ELSEVIER

Ceramics International 30 (2004) 1431–1433

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Study of piezoelectric, magnetic and magnetoelectric measurements on $SrBi_3Nb_2FeO_{12}$ ceramic

A. Srinivas [a,*], F. Boey [a], T. Sritharan [a], Dong Wan Kim [b], Kug Sun Hong [b], S.V. Suryanarayana [c]

[a] *School of Materials Engineering, Nanyang Technological University, Singapore 639798, Singapore*
[b] *School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 151-744, South Korea*
[c] *Department of Physics, Materials Research Laboratory, Osmania University, Hyderabad 500007, India*

Received 28 November 2003; received in revised form 9 December 2003; accepted 22 December 2003

Available online 15 July 2004

**Abstract**

$SrBi_3Nb_2FeO_{12}$ (SBNF) is a three-layered perovksite in the system $SrBi_2Nb_2O_9$ (SBN) + (*n*). $BiFeO_3$ (BF) system with $n = 1$. In order to achieve the magnetic and magnetoelectric (ME) nature, the material should consist of ferroelectric and magnetic ordering. In the present system, the addition of $BiFeO_3$ to SBN makes the material both ferroelectric and magnetic, to realise magnetoelectric output. The piezoelectric nature of the material is investigated by using the resonance and anti resonance measurement. The magnetisation measurements carried out at room temperature showed a slim hysteresis loop indicating the material consists of antiferromagnetic ordering. The dynamic magnetoelectric measurements performed at room temperature and at 77 K, showed that magnetoelectric output is high at 77 K.


*Keywords:* A. Powders: solid state reaction; C. Magnetic properties; D. Perovskites

## 1. Introduction

The solid solution of $BiFeO_3$ (BF)–$SrBi_2Nb_2O_9$ (SBN) was prepared at a concentration of 1:1 ratio, by solid state sintering method. This compound can be written as $SrBi_3Nb_2FeO_{12}$, which belongs to Aurivillius family of compounds with a general formula of $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ where A: $Bi^{3+}$, $Sr^{2+}$ and B: $Fe^{3+}$, $Ta^{5+}$, $Nb^{5+}$, $Ti^{4+}$ and "*n*" refers to the number of perovskite-like layers between $Bi_2O_2$ layers [1].

From the earlier reports, the two-layered compound SBN has tetragonal symmetry with a ferroelectric transition around 420 °C [2]. On the other hand BF is ferroelectric and also antiferromagnetic with rhombohedral symmetry at room temperature. It has ferroelectric $T_c$ at 850 °C and antiferromagnetic Neel temperature at 370 °C with cycloidal spiral magnetic ordering [3]. Combining SBN with BF in 1:1 ratio, the new compound obtained is $SrBi_3Nb_2FeO_{12}$, which is a three-layered compound.

The magnetoelectric (ME) effect, a coupled magnetic-ferroelectric effect characterized by the appearance of an electric polarization (ME output) on applying a magnetic field or by appearance of a magnetization on applying an electric field.

However, among the single-phase ME materials, (which are brittle), particularly strong ME effects, as initially envisioned, have not so far been found, which is the reason that they have not yet found applications in technology. To be technologically viable, ME materials must exhibit high ME coefficients. Important applications include magnetic-electric sensors in radioelectronics, optoelectronics and microwave electronics and transducers in instrumentation.

Magnetoelectric output can be realized in two types of materials, i.e. in single-phase materials and in composites. In single-phase materials, the magnetoelectric output arises due to the interaction between the ferroelectric and magnetic sub-lattices, while in composites, the ME output is a product property of piezomagnetic and piezoelectric phases.

The materials showing ferroelectric and magnetic ordering are termed as ferroelectromagnets [4]. In the present system, SBN is a pure ferroelectric material and BF is

* Corresponding author.
*E-mail address:* sadiraj@ntu.edu.sg (A. Srinivas).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.074

ferroelectric and magnetic in nature. By combining these two materials, one can obtain a ferroelectromagnetic material. The present paper aims at the study the piezoelectric nature, magnetic and magnetoelectric output at low temperature and at room temperature.

## 2. Experimental procedure

$SrBi_3Nb_2FeO_{12}$ was synthesized by the solid-state double sintering method. From the X-ray analysis, it was confirmed that the synthesized compound formed in single phase with tetragonal structure. The resonance and antiresonance measurements were performed from 100 Hz to 10 MHz frequency using a HP 4194A impedance analyser, interfaced to a computer. Prior to these measurements, the electrical poling was done at 5 kV/cm at a temperature of 120 °C for 30 min and cooled to room temperature by keeping the field on. The magnetization measurements were performed at room temperature using Lakeshore—vibrating sample magnetometer. The ME measurements were made using a dynamic ME set-up [5]. These measurements were performed at room temperature and at 77 K as a function of dc field (0–8 kOe) with a superimposed ac field of 18 Oe. Prior to the ME measurement, the sample was poled electrically at 5 kV/cm at 120 °C for 30 min and the magnetic poling was performed at 10 kOe at room temperature. For all the iso-structural compounds, fixed ac field of 18 Oe and a dc field of 1.3 kOe were applied. Point contacts were made on both sides of sample with silver paint using epoxy resin. The samples were cooled down to 77 K in a magnetic field of 1.3 kOe.

