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Electrical Characterization by Impedance Spectroscopy of $Zn_7Sb_2O_{12}$ Ceramic

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Impedance spectroscopy technique was used to investigate the electric properties of $Zn_7Sb_2O_{12}$, an electroceramic with inverse spinel type structure. The electric characterization of the $Zn_7Sb_2O_{12}$ semiconducting ceramic was performed at temperature from 250 to 550 °C, in the frequency range from 5 Hz to 13 MHz. Zinc antimoniate phase was synthesized by the polymeric precursors method. The bulk resistance curve as a function of temperature exhibits a thermistor behavior with negative temperature coefficient. The bulk conductivity follows the Arrhenius law with two linear branches of different slopes positioned at around a region of transition, $450\ °C \geq T \geq 350\ °C$. The activation energy values at low temperature (≤ 350 °C) and high temperature (≥ 450 °C) are equals to 0.78 and 0.61 eV, respectively. The existence of a phase transition limiting these regions is discussed.

Keywords: *varistor, spinel, semiconductor, impedance spectroscopy*

1. Introduction

Oxides with general formula AB_2O_4 exhibiting structure similar to $MgAl_2O_4$ mineral[1] are classified as spinel type oxides. These materials exhibit interesting properties giving potential application in a wide range of ceramic areas such as: catalyst, pigment magnetic and gas sensor. Furthermore, some spinels show interesting applications based on the semiconducting properties. As recent development, we can mention the non linear behavior at tension *vs.* current characteristic that has been engineered on $Zn_7Sb_2O_{12}$ ceramic[2]. This property is typical of ceramic varistor, which is a classic technological application of an effect based on the grain boundary phenomenon. Recently, fundamental electric and dielectric properties differences between the bulk and grain boundary regions have been reported for $Zn_7Sb_2O_{12}$ ceramic. This is further evidence for that grain boundary phenomenon is an intrinsic feature in this spinel, whether ceramic powder is synthesized by chemical route[3]. Another set of electroceramic spinel exhibits thermistors properties with negative temperature coefficient (NTC)[4].

In this work, a new negative temperature coefficient (NTC) thermistor property for high temperature is presented based on $Zn_7Sb_2O_{12}$ ceramic. $Zn_7Sb_2O_{12}$ powder was synthesized by a chemical route based on the modified polymeric precursors method.

2. Experimental Procedure

The starting reagents for spinel preparing were citric acid (99.5% Reagen), ethylene glycol (98.0% Synth), zinc acetate (99.0% Reagen), and antimony oxide (99.0% Riedel). $Zn_7Sb_2O_{12}$ powders were prepared by calcination of the precursor at 900 °C for one hour. Further details of synthesis procedure are described elsewhere[3]. Ceramic with 97% of theoretical density (6.00 g/cm^3) was sintered by constant heating rate process in a dilatometer up to 1250 °C at 10 °C/min, in air atmosphere.

The electrical properties were investigated by impedance spectroscopy. Measurements were performed on 8 mm × 2 mm cylindrical samples. Platinum electrodes were deposited on the parallel faces and mirror like polished of the sample by a platinum paste coating (Demetron 308 A), which was dried at 800 °C for 30 min. The measurements were carried out with an applied potential of 500 mV in the frequency range from 5 Hz to 13 MHz. A Solartron 1260 Impedance Analyzer controlled by a personal computer was used. The samples were placed in a sample holder with a

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two-electrode configuration. The measurements were taken from 250 to 550 °C with a 50 °C step, in atmospheric air. After each measurement, a interval of 30 min was used prior to the stabilization of the temperature and properties. No thermal hysteresis was detected during the measurements taken on the heating and cooling cycle. The data were presented in the complex plane formalism being analyzed throughout Boukamp's software EQUIVCRT. This program works in an environment developed for equivalent electric circuits being based on the simulation of the immitance spectra[5].

3. Results and Discussion

Figure 1 shows impedance diagrams of $Zn_7Sb_2O_{12}$ ceramic, at several temperatures. All diagrams show a slight decentralization of the semicircle. This phenomenon is typically related with the existence of a distribution of relaxation time, when electroceramics are considered. This behavior is in according to a Cole-Cole type response[6]. The diagrams shape indicates that the electric response is composed of, at least, two semicircles. However, in addition to semicircle decentralization, the semicircles exhibit a high overlapping degree.

The analysis of the electrical response can be investigated via the electric modulus M*(ω) formalism.

