# Multiferroic properties of 0.05 NZF - 0.95 $Ba_{0.9-3x/2}Sr_{0.1}La_xTiO_3$ magnetoelectric composites

**Renu Rani[1, 4], J. K. Juneja[2], Sangeeta Singh[3], K. K. Raina[4] and Chandra Prakash[5*]**

[1]*Electroceramics Research Lab, GVM Girls College, Sonepat 131001, India*
[2]*Department of Physics, Hindu College, Sonepat 131001, India*
[3]*Department of Physics, GVM Girls College, Sonepat 131001, India*
[4]*School of Physics & Materials Science, Thapar University, Patiala 147004, India*
[5]*Solid State Physics Laboratory, Timarpur, Delhi 110 054, India*

[*]Corresponding author. E-mail: cprakash2014@gmail.com

## ABSTRACT

For the present work, the magnetoelectric (ME) composites with composition 0.05 $Ni_{0.8}Zn_{0.2}Fe_2O_4$ - 0.95 $Ba_{0.9-3x/2}Sr_{0.1}La_xTiO_3$ (NZF-BSLT) with x = 0, 0.01 and 0.02 were synthesized by conventional solid state reaction route. The existence of both phases was confirmed by the X-Ray diffraction (XRD) technique. The dielectric properties such as dielectric constant and dielectric loss were measured as a function of temperature at different frequencies. P-E hysteresis loops and M-H hysteresis loops confirm the ferroelectric and ferromagnetic nature of the composite samples.La substitution in ferroelectric phase results in significant improvement in properties of composite samples. The investigated composites seem to be very attractive for multiple state memory devices where data can be stored both as polarization (P) and magnetization (M). Copyright © 2014 VBRI press.

Keywords: Magnetoelectric composites; ferroelectric; ferromagnetic; dielectric properties.

**Renu Rani** was born in Haryana, India on July 15th 1986. She received the M.Sc. degree in physics from M.D. University, Rohtak and the Ph.D. degree in material science from Thapar University Patiala (T.U. Patiala) in 2008 and 2013, respectively. Since 2008 she is a life time member of Material Research Society of India (MRSI). Her research interest and expertise are in ferroelectric materials, ferrite materials and magnetoelectric composites. She has coauthored more than 15 technical papers that were published in peer-reviewed journals or presented at national and international conferences. At present she is appointed as an Assistant Professor in Roorkee Institute of Technology, Roorkee, India.

**K.K. Raina** is Distinguished Prof of Physics & Materials Science at Thapar University, Patiala. He is Fellow of Punjab Academy of Sciences. He got MRSI Medal in 2012. His specialization is Physics & Materials Science specific to Ferroelectric Materials. He has published 200 papers in Peer refereed journals.

**Chandra Prakash** obtained his M.Sc. and M.Phil. in Physics from Institute of Advanced Studies, Meerut University in 1980 and 1981, respectively. He did Ph.D. from Delhi University in 1986 and M.B.A. from Sikkim Manipal University in 2010. He is presently Associate Director and Head of Functional Materials Group at Solid State Physics Laboratory (SSPL), DRDO, Delhi. He is Co-recipient of DRDO Technology awards for the years 1988, 1995 & 2002. He is Chairman of Delhi Chapter of Materials Research Society of India (MRSI) and was awarded MRSI Medal for the year 2012. He is Member of Executive Committee of Magnetics Society of India. He was Visiting Scientist at Penn State University, USA for one yr in 1994-95. He is visiting Professor at Thapar University, Patiala. He has more than 200 research papers published in peer reviewed journals and more than 100 papers in conference proceedings. He has 2 patents. His citation index is more than 1700, h-index is 23 and i-10 index is 54 (Ref: Google Scholar). He has guided 16 students for their doctoral degree. His current interests are focused on Advanced Ceramics: Ferroelectrics, Piezoelectrics, Microwave Dielectrics, Ferrites, Composites, etc.

