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Dielectric Dispersion in $Bi_3Zn_2Sb_3O_{14}$ Ceramic: a Pyrochlore Type Phase

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The electric and dielectric properties of $Bi_3Zn_2Sb_3O_{14}$ ceramic were studied by impedance spectroscopy. The measurements were performed in the frequency range 5 to 13 MHz and at temperature ranges from 25 to 700 °C. The permittivity was calculated by the variation of the imaginary part of the impedance (-Im(Z)) as function of 1/ω, where ω represents the angular frequency (2πf). The parameter ε = f(T) exhibits values in the range from 40 to 48. The dielectric losses (tanδ) show slight dependence with the temperature up to 400 °C. A strong increasing of the tanδ occurs at temperatures higher than 400 °C. In a general way, a decrease of the parameter tanδ occurs with the increasing frequency.

Keywords: *varistor, pyrochlore, impedance spectroscopy, dielectric*

1. Introduction

Pyrochlore type phases are materials potentially applicable in a variety of areas due to their wide range of semiconductor, electro-optic and dielectric properties[1,2]. $Bi_3Zn_2Sb_3O_{14}$ is formed during sintering process in ZnO-based varistors, a typical polyphasic ceramic. These polyphasic electroceramics are the result of a complex sequence of chemical reactions[3-6]. The pyrochlore phase does not generally make up the varistor microstructure since, after it is formed during heating cycle to temperatures very similar to 700 °C, it reacts with ZnO at around 1000 °C, forming the spinel type $Zn_7Sb_2O_{12}$ and bismuth oxide Bi_2O_3 phases. However, under specific sintering conditions, the pyrochlore type $Bi_3Zn_2Sb_3O_{14}$ phase may be retained[7]. The effects of this phase on the dielectric behavior of varistor ceramics are not yet known. Indeed, small number of technical and academic information are available on the $Bi_3Zn_2Sb_3O_{14}$ phase, particularly insofar as its dielectric characteristics, such as permittivity and dielectric loss, are concerned.

Studies of electrical properties of the electroceramics at fixed frequency do not give a complete set of properties about the evolution of the electric parameters as a function of temperature. Electroceramic shows a variety of the frequency dependent phenomena associated with grain boundaries region and intrinsic properties of the material[8-10]. Fortunately, the impedance spectroscopy allows measurements under wide range of frequencies, being useful to separate the contributions of the electroactive regions, such as grain boundary and grain.

In this study, the impedance spectroscopy technique was employed to investigate the permittivity of high density ceramics of the pyrochlore type $Bi_3Zn_2Sb_3O_{14}$ phase prepared by the chemical route based on the polymeric precursor method.

2. Experimantal Procedure

2.1 Synthesis

The chemical route developed by Pechini[11] was used to synthesize the pyrochlore phase $Bi_3Zn_2Sb_3O_{14}$ [7]. This synthesis process also called of polymeric precursor method[12] shows large applications in the preparation of the polycations oxides. In this process, several cationic species are randomly distributed at molecular scale into the polymer. The starting reagents to prepare the powders obtained *via* chemical route were zinc acetate $(CH_3CO_2)2Zn.2H_2O$ (99.0% Reagen), citric acid $H_3C_6H_5O_7.H_2O$ (99.5% Reagen), ethylene glycol $HOCH_2CH_2OH$ (98.0% Synth), antimony oxide Sb_2O_3 (99.0% Riedel) and bismuth oxide Bi_2O_3. Zinc acetate and citric acid were dissolved in ethylene glycol at 70 °C under

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continuous magnetic stirring of solution, in a beaker. Due to the low solubility of zinc acetate in ethylene glycol, nitric acid was added in sufficient amount for complete solubilization. In the sequence, stoichiometric amount of Sb_2O_3 and Bi_2O_3 were added. Distilled water and nitric acid were added in excess under stirring and heating to complete solubilization of oxides. A clear and colorless solution was obtained after complete oxides dissolution. Then, the in situ reactions consisted in the conversion of the oxides into citrates, which have high solubility of ethylene glycol. During the synthesis of pyrochlore phase the following ratios among the chelating agents and salts were used: 3 moles of citric acid for each mole of metallic cations to be chelated. The ratio between citric acid and ethylene glycol was 60% in mass of citric acid to 40% in mass of ethylene glycol. After complete solubilization of the starting reagents, the temperature was raised to 110 °C promoting polyestherification. In the sequence, the reaction of a polymeric gel was carried out. The temperature was then increased at 3 °C/min to 350 °C leading to partial decomposition of the polymer. The resulting expanded resin consisted of a partially decomposed polymer presenting very brittle characteristic. This material was deagglomerated in an agate mortar being called as precursor. This precursor was spread in an alumina substrate and calcined at 900 °C during 1 h.

