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On the approach to Mott's transition in glass-ceramic nanocomposite due to heat treatment

Iman A. Mahdy *[,1], Sh. Heikal [1], A.S. Abd-Rabo [1], A. Abdel Ghany [1], A.A. Bahgat *

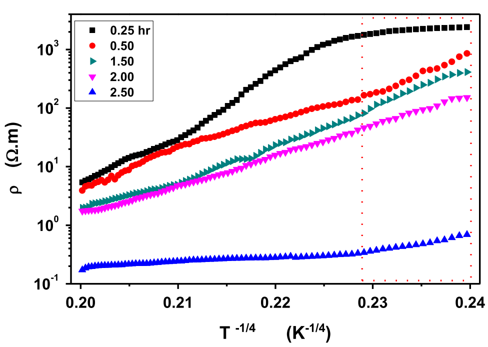
Department of Physics, Faculty of Science, Al-Azhar University, Nasr city 11884, Cairo, Egypt

HIGHLIGHTS

- The glass ceramic nanocomposite of 30[0.75 $BaTiO_3$+0.25 $PbTiO_3$]+70 V_2O_5 (mol%) are prepared by heat treatment at 723 K.
- The difference between glass and GCNC are seen in the XRD and HRTEM.
- The weak change of particle size according to the change in heat treatment time cause to approach to a nonmetallic–metallic transition.

GRAPHICAL ABSTRACT

Glass-ceramic nanocomposite of the composition 30[0.75 $BaTiO_3$+0.25 $PbTiO_3$]+70 V_2O_5 (mol%) was prepared by isothermal heat treatment (HT) at 723 K of the parent glass for different time intervals shows a nonmetallic–metallic transition.



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ABSTRACT

In the present work, the glass-ceramic nanocomposite (GCNC) of the composition 30[0.75 $BaTiO_3$+0.25 $PbTiO_3$]+70 V_2O_5 (mol. %) was prepared from the parent glass by isothermal heat treatment (HT) at 723 K for different time intervals 0.25, 0.5, 1.5, 2, and 2.5 h, respectively. The bulk density and some related parameters were calculated. X-ray diffraction and Hi-Resolution Transmission Electron Microscope (HRTEM) were used to identify different phases as well as particle size of the precipitated nanocrystals during the heat treatment process. The DC electrical conductivity was enhanced three orders of magnitudes (3×10^3) by increasing HT time. The resistivity measurements on the other hand as a function of time show an approach to nonmetallic–metallic transition for the prepared NCGC samples. Mott's VRH conduction mechanism was predicted as a result of the increase of the heat treatment time.

1. Introduction

Glass-ceramics materials are polycrystalline solids containing nanometers to micrometers size crystals produced by devitrifying their parent glasses. The first step toward this involves conventional techniques for glass production, followed by controlled crystallization [1,2]. The desired properties are achievable by controlling the microstructure and heat treatment process. Wide varieties of applications of these versatile materials have been developed because of their many outstanding properties and the distinct advantages of the glass ceramic method over conventional

* Corresponding authors.
E-mail addresses: imanmahdy@gmail.com (I.A. Mahdy), alaabahgat@hotmail.com (A.A. Bahgat).
[1] Girls branch.

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ceramic processing routes. Of particular importance in many applications is the high uniformity of the microstructures of glass ceramics, the absence of porosity and the minor changes in volume during the conversion of glass into glass ceramic [2].

The controlled crystallization process leads to the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals, where the number of crystals, their growth rate, microstructure and their final size are controlled by suitable heat treatment [1,2]. Glass-ceramic materials (so-called glass-ceramic nanocomposite with the size of crystallites smaller than 100 nm (nanocrystallites) which are still transparent like glass [1,3]. In the past few years, glass-ceramics containing ferroelectric crystals have received considerable interest, because of their easiness of preparation, promising dielectric, and excellent electro-optical properties [4,5]. Advantages in case of ferroelectric glass-ceramics include low levels of porosity and hence high breakdown voltages, this together gives the ability to develop different article shapes depending on the application required, with the least energy consumption and machining [4].

$BaTiO_3$ and $PbTiO_3$ based glass-ceramics have shown great potential in certain electronic applications. The advantages of ferroelectric glass-ceramic materials, such as lower sintering temperature and homogeneous mixing of ferroelectric phases with glass, have been utilized in ferroelectric and piezoelectric applications [6].

Barium titanate ($BaTiO_3$) is a very important and interesting ferroelectric material for applications in electronic devices such as capacitors, electro-optic devices, radio communication filter, thermal switches, piezoelectric sonar and ultrasonic transducers, stereo tweeters, buzzers, sensors and ferroelectric thin film memories, microwave, pyroelectric and piezoelectric sensors, non-volatile memories and optical waveguides [6,7].

