Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 897–900
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Temperature-dependent dielectric, impedance and tunability studies on bismuth zinc niobate ($(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_7$) ceramics

K. Sudheendran, K.C. James Raju *
School of Physics, University of Hyderabad, Hyderabad 500046, India

Available online 29 September 2007

Abstract

Bi_2O_3–ZnO–Nb_2O_5-based pyrochlore ceramics are receiving increasing attention due to their excellent dielectric properties in the microwave frequency range. Site disorder at the pyrochlore A-site is well known for lone pair active cations like Bi^{3+} and is attributed as the reason for this material's high dielectric constant and tunability. Bismuth zinc niobate ($(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_7$) [BZN] ceramics are prepared by the conventional solid-state reactions. The relative permittivity (ε_r) and the dielectric loss tangent (tan δ) of the BZN ceramics sintered at 1000 °C are found to be around 130 and 0.0004, respectively at a frequency of 1 MHz measured at room temperature. The impedance spectroscopy measurements are conducted at different temperatures to separate grain and grain boundary contributions to the dielectric constant. The tunability of these ceramics is studied under a constant dc bias voltage.

Keywords: D. Niobates; Dielectric constant; Pyrochlore; Tunability

1. Introduction

Microwave dielectric ceramics play an important role in the miniaturization of microwave components such as microwave oscillators and filters. High dielectric permittivity and a very low loss are the essential requirements of microwave materials in many applications. Recently researchers have been showing much interest in bismuth zinc niobate (BZN) as a possible microwave dielectric and for multilayer ceramic capacitor applications [1]. Apart from the high dielectric constant and low loss, these systems possess a field-dependent permittivity, which makes them potential materials for the present day frequency and phase agile devices. There have been many efforts to exploit the voltage-dependent dielectric constant of tunable dielectric materials such as $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$. So far these ferroelectric thin films have been successfully adapted to tunable phase shifters and tunable filters, on account of the non-linear behavior of their dielectric properties with respect to an applied dc voltage [2]. However, it is also important that dielectric materials for these applications posses a low dielectric loss (tan δ) or high quality factor Q, as well as a temperature-independent dielectric behavior. The ferroelectric materials have intrinsically high losses in the microwave regions below their Curie temperature and hence they are temperature-dependent materials. Consequently the development of new tunable materials with low loss rather than ferroelectrics is becoming important. The bismuth zinc niobate-based pyrochlore system has proved to have significant voltage tunability, with a medium dielectric constant and low loss. Reduction of the dielectric loss is one of the important tasks for improving the quality of the material. It is highly important to understand the dielectric loss mechanisms in microwave ceramics in detail. Temperature-dependent impedance and dielectric studies are important to understand the nature and origin of dielectric losses. In this work an investigation has been carried out on the dielectric and impedance characteristics of this ceramic system.

Impedance spectroscopy (IS) has been recognized as a powerful technique to distinguish the grain and grain boundary contribution of many oxide ceramic materials [3]. Data from the IS can be analyzed using different complex formalisms, impedance Z^*, admittance Y^*, permittivity ε^* and electric modulus M^*. Each consists of real and imaginary components. For example $Z^* = Z' - jZ''$, where Z' and Z'' are the real and

* Corresponding author. Tel.: +91 40 23134305; fax: +91 40 23010227.
E-mail address: kcjrsp@uohyd.ernet.in (K.C.J. Raju).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.09.055

imaginary components of the impedance, respectively. The four complex quantities are interrelated, i.e., $M^* = 1/\varepsilon^* = j\omega C_0 Z^* = j\omega C_0(1/Y^*)$, where ω is the angular frequency and C_0 is the empty cell capacitance. Data can be presented in complex plane plot. All the formalisms are valuable because of their different kinds of dependence on frequency. In the present study is made of the complex Z'–Z'' plots to identify the grain and grain boundary characteristics.

2. Experimental procedure

Ceramics samples were prepared by solid-state reaction. Raw materials used are the individual high purity oxide powders Bi_2O_3, ZnO and Nb_2O_5 (99.9%) of Sigma–Aldrich, USA. These oxide powders were weighed according to the composition $Bi_{1.5}ZnNb_{1.5}O_7$. The weighed powders were hand mixed in an agate mortar. After the mixing they were calcined at 950 °C. The formation of the compound is confirmed with X-ray diffraction analysis using a Philips powder X-ray diffractometer. For the electrical property measurements, the disks were pressed uniaxially at 6 MPa and were sintered at 1100 °C. The disk density estimated was approximately 93%. The microstructural analysis of the sintered sample surface was performed with scanning electron microscopy (SEM). Silver paint was applied on the faces of the pellets and they were annealed at 300 °C for 15 min. The impedance and dielectric measurements were carried out over range of 100 Hz–4 MHz using agilent 4294A impedance analyzer interfaced with PC in the temperature range of 300–430 K.

