ANTIFERROMAGNETIC TO PARAMAGNETIC PHASE TRANSITIONS IN BISMUTH FERRITE ($BiFeO_3$) CERAMICS BY SOLID STATE REACTION

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This paper describes the synthesis of multiferroic $BiFeO_3$ ceramics was prepared by solid state reaction and high energy ball milling method. The structural studies was carried out by using an X-ray diffraction pattern and demonstrated that the $BiFeO_3$ ceramic crystallizes in a rhombhohedral perovskite phase. The ferroelectric hystersis loop measured at room temperature demonstrates a lossy loop with unsaturated behavior and symbolize a partial reversal of polarization. A dielectric constant with temperature measurement for $BiFeO_3$ ceramic represents an anomaly around 350°C for all frequencies and intimately associated with antiferromagnetic to paramagnetic phase transition (TN) of $BiFeO_3$.

INTRODUCTION

Multiferroic materials shows coexistence of electric and magnetic order parameters together results in concurrent production of ferroelectricity and magnetism in a single phase [1,2]. On account of coupling between electric and magnetic parameter generates a unique phenomena known as magnetoelectric effect in which polarization can be tuned under the application of external magnetic field and magnetization can be tuned by external electric field provides an additional functionalities for device design [3]. These materials have earned a large amount of attention because of their potential applications in various fields such as information storage, spintronic sensors, memory, data storage media, digital memories, spin filters, electrically switchable spin valves, microelectronics, wireless sensors, high frequency filters and multiple state memory elements [4-9]. A multifunctional bismuth ferrite ($BiFeO_3$) has ferroelectric Curie temperature $T_c \sim 1103$ K and antiferromagnetic Neel temperature $T_N \sim 643$K [10-12].

There are many attempts have been made to improve the multiferroic properties of doped $BiFeO_3$ ceramics prepared by number of synthesis methods such as Gautam et.al. reported the multiferroic properties of single phase $Bi_{1-x}Ba_xFeO_3$ compounds depicts room temperature enhanced ferroelectric and magnetic properties formulated by solid state reaction [13]. Fruth et al. studied the dielectric properties of $BiFeO_3$ ceramics by solution combustion method under heating and cooling cycles [14].

EXPERIMENTAL

Synthesis of $BiFeO_3$

The Bi_2O_3 (Hi-Media) and Fe_2O_3 (Sigma Aldrich) were used as a starting precursors. The multiferroic $BiFeO_3$ ceramic was prepared using a solid state reaction in accordance with stiochiometric formula and high energy ball milling. Initially, Bi_2O_3 and Fe_2O_3 were dissolved in acetone in a stiochiometric proportion and ball milled for 24 hrs. The dried mixture was calcined at 650°C for 1 hr. The fine calcined powder was mixed with polyvinyl alcohol. Then $BiFeO_3$ was again grounded and pelletized with an organic binder and sintered at 750°C for 30 min. This pellet was then utilized for further characterization and measurements.

Characterizations

The structural study of pellet was carried out using CuKα radiation in the 2θ range of 20-60°. The two opposite surfaces of the pellet was polished with silver paste and fired at 300°C for 20 min in a furnace before performing ferroelectric and dielectric measurements. The room temperature ferroelectric measurement was performed on using Precision Premier II, Radiant technologies, USA. A dielectric constant and loss as a function of temperature were addressed using Agilent HP 4192A, Impedance analyzer.

RESULTS AND DISCUSSION

Structural studies

Figure 1 presents the room temperature XRD spectra of $BiFeO_3$. The XRD results depicted that $BiFeO_3$ ceramic has rhombhohedral perovskite structure having space group R3c. The obtained results shows good correspondence with reported data among an additional secondary phase subsequent to $Bi_2Fe_4O_9/Bi_2O_3$ has been seemed around 30° in 2θ range marked by stars. The average crystallite size was found to about 60 nm.