2.2 Sintering

Pellet of $Bi_3Zn_2Sb_3O_{14}$ powder was prepared by isostatic pressing at 100 MPa. The sintering process was carried out in a dilatometer up to 1250 °C (NETZSCH 402, Selb, Germany) using constant heating rate sintering of 10 °C/min. A relative density of 98% of the theoretical density was reached.

2.3 Electrical Measurements

Electrical measurements were carried out by impedance spectroscopy on 8 × 5 mm sample. Platinum electrodes were deposited on both faces of the ceramic sample by a platinum paste coating (Demetron 308A), which was dried at 800 °C for 30 min. The electrical measurements were performed in the frequency range of 5 to 13 MHz, using a Solartron 1260 impedance analyzer controlled by a personal computer. A nominal voltage equal to 500 mV was applied. The sample was characterized in a sample holder with a two-electrode configuration. The ac measurements were taken in the range from room temperature to 700 °C temperature. After each measuring temperature prior to thermal stabilization a 1 h of soaking time was used. All the measurements were carried out in dry air. The data were plotted in the complex plane formalism and analyzed using the "Equivalent Circuit" (Equivcrt) software program. This program works in an environment developed for equivalent electric circuits being based on the fitting of the immitance spectra data[13].

3. Results and discussion

3.1 Electrical Characterization

Figure 1 shows impedance diagrams of $Bi_3Zn_2Sb_3O_{14}$, at several temperatures. All diagrams exhibit the phenomenon of the decentralization, in which the centers of the semicircles that compose the total electric response are centered below of real axis. In addition, the shape of the diagrams suggests that electric response is composed of two semicircle. The high overlapping degree suggests that each contribution presents very similar relaxation frequency ($f = \frac{1}{2\pi\tau}$). The small semicircles definition is assigned to very similar values of most relaxation frequent, with relation to each relaxation phenomenon detected, one to the grain and another to the grain boundary. Therefore, the overlapping increase with decreasing of magnitude of the difference between of most relaxation frequent.

Figure 2 shows experimental points and theoretical curve, at 400 °C. An excellent agreement between the data and the fitting curve was obtained. Both the electric and dielectric properties of the $Bi_3Zn_2Sb_3O_{14}$ are well represented by two parallel RC equivalent circuits in series. The first relaxation phenomenon (< 10^4 Hz) represents the grain boundary contribution to electrical response. The second one, in the high frequency range (> 10^4 Hz), corresponds to specific properties of the grain or bulk.

Electrical conductivity of ceramic materials (σ_b) is thermally activated and follows an Arrhenius law:

$$\sigma = \sigma_o \exp(-E_a/kT) \quad (1)$$

where σ_o is a pre-exponential factor and a characteristic of the material, E_a, k and T are, respectively, the apparent activation energy for conduction, Boltzmann's constant, and the absolute temperature. Thus, the activation energy for conduction (E_a) can be calculated from the slope of the straight line given by log $\sigma \times 1/T$.

Figure 3 shows the electric conductivity of the grain as a function of temperature. The behavior observed follows Arrhenius's law, in accordance with the Eq. 1. The activation energy is equal to 1.37 eV. This magnitude of the values, when not linked to ionic conductivity, is usually associated to a hopping-type electronic transport mechanism which, in this case, suggests the existence of defects of the oxygen vacancy-type and/or of antimony cations with valences equal to 3 and 5. Between 400 and 700 °C, the conductivity values were, 10^{-7} $(\Omega.cm)^{-1}$ and 10^{-4} $(\Omega.cm)^{-1}$, respectively. Conductivity was defined by extrapolation method being a value derived equal to 1.0 x 10^{-20} $(\Omega.cm)^{-1}$ at room temperature, which is lower than the average value