3. Results and discussion

3.1. Structural

Fig. 1 shows the XRD patterns of the ceramic $((Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_7)$ prepared at two different calcination temperatures. The X-ray diffractogram clearly shows the formation of the cubic pyrochlore structure with all the major peaks corresponding to this crystal structure. Fig. 2 shows the SEM micrograph of the sample.

3.2. Complex impedance study

Fig. 3 shows the complex plots between the Z' and Z'' at different temperatures in the 60 Hz–4.5 MHz frequency range. On equivalent circuit analysis using the ‘‘Z-view’’ software, it is seen that all these plots can be resolved into two overlapping semicircles. These can be attributed to the contribution from grain as well as grain boundary. The poor separation of these overlapped semicircles can be attributed to the porosity of the sample as seen in Fig. 2. It is well known in electroceramics that if the pore size is greater than 1 μm then it will lead to the overlapping of the semicircles in the complex impedance plot [4]. Fig. 4 shows the variation of the Z'' as a function of frequency at two different temperatures. The figures do not show any peaks at this frequency of measurement; this implies that the relaxation occurs at very low frequencies for these samples. It is observed that the curves are shifting to the higher frequency side with increase of temperatures (see the inset of Fig. 4), which implies that the relaxation frequency increases with the increase of temperature. It is also clearly seen that irrespective of the temperatures at which the measurements are made all the curves merged at the higher frequency side. This is due to the fact that at higher frequencies the grain properties are predominant. This can be verified from the observed dielectric spectra of the material.

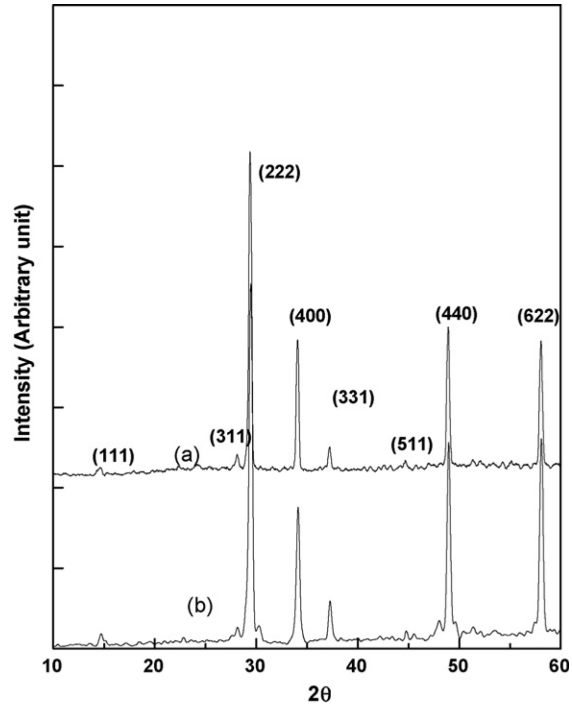

Fig. 1. XRD patterns of $((Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_7)$ calcined at (a) 850 °C and (b) 950 °C.

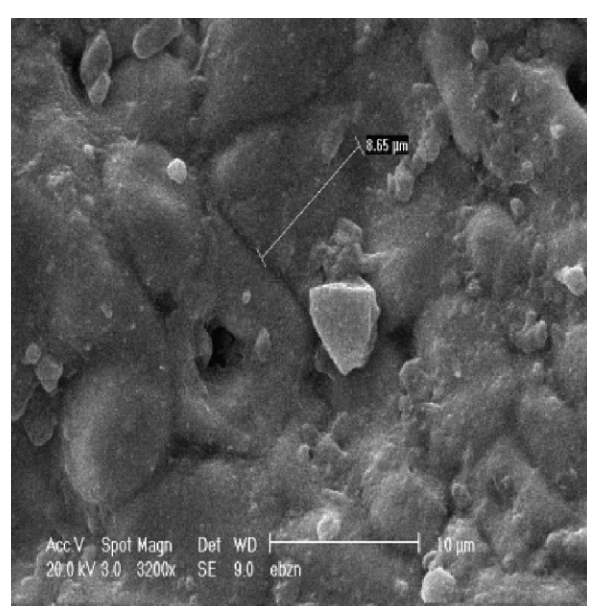

Fig. 2. Scanning electron micrograph of the BZN ceramics.