Ferroelectric studies

Figure 2 shows the P-E hystersis loop of $BiFeO_3$ ceramic at room temperature. The hystersis loop is lossy and exhibits an unsaturated behavior. However, the P-E loop could not achieve saturation polarization manifest a conducting behavior of ceramics.

Dielectric measurements

Figure 3 displays the variation of dielectric constant with temperature of $BiFeO_3$ sample at different frequencies of 1 kHz, 3 kHz and 5 kHz. As shown in the figure the dielectric constant demonstrates continues increase with temperature for $BiFeO_3$ ceramic. A comprehensible dielectric anomaly has been observed around 350°C for all frequencies. This anomaly indicates a phase transformation from antiferromagnetic to paramagnetic phase (T_N) of $BiFeO_3$ and possible coupling between

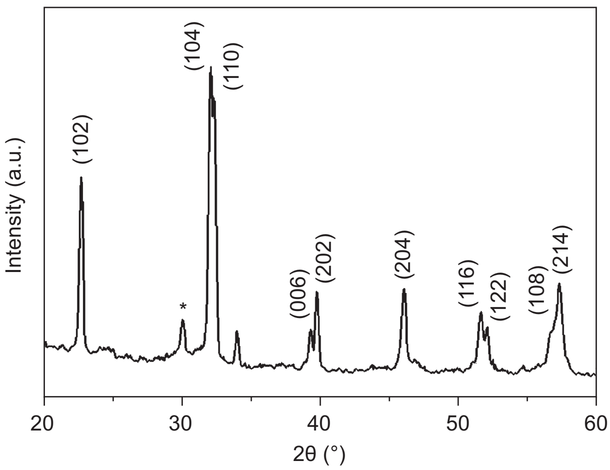

Figure 1. X-ray diffraction (XRD) pattern of $BiFeO_3$ ceramic at room temperature.

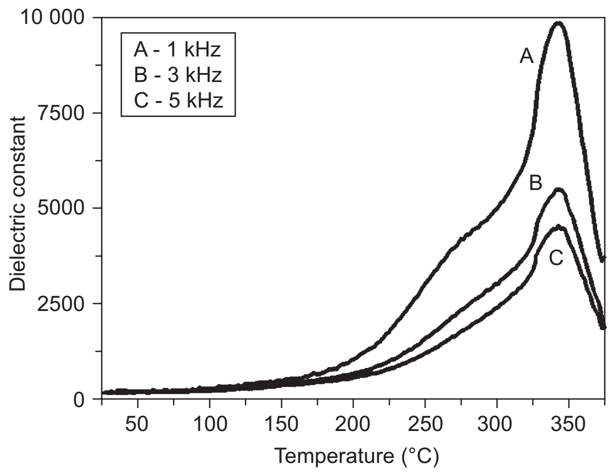

Figure 3. Variation of dielectric constant with temperature for $BiFeO_3$ ceramic.

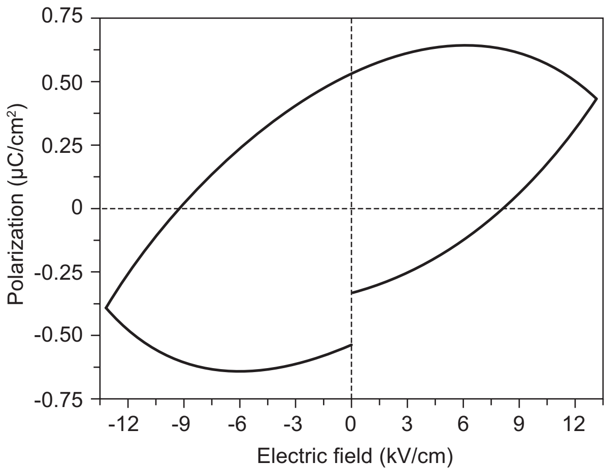

Figure 2. P–E hysteresis loop of $BiFeO_3$ at room temperature.

