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Electronic and ionic relaxations in strontium–borate glass and glass-ceramics containing bismuth and vanadium oxides

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ABSTRACT

The topography, microstructure, and electrical properties of strontium–borate glass and SBO glass containing bismuth and vanadium oxides, were studied. The structure was measured using X-ray diffraction (XRD), energy dispersive X-ray spectrometer (EDS), and scanning electron microscope (SEM) methods. The A.C. complex conductivity was investigated as a function of temperature and frequency. The influence of the quantity of bismuth and vanadium oxides present, on glasses microstructure and electrical properties, was discussed.

In order to obtain glass-ceramics, the glasses were subjected to crystallization at temperatures close to the exothermic processes indicated by the differential scanning calorimetry (DSC) measurements. X-ray diffraction (XRD) measurements were carried out to determine the presence of bismuth vanadate ($Bi_2VO_{5.5}$) crystalline phase in heat-treated samples. After heat treatment, there were still some traces of the glassy phase within the samples. The effect of the crystallization process on the microstructure, topography, and dielectric behavior of the material was analyzed. The A.C. dielectric permittivity, conductivity, and impedance were discussed at specific temperature and frequency region; in addition, conduction mechanisms were proposed.

1. Introduction

Borate glasses are known for their high thermal stability, low melting point, and good solubility of rare earth ions [1]. Boron in boron–oxygen structural units has the ability to change coordination number, that is a variety of B—O structural units may be present in the glass network [2,3]. The structure of glassy B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B—O—B linkages [4]. However, this glass easily becomes unstable due to its hygroscopic nature. Therefore, in order to obtain a stable borate glass, modifiers such as alkalies and alkaline earth ions are added [5,6]. Metal oxides like MgO, CaO, SrO, BaO, ZnO, and Al_2O_3 etc., are found to be stabilizers of borate glasses [4]. Apart from being stabilizers, these oxides also modify other physical properties of the glasses. For instance, strontium–borate glass SrB_4O_7 (SBO) has dielectric, thermal, and non-linear optical properties. It has a relatively low melting point and can be easily prepared by the traditional melting method. SBO glass is known as a good host matrix for easily dispersing a large number of ferroelectric crystallites [7].

Recently, borate glasses containing heavy metal oxides such as Bi_2O_3, PbO, and Ga_2O_3 have been also studied because of a wide number of promising applications in optical and electronic devices [8,9]. Bismuth oxide is a glass modifier which causes an increase in the density, linear, and non-linear refractive indices of glass. These properties enhance their applications in optical and optoelectronics [10,11]. Borate glasses containing Bi_2O_3 show improved chemical durability, thermal stability and reduce the phonon energy of the glasses [12].

Vanadium oxide is a transition metal oxide which within the structure of a glass may act as both a glass former and glass network modifier. Glasses containing a large amount of transition metal oxides exhibit electronic conductivity. Their electrical properties are determined by the presence of transition metal ions in two different valence states (for instance V^{4+} and V^{5+}). The conductivity of these systems is usually described by the mechanism of polaron hopping between such ions [13–16]. A general formula for the electrical conductivity of these glasses was proposed by Mott in which the conductivity, σ, is given by [16]:

$$\sigma = \frac{\upsilon_{ph} e^2 C(1-C)}{kTR} \exp(-2\alpha R) \exp\left(-\frac{W}{kT}\right), \tag{1}$$

where υ_{ph} is the phonon frequency, α is the rate of wave function decay, C is the ratio of ion concentration in the low valence state to the total concentration of transition-metal ions, R is the average hopping distance, W is the activation energy, e is the electron charge, k is Boltzmann's constant and T is the absolute temperature.

