ in K. Otherwise the sample D

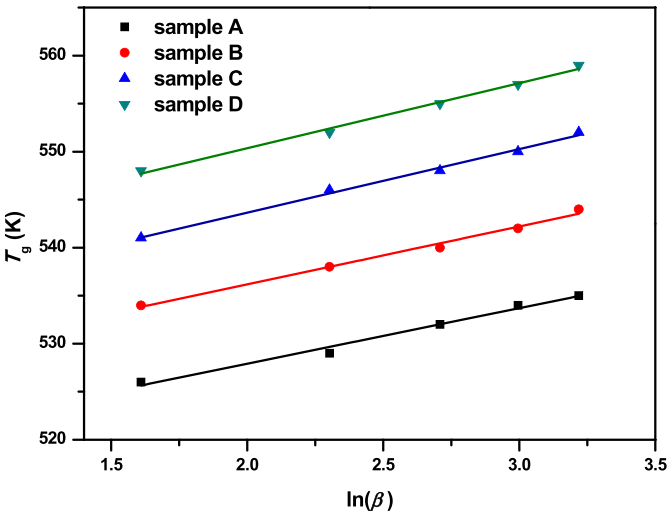

Fig. 2. Glass transition temperature T_g versus ln(β) in K min^{-1}.