## Introduction

In the recent years, there is renewed scientific interest in the study of the magnetoelectric materials because of their potential for applications as multifunctional devices. These magnetoelectric materials also show the unique property i.e. magnetoelectric effect (ME affect) which is not shown by their constituent phases. It occurs due to interaction between electric and magnetic dipole and it is defined as the induction of electric polarization by applying anexternal magnetic field or induction of magnetization by applying an external electric field **[1-4]**. These magnetoelectric materials are classified into two groups: single phase materials and two phase materials or composites.The first known single phase magnetoelectric material was $Cr_2O_3$ but these single phasematerials show so weak ME effect that

they have not yet found in any technological applications. Whereas two phase magnetoelectric materials (composites) show larger ME effect than the single phase materials [5]. These composite materials have large number of potential applicationssuch as magnetic field sensors, multiple state memory devices, transducers for magnetic field measurements, electro-optic devices, electrically tunable microwave devices such as filters, oscillators and phase shifters etc. [6-9]. However to improve the working of these devices, it is necessary to modify the properties of these composites. The modification can be done by two ways. i.e. either by modification of individual ferroelectric or ferrite phases because the property of the composites also depends on the properties of individual phases or by changing the ratio of two individual phases in composites. The ions such as $Zr^{4+}$, $Sr^{3+}$, $Pb^{2+}$, $La^{3+}$, $Sm^{3+}$ and $Ca^{2+}$ are extensively used as additives for enhancing the properties of the ferroelectric phase [10-12] whereas doping of Ni ferrite by other magnetic ions such as Mn, Co, Cu and Zn etc. improves the resistivity, permeability, magnetization and coercive field of the nickel ferrite [13-14].

For the present work Ni-Zn ferrite was selected as ferrite phase because of its high resistivity, high magnetic permeability, low dielectric loss, high Curie temperature, high mechanical hardness, low porosity, reasonable cost and chemical stability which helps to increase the efficiency of ME conversion factors of composite samples [15-16]. A small amount of Mn (0.5% by wt) was also substituted in ferrite phase because Van Uitert, reports that by incorporating small amounts of Mnto nickel ferrite, the resistivity of the nickel ferrite increases up to $10^{10}$ or $10^{11}\Omega$-cm and to obtain good magnetoelectric response in ME composite the ferrite phase should have high resistivity [17-18]. On the other hand, $Ba_{0.9-3x/2}Sr_{0.1}La_xTiO_3$was selected as a ferroelectric phase because of its high figure of merit, environment friendly nature and also shows superior dielectric and ferroelectric properties [19]. The addition of Sr at Ba site of barium titanate can shift the ferroelectric to paraelectric phase transition from high temperature to low temperature, resulting in a BST material with high dielectric constant at room temperature. Moreover, La substitution at Ba-site has also been found to be an effective way to decrease the $T_c$ and exhibited several interesting features in the dielectric behavior of $BaTiO_3$ ceramics [20-21].

From literature it was found that the properties of these composites have been studied only by changing the ratio of ferrite phase and ferroelectric phase. However the effect of substitution in ferroelectric phase by keeping fixed ratio of both phases has not yet been studied. In this context we have prepared the composites of $Ni_{0.8}Zn_{0.2}Fe_2O_4$and $Ba_{0.9-3x/2}Sr_{0.1}La_xTiO_3$by solid state reaction route and these composites were investigated for their structural, electrical and magnetic properties in detail as discussed in present paper.

## Experimental

The individual phases (ferrite and ferroelectric) were prepared by conventional solid state reaction method.

The ferrite phase was prepared by using AR grade NiO, ZnO and $Fe_2O_3$ (Loba cheme, Purity – 99.9%) raw materials. The powder mixture was ball milled in distilled water using zirconia balls. After drying the powder was calcined at 1000 $^o$C for 4h. A small amount of $MnO_2$ (0.5% by wt.) was added to the calcined powder to increase the resistivity of the ferrite phase. After ball milling and drying the powder mixture was recalcined at 1000 $^o$C for 4h.The ferroelectric phase was prepared using AR grade $BaCO_3$, $SrCO_3$, $La_2O_3$ and $TiO_2$ (Loba cheme, Purity – 99.9%) raw materials. The powder mixture was ball milled, dried and then calcined at 1100 $^o$C. The calcined powder was again ball milled, dried and then recalcined at 1100 $^o$C. The recalcined powder of both phases was then ball milled again and dried separately.