There are a large number scientific papers which describe glasses containing significance quantities of V_2O_5 (>50 %mol) for instance: V_2O_5—P_2O_5 [17], Fe_2O_3—V_2O_5—P_2O_5 [18], V_2O_5—Bi_2O_3 [19],

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$ZnO—V_2O_5—P_2O_5$, $GeO_2—V_2O_5—P_2O_5$ [20], and $V_2O_5—TeO_2$ glasses [21]. When comparing the electrical properties of vanadium oxide glasses, one may notice that vanadium–bismuth oxide glasses exhibit higher D.C. conductivity than those of the corresponding $V_2O_5—P_2O_5$ and $V_2O_5—TeO_2$ glasses [19].

The bismuth vanadate $Bi_2VO_{5.5}$ ceramics (BiV) have ferroelectric properties at room temperature which show promise across a range of potential applications. Bismuth vanadate crystallizes in a polar orthorhombic form. It exhibits three main polymorphs which are stable at different temperature ranges. A non-centrosymmetric α-phase which is stable below 730 K, a centrosymmetric β-phase between 730 K and 835 K, and a centrosymmetric γ-phase which is stable above 835 K. BiV melts at 1153 K. The high-temperature γ-phase consists of $(Bi_2O_2)^{2+}$ sheets interleaved with perovskite like layers of $(VO_{3.5}\square_{0.5})^{2-}$ where □ denotes oxygen ion vacancies [22–24]. In BiV systems, oxygen vacancies could be caused by the presence of reduced valance state of vanadium ions (V^{4+}). One oxygen ion vacancy will form with two tetravalent vanadium ions entering into the crystal structure, in order to maintain the electrical neutrality. This reaction could be described using Kroger–Vink notation:

$$2V^{+5}+O^{x}_{o}\rightarrow 2V^{+4}+V_{o}^{\bullet\bullet}+{}^{1}/_{2}O_{2(g)}$$

where $V_o^{\bullet\bullet}$ is the oxygen vacancy with two effective positive charges and O^x_o is the oxygen ion in the oxygen site with zero effective charge [25]. The BiV γ-phase exhibits a high ionic conductivity which may be attributed to the presence of doubly charged oxygen ion vacancies $V_o^{\bullet\bullet}$ in the perovskite layer, considered to be the most mobile charges in perovskite ferroelectrics. The oxygen vacancies in α and β-phases of BiV also give rise to non-negligible ionic conductivity of the order of 10^{-6} to 10^{-3} $\Omega^{-1}cm^{-1}$ [22–24]. In oxygen ion conductors, current flow occurs through the movement of oxygen ions or vacancies through the crystal lattice. This movement is a result of thermally activated hopping of the oxygen ions, moving from crystal lattice site to crystal lattice site, with a superimposed drift in the direction of the electric field. The ionic conductivity is consequently strongly temperature dependent and is also closely related to the disorder of oxygen vacancies. The number of oxides needed to consider ion oxygen conduction is relatively low and the energy involved in the process of migration from one site to the unoccupied equivalent site must be small, certainly less than about 1 eV [26].

Ferroelectric glass–ceramics have shown great potential in certain electronic applications such as thermal switches, capacitors, electrooptic devices, piezoelectric sonar and ultrasonic transducers, radio communication filters, pyroelectric security surveillance devices, tweeters, buzzers, sensors, and ferroelectric thin film memory [27–32]. Their dielectric permittivity is very sensitive to changes in grain size and to the structure of agglomerates and grain boundaries [27–32]. The most common method for obtaining such materials is using a conventional glass melting technique followed by a controlled crystallization of the glasses obtained [27]. Numerous studies of glass–ceramic composites prepared from two or more components include materials containing ferroelectric titanate and niobate crystallites such as $LiNbO_3$, $NaNbO_3$, $LiTaO_3$, $PbTiO_3$, $BaTiO_3$, dispersed within an amorphous matrix formed by glass forming oxides (SiO_2, V_2O_5, B_2O_3, PbO) [27–32].

There are only a few literature reports regarding the properties of strontium–borate glasses, bismuth and vanadium oxides containing strontium–borate glasses, and glass-ceramics [7,33,34]. Moreover, there is a lack of complex analysis of the electrical behavior of these systems. The aim of the present study is to investigate the electrical properties, morphology and structure of strontium–borate glass and strontium–borate glass containing bismuth and vanadium oxides. Moreover, the influence of the crystallization process on their structure and electrical behavior was studied.