Modulus is derived from impedance data by equation $M^*(\omega) = j\omega C_o Z^*(\omega)$, where $j = \sqrt{-1}$ and C_o is the vacuum capacitance of the cell. The modulus representation is suitable to detect some phenomena as electrode polarization[7] and conductivity relaxation time[8]. The modulus representation might lead to a higher clear picture of polarization phenomena than impedance one[9]. In this work, the formalisms Z*(ω) and M*(ω), represented in the complex plane, do not exhibit advantage on the identification of the semicircles number. Thus, these formalisms take into account both bulk and grain boundary contributions in a coupled way.

Figure 2 shows M''(ω) and Z''(ω) as a function of logarithmic frequency at 550 °C. The M''(ω) exhibits only a peak at high frequency and it tends to zero at low frequencies. This suggests that electrode polarization phenomenon is negligible or absent. In Z''(ω) against log f plot, an asymmetric peak is identified, which is shifted to a low frequency with relation to M''(ω) peak position. The slight mismatch of the peaks and asymmetry development give further evidence of existence of two polarization phenomena[10]. In the same way, this is in accordance with previous comment, where using Z*(ω) or M*(ω) representation does not lead any advantage on the semicircles recognition. Characteri-

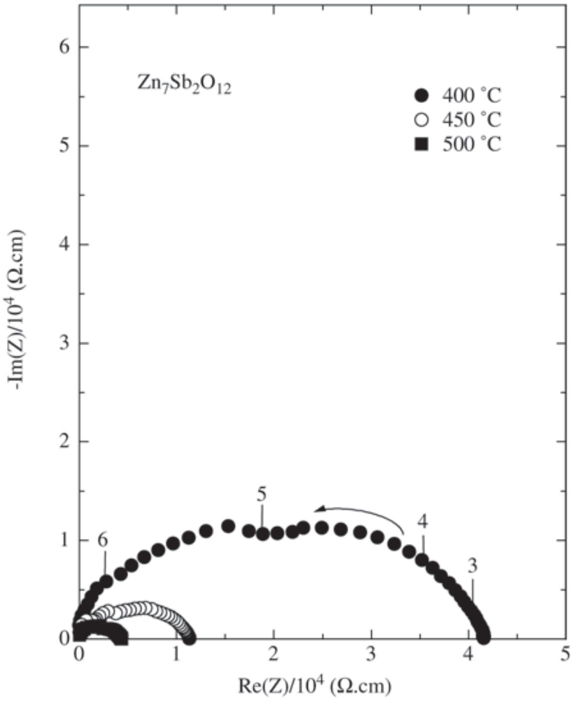

Figure 1. Impedance diagrams of $Zn_7Sb_2O_{12}$ at several temperatures. Numbers 4, 5 and 6 give the $\log_{10}$ (signal frequency) for the corresponding point.

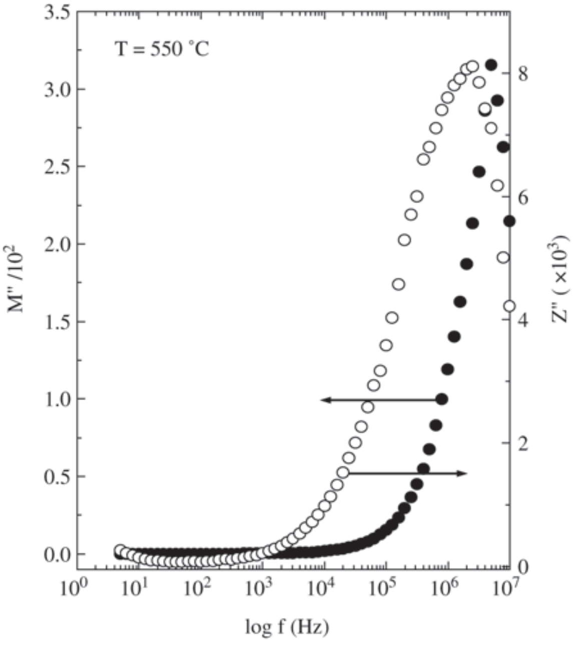

Figure 2. (M'') and (Z'') as a function of frequency logarithmic measured at 550 °C.