The composite were prepared by mixing 5% by wt. $Ni_{0.80}Zn_{0.20}Fe_2O_4$ (NZF) phase to the 95% by wt $Ba_{0.9-3x/2}Sr_{0.1}La_xTiO_3$ (BSLT) phase. The mixing process was carried out by ball-milling using Zirconia balls and distilled water as milling media. After drying the mixture, small amount of diluted poly vinyl alcohol was added as binder to the powder mixture and then the powder mixture was pressed into circular disks having thickness 2-3 mm and diameter 15 mm using a uniaxial hydraulic press. The composite pellets were finally sintered at 1325 $^o$C for 4 hours with constant heating rate of 5 $^o$C/min in a programmable furnace.
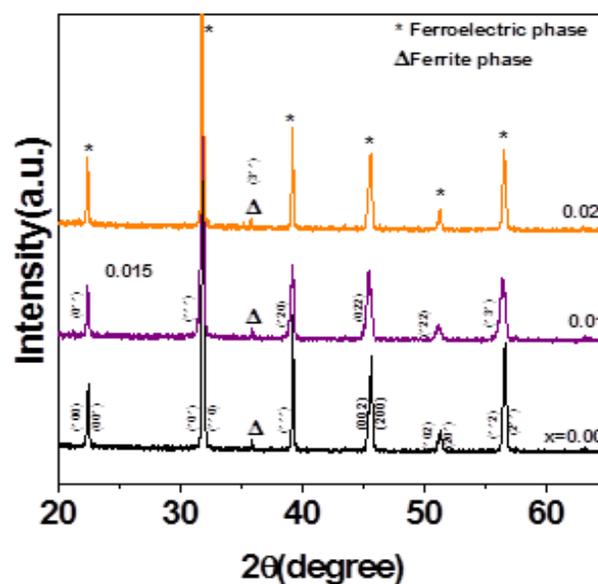


**Fig. 1.** XRD patterns of the samples.

## Characterization

After sintering,phase identification of sintered pallets was done by using Bruker, D-8 Advance model at room temperature in a range of Bragg angles ($20^o \leq 2\theta \leq 65^o$) with step size of $0.02^o$. For measuring electrical properties, the sintered pellets were lapped and then electroded by using silver epoxy and heated at 400 $^o$C for 30 min to ensure good ohmic contact. The dielectric properties of the samples as a function of temperature at discrete frequencies were measured by using Agilent 4263B LCR meter. P-E hysteresis loops were recorded by using an automated P-E loop tracer based on sawyer tower circuit. Lake shore 735 VSM controller was used for recording M-H hysteresis loops.

## Results and discussion

### Structural properties

To study the phase analysis of the samples all samples were subjected to XRD.XRD pattern for all samples are shown in **Fig. 1**. From the figure it is observed that all XRD patterns exhibit the characteristic peaks of both phases i.e. (110) for ferroelectric phase and (311) for ferrite phase and hence confirms the presence of both phases. For all samples all peaks could be indexed and no extra peaks were observed hence it is clear that no chemical reaction took place between two phases and they maintained proper stoichiometry. From XRD pattern it is also clear that theintensity of peaks corresponding to ferrite phase is very small that may be due to very low concentration of ferrite phase in composite samples.

**Table 1.** Structural and dielectric parameters for all samples.

| Parameters | 0.00 | 0.01 | 0.02 |
|---|---|---|---|
| Lattice Constant (Å) (BSLT phase) a | 3.986 | 3.983 | 3.976 |
| c | 4.003 | 3.997 | 3.988 |
| c/a | 1.0043 | 1.0035 | 1.0030 |
| Lattice Constant (Å) (NZF phase) | 8.324 | 8.335 | 8.339 |
| $T_c$ (ºC) | 134 | 106 | 70 |
| $\varepsilon_{RT}$ | 2254 | 3441 | 4314 |
| $\varepsilon_{max}$ | 3834 | 4598 | 4346 |
| $\tan\delta_{RT}$ | 0.081 | 0.019 | 0.015 |
| $\tan\delta_{max}$ | 0.046 | 0.016 | 0.020 |

The calculated values of lattice parameters for both phases are given in **Table 1**. From table it is observed that with the increase in La content lattice parameters corresponding to ferroelectric phase decreases (c,a) because larger ion $Ba^{2+}$ (ionic radii 1.49Å) are being replaced by smaller ion $La^{3+}$ (ionic radii 1.17 Å) and hence decrease in lattice parameter is expected. It can also be observed that there is change in the lattice parameter of ferrite phase while the amount of ferrite phase is fixed. This may be due to the stress exerted by two individual phases on each other's crystal lattice [22].

