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Effect of sintering temperature on the developed crystalline phases, optical and electrical properties of $5ZnO\text{-}2TiO_2\text{-}\ 3P_2O_5$ glass

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ABSTRACT

Glass of the composition $5ZnO\text{-}2TiO_2\text{-}\ 3P_2O_5$ was prepared by the melt-quenching technique. The prepared samples were heat-treated at the nucleation (625 °C) and crystallization (875 °C) temperatures for different soaking times. SEM, XRD, UV–Vis, DSC and electrical measurements were used. $Ti(PO_4)$ and $Zn_3(PO_4)_2$ phases were formed at the nucleation temperature; while, $Ti_5O_4(PO_4)_4$ and $\alpha\text{-}Zn_2P_2O_7$ phases were observed at the crystallization temperature. Long soaking time caused color fading or formation of opaque white samples due to the decrease of Ti^{3+} ions or increase of Ti^{4+} ions, respectively. The formation of Ti^{3+} ions causes a development of violet color with absorption bands in the range 400–800 nm. SEM suggested that prolonged heating at the crystallization temperature caused disintegration of the formed phases. The electrical conductivities of the studied samples at the low and high measuring temperatures occur via electrons revealing their suitability to be applied as semiconductors. The values of σ_{ac} and dielectric constant ε' increase with rising the sintering temperature. The ε' of the as-prepared sample (19.23) is increased to 152.45 or 189.11 when heat-treated at the nucleation temperature for 4 h and at crystallization temperature for 15 min, respectively. Samples of high ε' values represent promising candidates for energy storage in electronic devices.

1. Introduction

Phosphate compounds have been involved in many materials (e.g., ceramics, fluorescent, catalysts … etc) [1]. In addition, they are used in the formation of low melting temperature phosphate glasses. This type of glass possesses various advantages including high thermal expansion coefficient, biocompatibility, low dispersion and relatively high refractive indices relative to the traditional glasses such as silicate and borate glasses [2,3]. These advantages qualify phosphate glasses to be used for a variety of applications for instance industrial processing of hard water and optical technologies [3].

Phosphate glasses containing ZnO is motivating because, at the metaphosphate composition, these glass systems exhibit uncommon variations between the structural and physical properties [3]. Hence, zinc phosphate glasses were utilized as LED light sources [4] and as substrates for optical waveguides written by f-sec lasers [5]. Such glasses have greater coefficients of thermal expansion and low processing temperatures, which make them useful as sealing glasses [6]. On the other hand, chemical durability, thermal stability and other physical properties of phosphate glasses could be improved by the addition of TiO_2 because of the formation of Ti–O–P and/or Ti–O– Ti bonds into the phosphate structural network [7]. Many investigations of the role of Ti^{4+} ion in these titanophosphate glasses have been carried out [7–13]. The thermal and optical properties, structures and glass forming region of $TiO_2\text{-}ZnO\text{-}P_2O_5$ glasses were investigated and the fabrication of titanophosphate formed below 1600 °C was also examined [14]. The Structure and properties of titanium–zinc borophosphate glasses were investigated using Raman spectra [11]. Titanophosphate glasses have been found applications as electric conduction glasses [15].

The ternary system $TiO_2\text{-}ZnO\text{-}P_2O_5$ has received to the best of our knowledge less attention. More insight, in the present work, will be given to explore the properties of this ternary system. We investigated glass samples of the composition $5ZnO\text{-}2TiO_2\text{-}3P_2O_5$ and their related glass ceramics. The effects of heat-treatment temperature and soaking time at the nucleation and crystallization temperatures on the phases formed and on their optical and

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electrical properties were also investigated.

2. Experimental

Glass of composition $5ZnO\text{-}2TiO_2\text{-}3P_2O_5$ was prepared by the melt-quenching technique. Analytical grade ZnO, TiO_2, and $H_2(NH_3)PO_4$ were used for the preparation of the glass samples. A glass batch of 50 g glass was pulverized in an agate mortar, and then melted at 1250 °C for 1 h in an alumina crucible. The melt was poured into rectangular molds of $3 \times 10 \times 30$ mm at room temperature, and the samples were quickly transferred into electrically heated furnace pre-heated at 550 °C; the furnace was then switched off immediately to cool naturally to room temperature. The obtained samples appeared visually black and glossy. The prepared samples were coded as described in Table 1.

Differential Scanning Calorimetry (DSC) analysis was performed on the powder of the as-prepared glass sample using STDQ 600 TA Company (USA) instrument. In this analysis, the sample was placed in a Pt-holder with another Pt-holder containing Al_2O_3 as a reference material under an atmosphere of nitrogen at a flow rate of 30 mL/min and heating rate of 10 °C/min. The nucleation and crystallization temperatures were determined from the collected DSC trace.