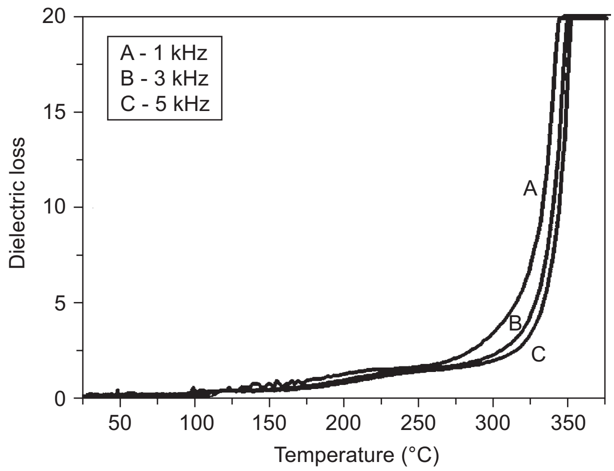

Figure 4. tanδ-T graph of $BiFeO_3$ ceramic.

electric and magnetic dipoles of $BiFeO_3$ [15]. The measured values of dielectric constant were found to be 176, 172 and 163 for 1kHz, 3kHz and 5kHz respectively at room temperature.

A dielectric constant with temperature plot of $BiFeO_3$ ceramic as shown in Figure 4. The frequency variation is ranging from 1kHz-5kHz and displays that the dielectric constant increases with increasing temperature. The measured values of dielectric loss were found to be 0.11, 0.04 and 0.01 for 1kHz, 3kHz and 5kHz respectively at room temperature.

CONCLUSIONS

The $BiFeO_3$ ceramic depicts a rhombhohedral perovskite structure. Room temperature ferroelectric measurement presents a lossy and unsaturated loop without any saturation. The dielectric constant with temperature exhibits an anomaly around 350°C corresponds to antiferromagnetic to paramagnetic phase transition in $BiFeO_3$. and loss as a function of temperature shows the dielectric constant and loss increases with increasing temperature. The room temperature dielectric measurement with frequency reveals the dielectric constant and loss decreases with increasing frequency for $BiFeO_3$ ceramics.

References

1. Yang C.H., Koo T.Y., Jeong Y.H.: Solid State Comm. *13*, 299 (2005).
2. Cheong S.W., Mostovoy M.: Nat. Mater. *6*, 13 (2007).
3. Jiang Q.H., Nan C.W., Shen Z.J.: J. Am. Ceram. Soc. *89*, 2123 (2006).
4. Kumar M., Yadav K.L.: Appl. Phys. Lett. *91*, 242901 (2007).
5. Lee Y.H., Wu J.M., Lai C.H.:, Appl. Phys. Lett. *88*, 042903 (2006).
6. Qi X., Tsai P.C., Chen Y.C., Ko C.H., Andrew Huang J.C., Chen I.G.: J. Appl. Phys. *41*, 232001 (2008).
7. Shannigrahi S.R., Huang A., Tripathy D., Adeyeye J.: J. Magn. Magn. Mater. *320*, 2215 (2008).
8. Naik V.B., Mahendiran R.: Solid State Comm. *149*, 754 (2009).
9. Tzvetkov P., Petrova N., Kovacheva D.: J. Alloy. Comp. *485*, 862 (2009).
10. Wei J., Xue D., Wu C., Lai Z.: J. Alloy. Comp. *453*, 20 (2008).
11. Kothari D., Reddy V.R., Sathe V.G., Gupta A., Banerjee A., Awasthi, A.M.: J. Magn. Magn. Mater. *320*, 548 (2008).
12. Reddy V.R., Kothari D., Gupta A., Gupta S.M.: Appl. Phys. Lett. *94*, 082505 (2009).
13. Gautam A., Rangra V.S.: Cryst. Res. Tech. *45*, 953 (2010).
14. Fruth V., Mitoseriu L., Berger D., Ianculescu A., Matei C., Preda S., Zaharescu M.: Prog. Sol. Stat. Chem. *35*, 193 (2007).
15. Jia D.C., Xu J.H., Ke H., Wang W., Zhou Y.:, J. Eur. Ceram. Soc. *29*, 3099 (2009).