### Dielectric properties

The variation of dielectric constant with temperature at different frequencies (1 kHz, 10 kHz and 100 kHz) for all samples is shown in **Fig. 2**. From figure it is observed that dielectric constant increases with increase in temperature for all samples and reaching to maximum value at a particular temperature called Curie temperature of ferroelectric phase and after that dielectric constant decreases. This is a typical characteristic of ferroelectric materials. As the amount of La content increases in ferroelectric phase the dielectric peak shift towards room temperature. All dielectric parameters like room temperature dielectric constant ($\varepsilon_{RT}$), dielectric loss, dielectric constant at $T_c$ ($\varepsilon_{max}$), dielectric loss at $T_c$, and Curie temperature for all samples is given in table1. From table it can be observed that La has very prominent effect on the dielectric properties of composite samples.
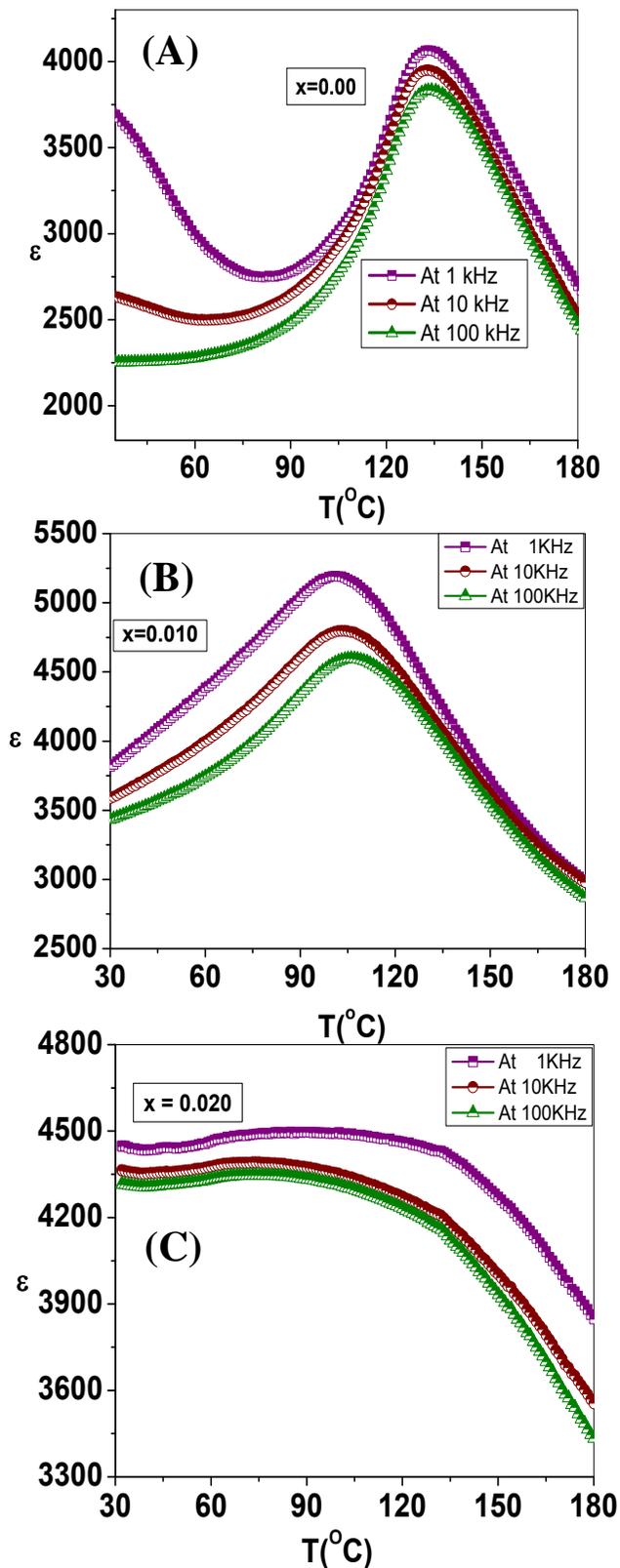


**Fig. 2.** Variation of dielectric constant as a function of temperature at different frequencies for all value of x.

From **Fig. 2** it is also observed that dielectric peak get suppressed and become broadened with the increase of La content.Thebroadening of dielectric peak occurs mainly due to the compositional fluctuations and structural disordering