zation at another temperatures gives raise similar feature. In fact, these polarization are due the bulk and grain boundary contributions to electric response. A powerful tool to derive both bulk and grain boundary contributions is carried out the theoretical deconvolution of the electrical response. Boukamp's formalism can be used. In this formalism, the non-ideal character of the polarization phenomenon is represented by a parameter Q. This parameter can be interpreted as a non-ideal capacitance (C) being physically determined by the parameters Y_o and exponent n being $n \leq 1$. When the exponent n tends to unity, the parameter Y_o tends to C, an ideal capacitance. Thus, the non-ideal character of the parameter Q is only assigned to a distribution of relaxation times. In the Boukamp's formalism, the impedance of a circuit (RQ) serie is given by the following equation:

$$Z = \frac{R}{1 + RY_o(j\omega)^n} \tag{1}$$

where R_1 is the intercept of the curve at high frequency with real axis. The parameters R, Y_o and n are extracted by theoretical fitting of data. The C can be derived by the following equation:

$$C = R^{\left(\frac{1-n}{n}\right)} Y_O^{\left(\frac{1}{n}\right)} \tag{2}$$

Thus, the relaxation time (τ) is extracted by the classical equation $\tau = RC$. It is interesting to note that despite a simple and concise physical interpretation of n exponent, it allows to extract capacitance and resistance.

The capacitance values derived are experimental meaningful. Recently, the bulk capacitance has been extracted from alternative approach at ceramics and single crystals[11-15]. This method is based on the following equation:

$$-\mathrm{Im}(Z^*) = 1/j\omega C \tag{3}$$

The advantage obtained using Eq. 3 is twofold. The first advantage is that no data fitting are necessary to determine the bulk capacitance. The second one is that C can be derived in trivial manner. Bulk capacitance derived using Eq. 3 gives very similar values that one extracted *via* Eq. 2. In fact, considering typical error, at around ± 3%, both values are the same. These data are not shown here.

Figure 3 shows experimental and fitting curve of impedance data measured at 500 °C. The electrical behavior of $Zn_7Sb_2O_{12}$ is well represented by two parallel RC equivalent circuits in series. The first semicircle, at low frequency, represents the grain boundary contribution. The second one positioned for high frequency domain corresponds to the grain or bulk properties.

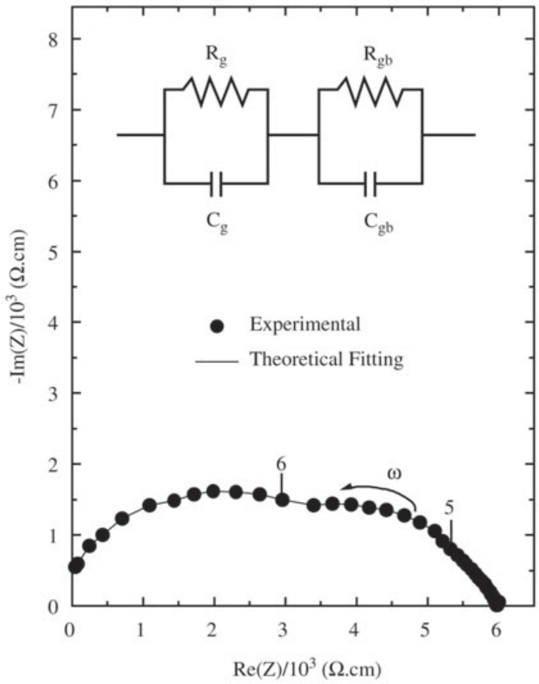

Figure 3. Experimental and theoretical curves of $Zn_7Sb_2O_{12}$ with corresponding equivalent circuits obtained at 500 °C. Numbers 5 and 6 give the $\log_{10}$ (signal frequency) for the corresponding point.

Figure 4 shows the bulk resistance and relaxation time as a function of temperature. The resistance decreases with increasing of temperature. τ exhibits long relaxation time, in the temperature range studied. These values suggest a conduction process of type hopping, similar to another inverse spinels[4]. The hopping mechanism requires that the cations with distinct valences occupy octahedral holes[4]. $Zn_7Sb_2O_{12}$ has antimonium cations with oxidation state equal to 5 occupying octahedral sites. However, the presence of the Sb^{+3} has been reported[2]. This is not sufficient to attain a conduction mechanism based on the hopping approach, since the hopping of the carrier should occur between cations positioned at crystallographic equivalent lattice-sites with valence differing of one unit only. The existence of the Sb^{+4} has been hypothesized[3]. According to Fig. 4, there is a region of anomaly in the resistance and relaxation time curves. As a whole, this electrical behavior is characteristic of negative temperature coefficient thermistor. This property has been observed at another thermistors ceramics being further evidence that the conduction mechanism actuating on the bulk is of the hopping type. Furthermore, in the region between 350 to 450 °C, the simultaneously anomalies observed in both curves suggest a phase transition phenomenon of the order-disorder type, which requires a broad