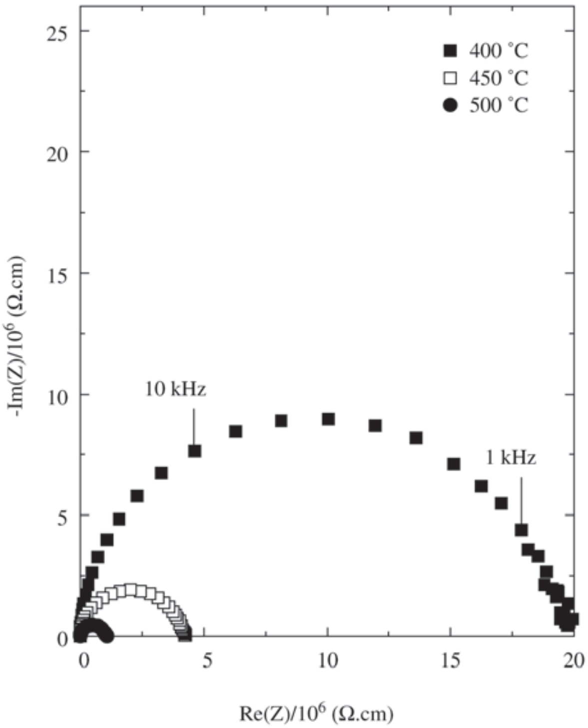

Figure 1. Impedance diagrams of the $Bi_3Zn_2Sb_3O_{14}$ ceramic at 400, 450 and 500 °C.

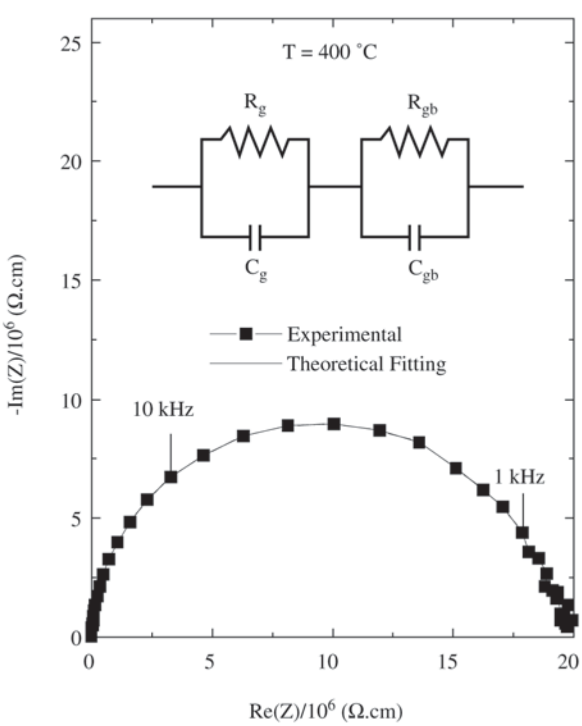

Figure 2. Experimental and theoretical curves of the $Bi_3Zn_2Sb_3O_{14}$ ceramic obtained at 400 °C with the corresponding equivalent circuits.

reported for ZnO grain boundaries in ZnO-based varistors (in the order of 10^{-12} $(\Omega.cm)^{-1}$). Based on this data, the presence of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore-type phase in ZnO-based varistors would exert small direct influence on the electric properties of these varistors.

Figure 4 shows the relaxation frequency of the grain as a function of temperature. The relaxation frequency of the material f_b, independently of the geometrical parameter of the sample, is identified by a simple inspection of the impedance diagram and fulfills the condition:

$$2\pi f_b R_b C_b = 1 \quad (2)$$

where f_b, R_b and C_b are the relaxation frequency, the bulk resistance and bulk capacitance of the material, respectively. According to Fig. 4, the evolution of the relaxation frequency follows Arrhenius's law, with activation energy equal to 1.38 eV. This is in excellent agreement with the value previously calculated through the conductivity parameter of 1.37 eV.

3.2 Dielectric Characterization

The electric response presents a semicircle form, when the complex plane representation is considered. The impedance diagram is not completely defined, when the sample exhibits high resistivity, normally at a low temperature. In this case, a typical fitting process is inadequate, since it leads to a gross error. Thus, an alternative approach to extract the capacitance and permittivity can be used[14]. Considering the electrical response in a high frequency range ($10^5 - 10^7$ Hz), C_b might be extracted by the following equation:

$$-\mathrm{Im}(Z) = 1/jC_b 2\pi f \quad (3)$$

where -Im(Z) is the opposite of the imaginary part of impedance (Z), j is the operator $\sqrt{-1}$ and ω is the angular frequency ($\omega = 2\pi f$).