## 3. Results and discussion

Fig. 1 shows the plot of admittance versus frequency at room temperature for the sample $SrBi_3Nb_2FeO_{12}$. The

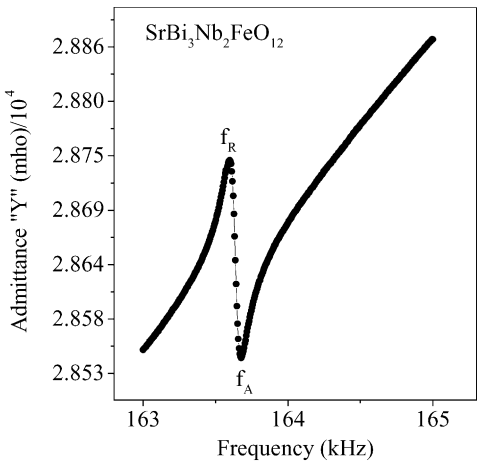


Fig. 1. Admittance vs. frequency of $SrBi_3Nb_2FeO_{12}$.

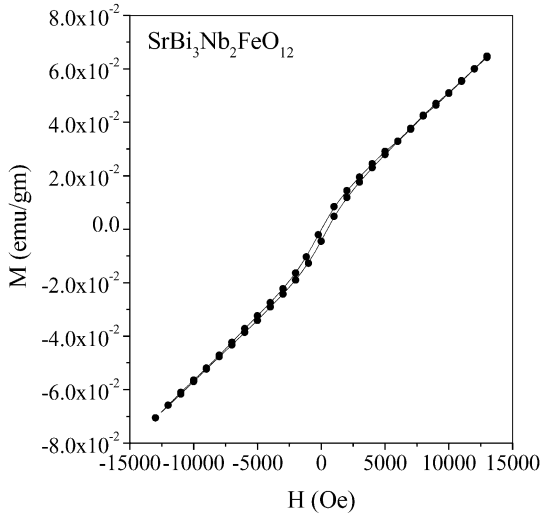


Fig. 2. *M* vs. *H* plot of $SrBi_3Nb_2FeO_{12}$ at room temperature.

electromechanical coupling coefficient—$K_P$ is calculated from the resonance and antiresonance method. Prior to the measurements, the sample is electrically poled. The percentage value of $K_P$ obtained from the calculations is 3.46. There are a few reports on resonance and antiresonance measurements in these layer compounds. The obtained value of $K_P$ is less when compared to $BaTiO_3$, which has a value about 38% and PZT with a value around 58%. Further studies are on to understand the piezoelectric nature of the material at different temperatures and also to improve the value of the coupling coefficients.

Fig. 2 shows the magnetization versus field at room temperature for $SrBi_3Nb_2FeO_{12}$ ceramic. A slim loop was observed from the plot. The loop is not saturated at 15 kOe field. The loop is not saturated at the field of 15 kOe. The interesting aspect is that the loop area is more at the origin and gets narrower with the increase of field. This type of behaviour is also observed in other layer compounds [6]. The structure consists of perovskite like slabs in between the two $Bi_2O_2$ layers. The $Fe^{3+}$ ions are statistically distributed in the octahedral sites. The interactions are taking along the chain Fe–O–Bi–O–O–Fe indicating a possibility of super exchange. The minor loop in the plot is due to canting of spins. Presumably, the Fe–O–Fe chain will not be equal to zero but gives rise to a small moment and hence the minor loop in the *M* versus *H* plot. The strength of exchange interactions would accordingly influence the magnetic nature of the compound.

Fig. 3 show the plot of ME output versus field at room temperature at four different frequencies. With the increase of frequency from 0.5 to 1.5 kHz, the value of ME out put has increased. The maximum value of out put was observed at 8 kOe field was around $3.1 \times 10^{-4}$ V/cm at 1.5 kHz frequency. The nature of the output was getting saturated around 4 kOe field. There is not much change in the signal from 4 to 8 kOe field. Fig. 4 shows the plot of ME out put