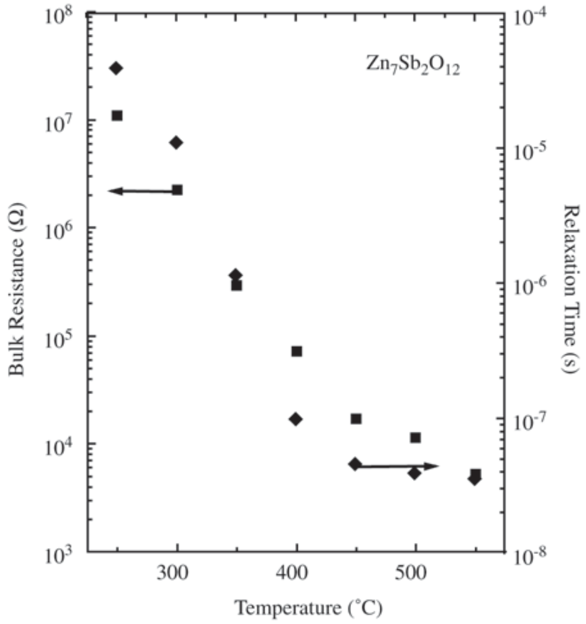

Figure 4. Bulk resistance and relaxation time as a function of temperature.

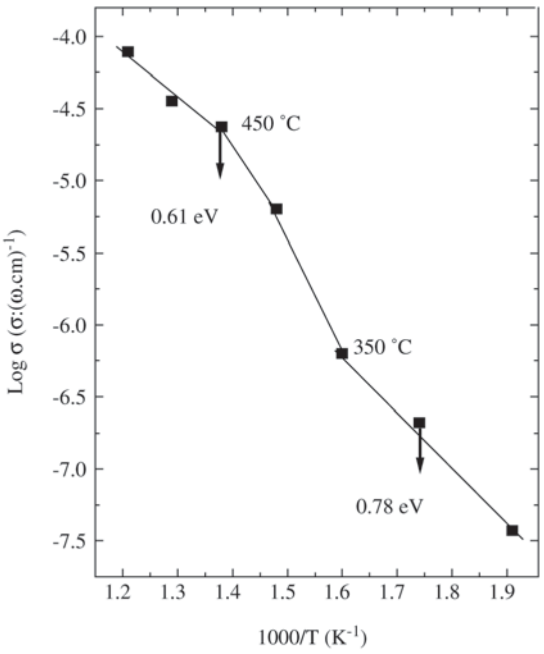

Figure 5. Arrhenius plot of bulk conductivity of the $Zn_7Sb_2O_{12}$.

interval of temperature. Thus, based on the wide temperature range we can speculate that another physico-chemical process is responsible for the phenomenon observed, such as an oxi-reduction of antimony cations. The phase transition is a favorable phenomenon due the open character of the structure and great number of vacant sites.

Figure 5 shows the Arrhenius' diagram of the bulk conductivity as a function of reciprocal temperature. The behavior observed is given by the following equation:

$$\sigma = \sigma_o \exp\left(-E_a / kT\right) \qquad (4)$$

where $\sigma_0$represents a pre-exponential factor and E_a, k and T are, respectively, the apparent activation energy for conduction, Boltzmann's constant and the absolute temperature.

The Arrhenius diagram (Fig. 5) shows two linear regions with different slopes positioned at T ≥ 450 °C and T ≤ 350 °C. The region between 350 °C ≤ T ≤ 450 °C is further evidence of a phase transition, as mentioned above. $Zn_7Sb_2O_{12}$ ceramic presents distinct values for E_a at low temperature (≤ 350 °C) and high temperature (≥ 450 °C) regions being equal to 0.78 and 0.61 eV, respectively. In the transition region, the E_a exhibits an unrealistic value of 1.40 eV.