Crystallized samples were prepared by heating the glass samples by one-step heat treatment regime based on the data obtained from DSC technique. Heat treatment was carried out at the nucleation and crystallization temperatures. The samples were soaked for different periods at each temperature and the phases formed were identified using X-ray diffractometer (Bruker D8 Advanced Instrument (Germany# D8 ADVANCE Cu target 1.54 Å, 40 kV, 40 mA).

The microstructure of the heat-treated glass samples was investigated using a scanning electron microscope of the type SEM-EDX, Jeol-840A Electron Probe Microanalyzer operating at 20 kV.

Reflection spectra were measured in the range 200–1100 nm for highly polished samples using a double beam spectrophotometer (JASCO corp. V-570, Rel-OO, Japan) equipped with special reflection sample holder.

The electrical measurements were carried out on rectangular samples of thicknesses ranging from 1.0 to 2.0 mm. The surfaces were polished and the opposite sides for each sample were brush painted with silver paste. The sample was mounted between two stainless steel disc electrodes, one of them was kept fixed and the other disc was positioned using perfect spring contact. Electrical connections and measurements using LCR Hi Tester (HIOKI, 3532-50), Japan, at frequency range 0.042 kHz–5 MHz, and temperature range from 25 to 350 (°C) are described elsewhere [16]. The a.c. conductivity (σ_{ac}) of the studied samples has been calculated using the following relation [17]:

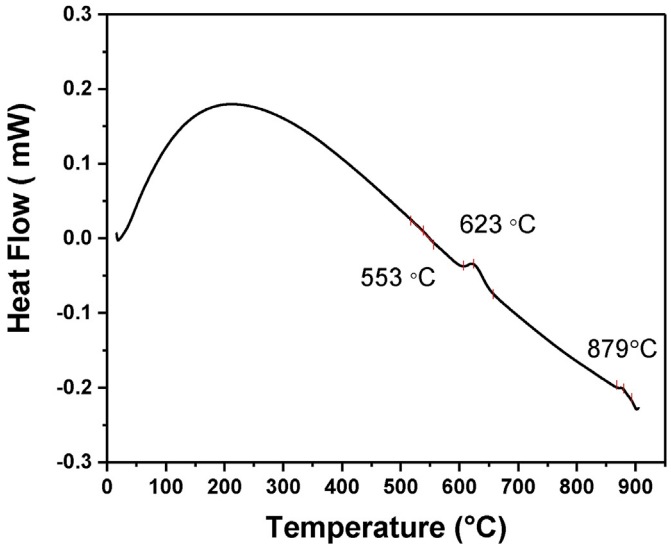

Fig. 1. DSC of the as-prepared glass sample (Z-0).

$\sigma_{ac} = \acute{\varepsilon}\ \varepsilon_o\ \omega\ \tan\delta$, where, ε_o is the permittivity of free space equals $8.85\ 9 \times 10^{-12}$ F m^{-1}, and $\acute{\varepsilon}$ is dielectric constant calculated as described elsewhere [16], $\omega = 2\pi f$ is the angular frequency at frequency f and tan δ is the dissipation factor obtained directly from LCR bridge.

3. Results and discussion

Fig. 1 shows the DSC trace of the as-prepared glass sample after being melted, annealed and cooled to room temperature (Z-0 sample).It can be noticed that the glass has a glass-transition temperature (T_g) at 553 °C, the two exothermic peaks at 623 °C and 879 °C indicate the nucleation and crystallization temperatures, respectively. The latter temperature is very close to the deformation temperature therefore, the crystallization of the glass samples was performed at 875 °C and this temperature will be referred hereafter as the crystallization temperature. Due to the large thickness of the as prepared samples (greater than 3 mm), the nucleation was carried out at 625 °C, and will be denoted as the nucleation temperature.

3.1. Heat treatment effect

The as-prepared sample appeared visually black in color (Fig. 2). This color has been attributed to the presence of Ti^{3+} and Ti^{4+} ions [18]. On the other hand, the heat-treated samples showed different

Table 1
The dielectric constant (ε') and activation energy (E_a) values of the studied samples.

Sample code	Sintering temperature (°C)	E_a (eV) in HTR[a]	E_a (eV) in LTR[a],	ε' at RT[a],1 kHz
Z-0	RT	0.209	0.007	19.23
Z-1h	625	0.228	0.014	35.63
Z-2h	625	0.182	0.031	110.06
Z-4h	625	0.241	0.015	152.45
Z-7h	625	0.323	0.043	30.41
Z-10h	625	0.405	0.027	16.19
ZP-¼h	875	0.155		189,11
ZP-½h	875	0.140		101.12
ZP-1h	875	0.142		48.41
ZP-2h	875	0.104		34.38
ZP-4h	875	0.106		31.40

[a] HTR = high temperature region, LTR = low temperature region, RT = room temperature.