Based on Eq. 3, the capacitance of the sample (C_b) is derived by the slope of the straight line determined by the variation of -Im(Z) as a function of $1/2\pi f$. Since C_b was determined, the permittivity (ε) can be derived.

Figure 5 shows the permittivity of $Bi_3Zn_2Sb_3O_{14}$ phase as a function of temperature. Two anomalies in the permittivity curve as a function of the measuring temperature were observed. The first anomaly is located at approximately 200 °C, while the second one is close to 320 °C. This latter showing a low intensity, fairly diffuse peak. Peaks in the permittivity curve as a function of temperature typically suggest the presence of a polarization phenomenon[15]. The most common polarization phenomena are those associated to lattice and to carrier polarization. These phenomena are physically compatible with the formation of dipoles and the movement of carriers (electrons). Considering that the pyrochlore phase has a cubic symmetry, it may be assumed

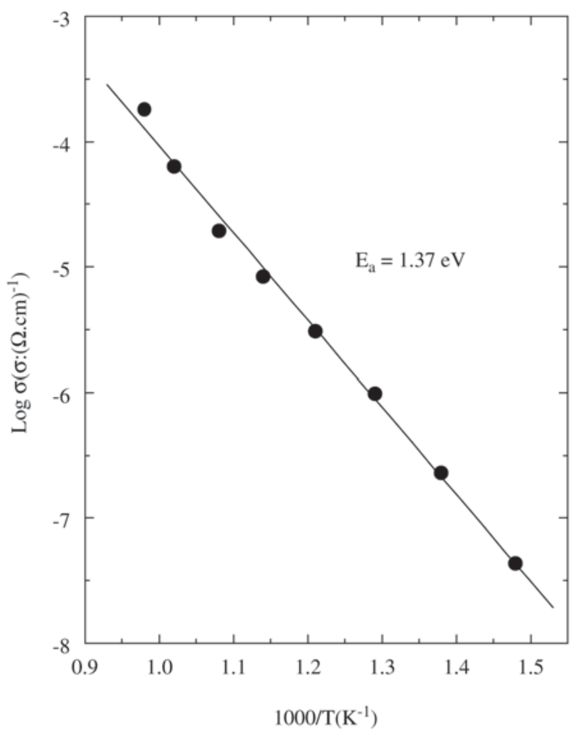

Figure 3. Arrhenius diagram for conductivity of the $Bi_3Zn_2Sb_3O_{14}$ ceramic.

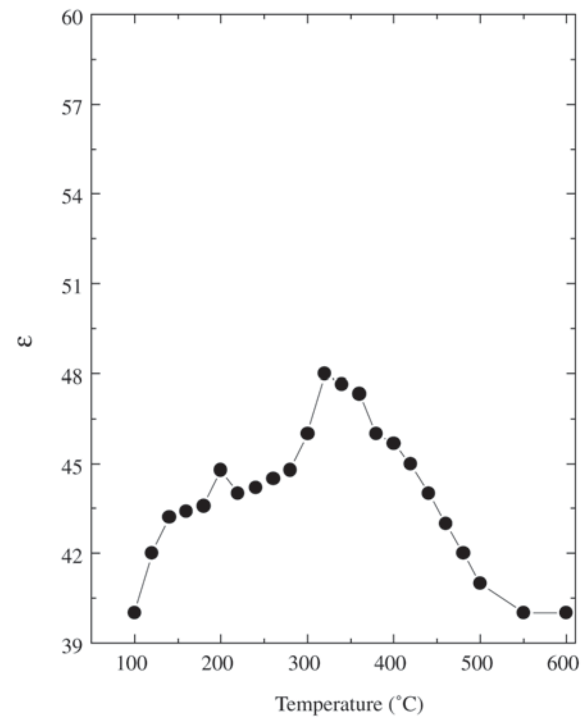

Figure 5. Permittivity of the $Bi_3Zn_2Sb_3O_{14}$ ceramic as a function of temperature.