The total conductivity has been studied as a function of temperature in the frequency range from 10^2 to 10^6 Hz. Figure 6 shows the frequency dependence of total conductivity at different temperatures. The frequency dependence of ac conductivity, σ_{ac}, follows a power relation $\sigma_{ac} \propto \omega^s$, at high frequency. At low frequency domain, a plateau can be observed. As matter of fact, this behavior is further evidence of d.c. conductivity, which conductivity contribution to total-conductivity is independent of the frequency. Thus, the total conductivity could be given by the following equation:

$$\sigma_{tot} = \sigma_{dc} + A\omega^s \qquad (5)$$

where σ_{dc} is d.c. conductivity due excitation of electron from localized states to the conduction bands and Aw^s is the a.c. conductivity typically assigned to the hopping conduction being "A" a frequency independent constant and "s" a power with values $0.0 < s < 1.0$. As a whole, the conductivity behavior is in accordance with conduction mechanism based on the hopping process. Furthermore, there is a large increase of conductivity level at region between 350 and 450 °C being further evidence of the phase transition, as discussed previously. Accordingly, the dielectric permittivity undergoes gradual increase of values with increasing of the temperature of measurement for temperature phase-transition range, at low frequency range (< 10^2 Hz). Figure 7 shows dielectric permittivity as a function of frequency at several temperatures. At temperature above 450 °C, the permittivity exhibits a significant increment of values.

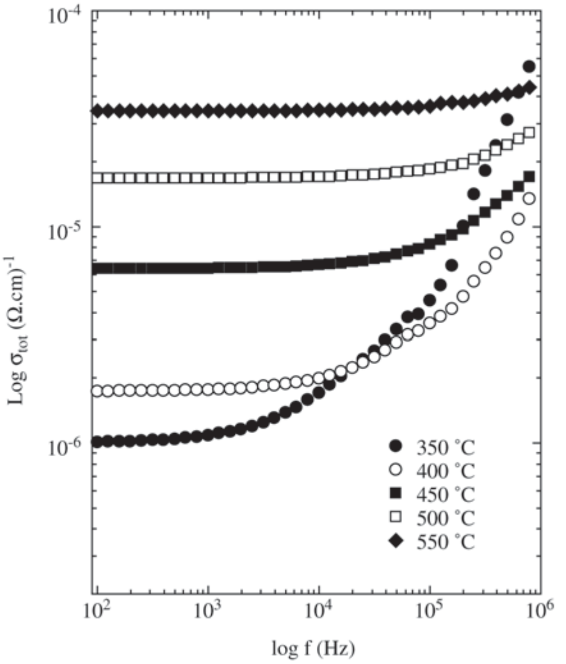

Figure 6. Total conductivity as a function of frequency at different temperatures.

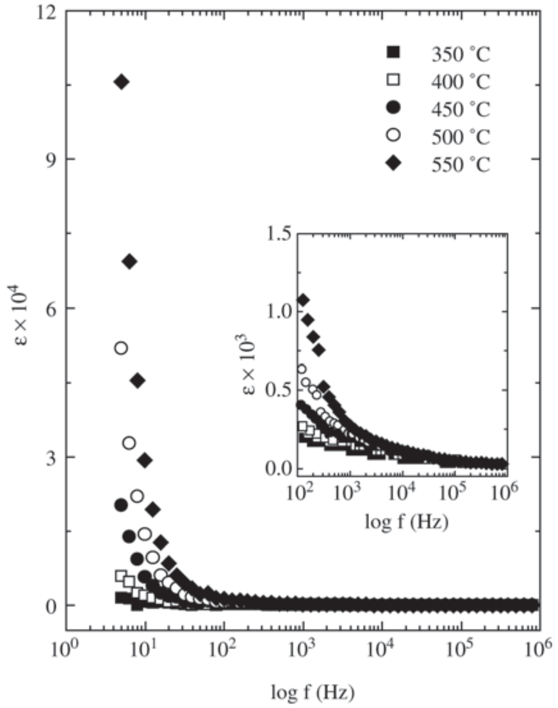

Figure 7. Dielectric permittivity as a function of frequency at several temperatures.

4. Conclusion

$Zn_7Sb_2O_{12}$ ceramic exhibits electrical behavior with thermistor's feature being the temperature coefficient of characteristic negative. The electric and dielectric properties of the bulk are correlated to actuating of a conduction mechanism of the hopping type expected to NTC material. According to conductivity and dielectric permittivity properties, in the temperature range from to 450 °C, the spinel undergoes a phase transition based on the order-disorder process, which is an eventual phenomenon at inverse spinels.

Acknowledgments

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