2. Experimental

The polycrystalline strontium–borate, SrB_4O_7 was synthesized via a solid state reaction route that involved heating stoichiometric mixtures of analytical grade $SrCO_3$ and H_3BO_3 at 1073 K for 12 hours. Next, samples of a composition of $x(2Bi_2O_3—V_2O_5)$-(100-x)SrB_4O_7, where x = 5 and 50 (in %mol) were prepared from reagent-grade Bi_2O_3, V_2O_5 and pre-prepared SrB_4O_7. While SBO glass samples (x = 0) were prepared from reagent-grade $SrCO_3$ and H_3BO_3. Samples of glass were prepared by the conventional melt quenching technique. The melting was conducted in alumina crucibles at 1373 K for 2 hours. The melt was poured onto a preheated (573 K) brass plate and pressed by another plate to obtain flat circular disks of 1–2 mm thickness and 20–30 mm in diameter.

Differential scanning calorimetry (DSC) measurements were performed on powdered samples in a flow of nitrogen at 50 cm^3 min^{-1} using a Netzsch STA 449F1 thermal analyzer. The heating rate was maintained at 15 K min^{-1} within a temperature range of 373–813 K. The presence of crystalline phases and their phase composition were studied using an X-ray diffraction (XRD) method using a Philips X'Pert Pro MPD system with CuKα radiation. The XRD measurements were conducted at room temperature.

The Raman spectra were recorded by using a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation by means of an argon ion laser emitting at 514 nm and operating at a power level of 50 mW. They were excited in the range between 100 and 1200 cm^{-1} five times for every sample.

The topography of the samples was investigated using a scanning electron microscope (SEM), FEI Company Quanta FEG250 with Energy Dispersive X-ray Spectrometer (EDS) QUANTA. SEM measurements were conducted on samples which had been fractured and then given a 7 nm gold coating, using a 30 kV beam accelerating voltage with a SE-ETD detector (secondary electron—Everhart-Thornley detector) working in the high vacuum mode (pressure 10^{-4} Pa).

For electrical measurements, gold electrodes were evaporated onto the surface of the polished samples. Impedance measurements were carried out in a frequency range from 10 mHz to 1 MHz with an A.C. voltage of 1 V_{rms} in a temperature range from 373 to 813 K with a step of 10 K using a Novocontrol Concept 40 broadband dielectric spectrometer and high-temperature Novotherm HT 1600 at atmosphere pressure. A single measurement was carried out both while increasing and decreasing the temperature and in total this process lasted for about 3 days. Each data point was saved when the temperature achieved did not deviate from the set temperature by more than 0.5 K and was stable for 60 sec.

Two types of samples were studied: as-quenched and heat-treated (SrB_4O_7, $5(2Bi_2O_3—V_2O_5)$-95SrB_4O_7, $50(2Bi_2O_3—V_2O_5)$-50SrB_4O_7). Sample names were simplified to SBO, as-quenched and heat-treated 5BiV-95SBO, as-quenched, partially crystallized, and fully crystallized 50BiV-50SBO. Heat-treated 5BiV-95SBO samples were obtained after a full cycle of high-temperature electrical measurements. Partially crystallized 50BiV-50SBO samples were obtained by heat treating in air at a temperature of 693 K for 3 hours and then kept the samples in the furnace to cool to room temperature. The crystallization temperature was determined on the basis of the DSC spectrum. During high-temperature electrical measurements of partially crystallized 50BiV-50SBO samples, further crystallization process took place. Samples after this process were described as fully crystallized.

3. Results

3.1. Structure and morphology

Fig. 1 shows the DSC spectrum for the as-quenched 50BiV-50SBO sample. This sample exhibits one exothermic process and two endothermic processes. Glass and phase transitions identified by DSC for all the samples studied are listed in Table 1 together with reference values