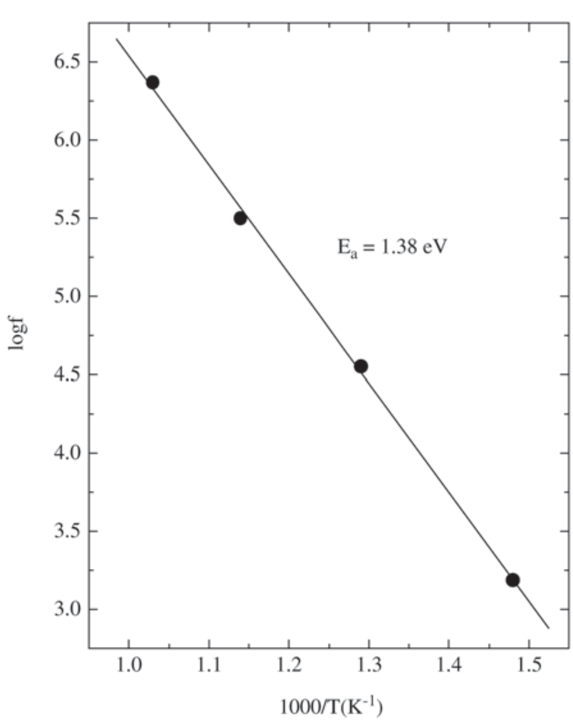

Figure 4. Arrhenius diagram for relaxation frequency of the $Bi_3Zn_2Sb_3O_{14}$ ceramic.

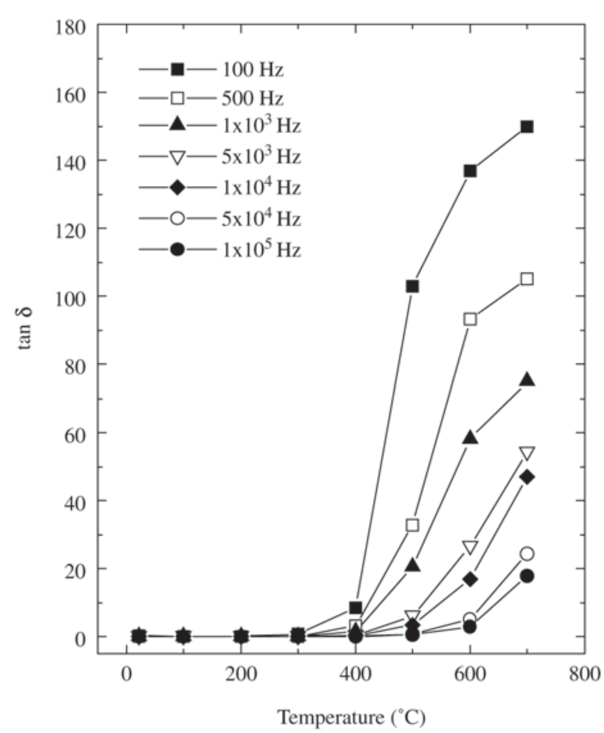

Figure 6. tan(δ) as a function of temperature at several frequencies.

that a polarization process is related to a phenomenon involving the charge carriers (electrons). The complex dielectric permittivity ε* is expressed as:

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' \quad (4)$$

where ε' and ε'' are the real and imaginary parts of the dielectric permittivity. The ε' and ε'' behavior may be interpreted in terms of dielectric loss using the relation $\tan\delta = \varepsilon''/\varepsilon'$, where tanδ is the loss tangent.

Figure 6 shows the parameter tanδ as a function of temperature, at several frequencies. All curves showed a similar behavior at temperatures below 400 °C. However, an intense increases of the loss was observed for every frequency measured, at temperatures above 400 °C. Generally speaking, such losses are strongly dependent on the frequency, with losses at high frequencies much lower than those occurring at low frequencies. This kind of dependence of tanδ with frequency is typically associated with losses by conduction. This finding is compatible with the anomaly observed in Fig. 5, which clearly shows an anomaly in the dielectric behavior in the temperature interval between 270 and 350 °C as well as a tendency for diminished permittivity. Furthermore, considering the permittivity value magnitude and low losses at high frequencies, the phase presents a high potential for applications at high frequencies, in the microwave (GHz) region.

4. Conclusions

Impedance technique proved suitable to characterize electric and dielectric properties of $Bi_3Zn_2Sb_3O_{14}$ ceramic. The conduction process is purely electronic in the ambient atmosphere and temperature studied. A high activation energy in the order of 1.37 eV was measured, in agreement with high resistivity to room temperature in the order of 10^{20} Ω.cm. The dielectric behavior is compatible with that of a linear dielectric.

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