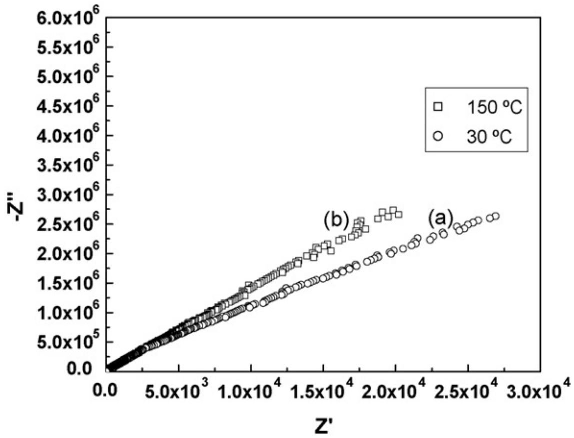

Fig. 3. Z'–Z'' plot of BZN ceramic plot at (a) room temperature and (b) 150 °C.

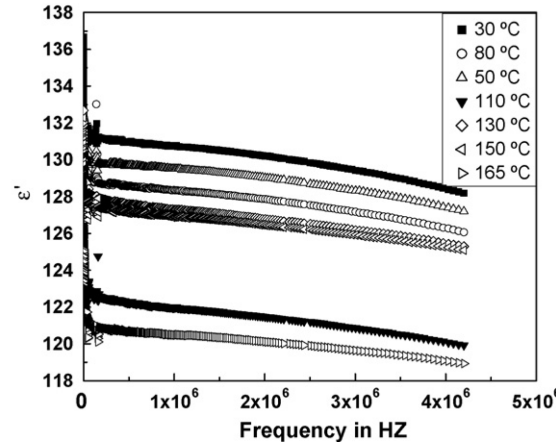

Fig. 5. Variation of the dielectric constant of the BZN samples at different temperatures.

3.3. Complex permittivity study

The dielectric constant and loss of the BZN samples measured at different temperatures are given in Figs. 5 and 6. It is seen that the dielectric constant is steeply decreasing in the lower frequency region and has an almost constant value at the higher frequency region. The dielectric loss tangent is also found to be decreasing and remains almost constant at higher frequency region. This shows that there is not much frequency dispersion in the dielectric properties for these materials, which is an important property suitable for many applications. Also it can be concluded that the resistance and capacitance of the material are not constant but vary in the lower frequency range. At frequencies below 1 kHz the dielectric constant is found to be high and this is attributed to the contribution from the grain boundaries. But for the frequencies above this the dielectric constant depends on the combined effect of both grain and grain boundaries and can be estimated as [5]:

$$\varepsilon = \frac{\varepsilon_b \varepsilon_{gb}}{\varepsilon_b + \varepsilon_{gb}} \tag{1}$$

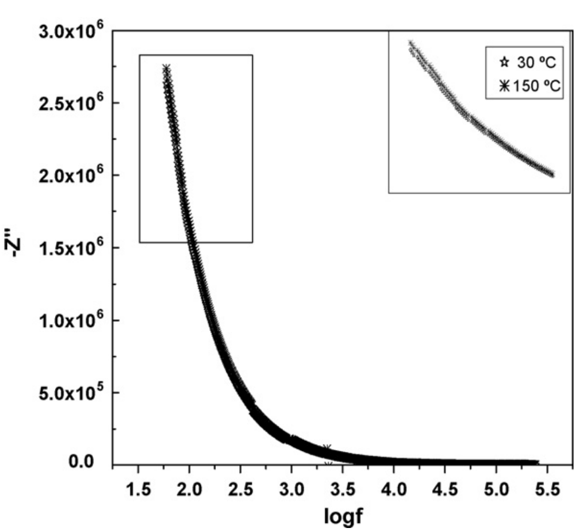

Fig. 4. The frequency dependence of the imaginary part of impedance of BZN ceramics at different temperatures.

where ε_b is the bulk permittivity and ε_{gb} is the permittivity from the grain boundaries. Since $\varepsilon_{gb} > \varepsilon_b$ in the higher frequency region we can approximate $\varepsilon \approx \varepsilon_b$. From the graph it is seen that at higher frequencies the ε versus f plots are almost linear and the value of ε at room temperature is around 130 at a measurement frequency of 1 MHz, this value can be taken as the ε_b values for these ceramics. So it is concluded that at higher frequencies only the grains contribute to the dielectric constant of these materials and the grain boundary effects can be neglected.