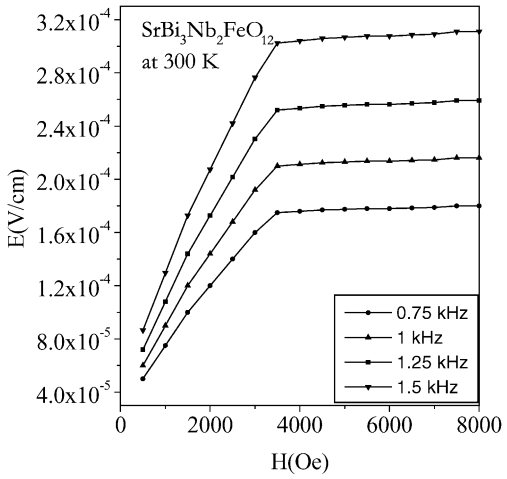


Fig. 3. Magnetoelectric output vs. field at room temperature.

versus field at 77 K at four different frequencies. The maximum value of output observed at 77 K was around $7 \times 10^{-4}$ V/cm at 1.5 kOe field. There is a gradual increase in the signal with the increase of field at 77 K. The value of ME output is more at 77 K than at room temperature. This shows the materials are more ordered at low temperatures. From the plots, it is clear that the signal obtained is not a linear one.

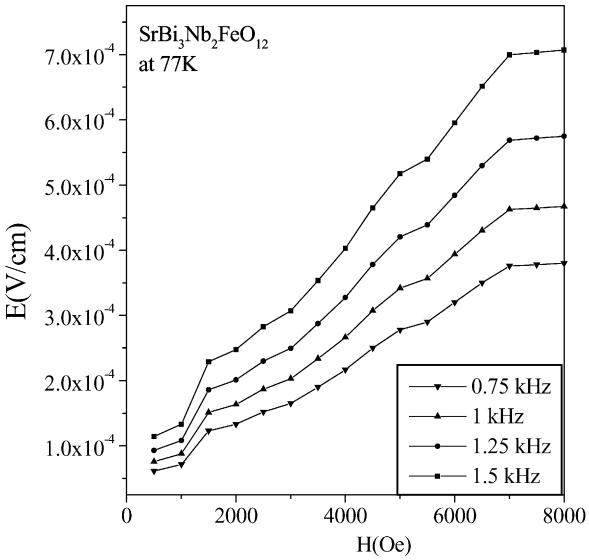


Fig. 4. Magnetoelectric output vs. field at 77 K.

In a magnetically ordered crystal only a linear signal can be predicted. But for a ceramic even if it is magnetically ordered, the true linear signal cannot be detected unless it is totally magnetically poled. In a partially poled state, we get a signal, which is superimposition of both linear and quadratic terms as it is in the present case. The antiferromagnetic nature of the material from the *M* versus *H* plot should give rise to linear effects, where as a quadratic signal may be arising due to slight canting of the Fe–O–Fe chains of spins in the regular octahedra, which is slightly tilted. Apart from this, the $BiFeO_3$, which has a cycloidal magnetic spin and incommensurate structure, gives rise to non-linear effects with a spin flop [3]. Addition of BF to SBN reduces the degree of incommensurate structure but preserves the non-linearity.

## 4. Conclusions

The resonance and antiresonance measurements indicates that the material consists of low coupling coefficient values. Further studies are to be undertaken to improve the coupling coefficients. The magnetization measurements show that the synthesized material consists of antiferromagnetic ordering at room temperature. The magnetoelectric measurements indicate that $SrBi_3Nb_2FeO_{12}$ ceramic is a magnetoelectric material at room temperature and at low temperatures. Further studies are on to study the material for a possible application in a thin film form.

## References

[1] B. Aurivillius, Mixed bismuth oxides with layer lattices, Arkiv Kemi 1 (1949) 499.
[2] P. Duran-Martin, A. Castro, P. Millan, B. Jimenez, Influence of Bi-site substitution on the ferroelectricity of the Aurivillius compound $Bi_2SrNb_2O_9$, J. Mater. Res. 13 (1998) 2565–2571.
[3] M. Mahesh Kumar, A. Srinivas, S.V. Suryanarayana, Structure property correlations in $BiFeO_3/BaTiO_3$ solid solutions, J. Appl. Phys. 87 (2000) 855–862.
[4] A. Srinivas, Dong-Wan Kim, Kug Sun Hong, S.V. Suryanarayana, Observation of ferroelectromagnetic nature in rare-earth-substituted bismuth iron titanate, Appl. Phys. Lett. 83 (2003) 2217–2219.
[5] M. Mahesh Kumar, A. Srinivas, S.V. Suryanarayana, G.S. Kumar, T. Bhimasankaram, An experimental setup for dynamic measurement of magnetoelectric effect, Bull. Mater. Sci. 21 (1998) 251–255.
[6] S.V. Suryanarayana, A. Srinivas, Structure property correlations in $Bi_5Mn_xFe_{1-x}Ti_3O_{15}$, Electron. Ceram. Mater. Dev. 106 (2000) 277–299.