Glass-ceramic nanocomposite in system containing V_2O_5 belong to the best electronic conductors [4,8–10]. They inherit some structural features and transport properties from the nanocrystalline forms of V_2O_5 and in particular of its α-phase, being often cited as a model of an electronic conductor [8,9]. On the other hand, in recent years it has been established that the presence of fine grain of foreign phases distributed in moderately conducting matrices (glasses, but also polymer electrolytes or poly-crystalline materials) can significantly improve their conductivity [1–10].

Oxide glasses and corresponding glass-ceramics nanocomposite containing large amounts of transition metal oxides (TMO) such as V_2O_5 show semiconducting behavior and have interesting electrical properties. This behavior is strongly influenced by the simultaneous presence of transition metal ions in two different valence states in the glass network. This is due to the redox processes accruing in the melt at high temperatures during the course of preparation [4]. In the conduction of V_2O_5, containing glasses changes between $V^{4+} \leftrightarrow V^{5+}$ sites takes place by hopping [10–12]. The electrical conductivity for such glasses depends strongly upon the local interaction of an electron with its surroundings and the distance between vanadium ions.

The aim of this work is studying the Mott variable-range-hopping model (VRH) for the glass-ceramic nanocomposite (GCNC) sample of 30[0.75 $BaTiO_3$+0.25 $PbTiO_3$]+70 V_2O_5 in mol% obtained by isothermal heat treatment of the glass at 723 K for a different HT time intervals. Where, Mott's variable-range-hopping model (VRH) will be applied when nonmetallic–metallic transition would take place.

2. Experimental

Glass-ceramic nanocomposite samples of the composition 30 [0.75 $BaTiO_3$+0.25 $PbTiO_3$]+70 V_2O_5, in mol% were prepared by the isothermal annealing of the parent glass obtained by conventional melt quenching technique as explained recently [12]. The parent glass sample was heat treated (HT) at 723 ± 5 K, which selected to be greater than the crystallization temperature [12]. The HT achieved at different time intervals 0.25, 0.5, 1.5, 2 and 2.5 h, respectively.

The bulk densities measured at room temperature by Archimedes method with carbon tetrachloride (CCl_4) as the immersing liquid of density (1.593 g/cm^3). Crystalline nature was studied by X-ray diffraction (XRD) using Panalytical (X'Pert Pro MRD) diffractometer with Cu(K_α)-radiation in the angular range (2θ=4–70°). Alternatively, high-resolution transmission electron microscope (HRTEM) used to verify the structural nature and homogeneity of the glass-ceramic samples using HRTEM JEOL (model: Jem-2100). Moreover, DC electrical conductivity of the glass-ceramic was measured by means of the two-probe method over the temperature range (303–623 K) using a chromel–alumel (type-K) thermocouple as a temperature sensor. In addition the dielectric permittivity was measured using RLC bridge type: Stanford Res (Model: SR-720) at frequency of 120 Hz by the two probe method.

3. Results and discussion

3.1. Density and related parameters

The bulk density is an important physical property to elucidate the structure nature of any glass matrix and glass-ceramic nanocomposite. Generally, the bulk density is affected by the structural softening and compactness, changes in geometrical conuration, coordination number, cross-link density and dimension of interstitial spaces of the glass [13]. Density values of the glass-ceramic nanocomposite shows a change from 3.69 to 4.10 g/cm^3 due to changing HT time at the proposed annealing temperature, Table 1 list the obtained results.

The molar volume V_m (cm^3/mol) for the glass-ceramic nanocomposite samples are calculated using the formula $V_m = M/d$

Table 1
The physical parameters calculated for glass-ceramic nano-composite samples. Where; d: is the density, V_m: the molar volume, N: density of states (number of ions per unit volume), D: particle size; ε lattice strain %; R: hopping distance (average cation–cation separation).

HT time (h)	Structural parameters						
	d (g/cm3)	V_m (cm^3/mol)	N (cm^{-3}) × 10^{22}	D (nm)	D_{av} (nm)	$\varepsilon \times 10^{-2}$ %	R (nm)
0.25	3.717	54.486	1.105	29.4	32	6.63	0.449
0.5	4.103	49.358	1.220	31.6	32.8	2.05	0.434
1.5	3.936	51.459	1.170	25.1	34	1.21	0.440
2	4.015	50.442	1.194	29.3	33.8	14.0	0.437
2.5	4.096	49.441	1.215	25.2	30	3.37	0.435