3.4. ac conductivity study

Fig. 7 shows the variation of the dielectric constant (ε') and ac conductivity (σ) with frequency for the BZN samples measured at room temperature. It is observed that the room temperature conductivity of this material is very low. It is also noticed that initially the conductivity increases slightly with the frequency and it starts decreasing gradually at the higher frequency side. This may be due to the fact that in the lower frequency range some charge transport mechanism is active through the barriers present in the materials such as grain boundaries. But in the higher frequency range this mechanism

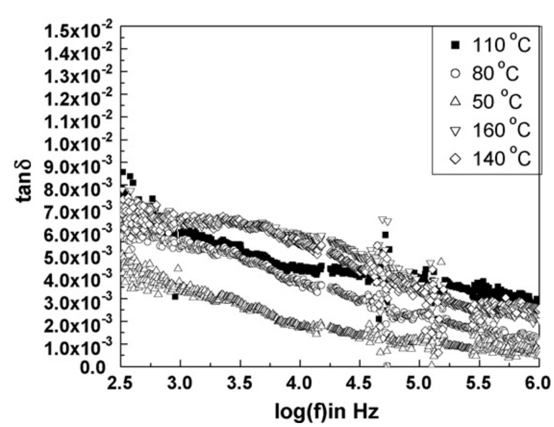

Fig. 6. Variation of the dielectric loss tangent of the BZN samples at different temperatures.

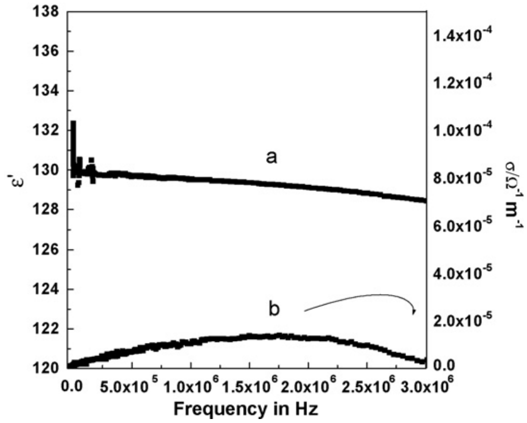

Fig. 7. Measured electrical properties of BZN ceramics at room temperature (a) ε vs. *f* and (b) σ vs. *f*.

fails and the conductivity decreases. The relatively high loss observed in this material at the lower frequency region is attributed to the grain boundary-related charge transport [6]. So at the higher frequency range only the grain contributes both to the loss and dielectric constant.

The tunability of the BZN prepared is checked by applying a voltage of 100 V across the sample whose thickness is around 1 mm. It is observed that the dielectric constant of this sample decreases its RT value of 130–121 exhibiting a tunability of around 6%. Further investigation at high voltages and high temperatures are being carried out to understand the exact mechanism of tunability in these materials.

4. Conclusions

Bismuth zinc niobate (BZN) having the composition ($(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_7$) is prepared through the solid-state reaction procedure. The impedance and dielectric measurements are carried out as a function of frequency and temperature. The complex impedance plot shows the grain- and grain boundary-related mechanism present in the material. At the lower frequency side grain boundaries contribute more than the grains to the observed properties such as dielectric constant, impedance and dielectric loss. The dielectric constant of these ceramics is found to change with the applied voltage, which shows that the material can be used for tunable application. From the impedance study it is clear that at higher frequencies region only grains contribute to the control the dielectric properties. A further systematic investigation is required to understand the effects of grain size on the dielectric and impedance characteristics of these materials.

Acknowledgements

The authors acknowledge UGC (SAP, UPE and Plan), DST and ISRO for financial support for this work. K.S. acknowledges DLRL and UGC for a fellowship.

References

[1] D.P. Can, C.A. Randall, T.R. Shrout, Investigation of the dielectric properties of bismuth pyrochlore, Solid State Commun. 7 (1996) 529–534.
[2] E.G. Erker, A.S. Nagra, Y. Liu, P. Periaswamy, T.R. Taylor, J.S. Speck, R.A. York, Monolithic Ka-band phase shifter using voltage tunable $BaSrTiO_3$ parallel plate capacitors, IEEE Microw. Guidew. Lett. 10 (2000) 10–12.
[3] J.T.S. Irvine, D.C. Sinclair, A.R. West, Electroceramics: characterization by impedance spectroscopy, Adv. Mater. 2 (3) (1990) 132–138.
[4] M.C. Steil, F. Thevenot, M. Kleitz, Densification of yttriya stabilized zirconia, impedance spectroscopy analysis, J. Electrochem. Soc. 144 (3) (1997) 390–395.
[5] A.R. West, D.C. Sinclair, N. Hirose, Charecterization of electrical materials, especially ferroelectrics by impedance spectroscopy, J. Electroceram. 1 (1) (1997) 65–71.
[6] A.S. Nowick, A.V. Vaysleyb, I. and, Kuskovsky, Universal dielectric response of variously doped CeO_2 ionically conducting ceramics, Phys. Rev. B 58 (13) (1998) 8398–8406.