in the arrangement of cations in one or more crystallographic sites in the structure which results in microscopic inhomogeneity in the samples with local Curie points [23]. Variation of dielectric loss with temperature at 100 kHz frequency is shown in **Fig. 3**. From figure it is also observed that dielectric loss of composite samples decreases from 0.081 to 0.015 with increase in lanthanum content in ferroelectric phase. From **Table 1** it is also observed that La substitution in ferroelectric phase increase the room temperature dielectric constant, dielectric constant at maxima and decreases the dielectric loss of composite samples.
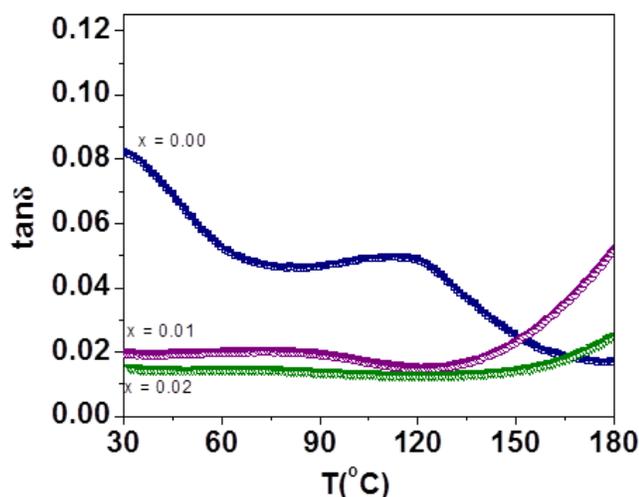


**Fig. 3.** Variation of tanδ as a function of temperature for all samples at 100 kHz.

**Table 2.** Ferroelectric and ferrimagnetic parameters variation of tanδ as a function of temperature for all samples at 100 kHz.

| y | $P_r$ ($\mu C/cm^2$) | $E_c$ (kV/cm) | $P_{max}$ ($\mu C/cm^2$) | $M_r$ (emu/g) | $M_s$ (emu/g) | $H_c$ (Oe) |
|---|---|---|---|---|---|---|
| 0.00 | 7.70 | 7.8 | 16 | 0.162 | 1.60 | 69.82 |
| 0.01 | 4.43 | 3.74 | 12.9 | 0.196 | 1.68 | 74.37 |
| 0.02 | 4.22 | 1.68 | 6.26 | 0.22 | 1.64 | 70.27 |

*Ferroelectric and Ferromagnetic Properties*

In order to understand the ferroelectric and ferromagnetic nature of the sample the P-E and M-H hysteresis loops were taken for different compositions as shown in **Fig. 4** (**A & B**) respectively. The various parameters such as saturation polarization ($P_s$), remnant polarization ($P_r$), electric coercive field ($E_c$) and saturation magnetization ($M_s$) for all samples are given in **Table 2**.

From **Table 2** it is observed that value of saturation magnetization varies in random manner while the amount of ferrite phase is fixed that may be due to non-uniform mixing of two individual phases because the effective value of magnetic and electric properties of a composite material consisting of two phases can be predicted as a function of individual components [24]. The value of polarization decreases with increase in La content in ferroelectric phase. That can correlate to microstructure of the samples.
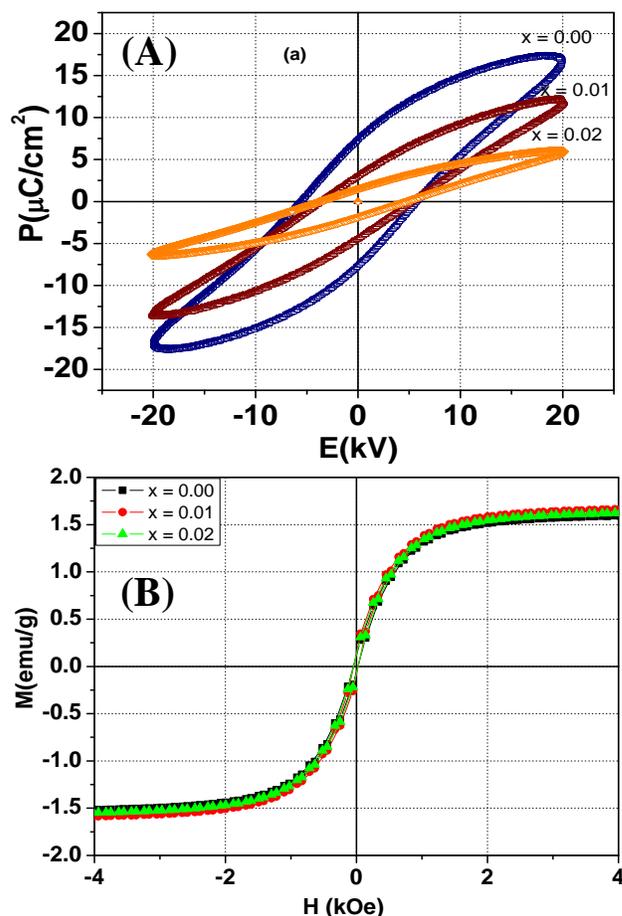


**Fig. 4** (**A**) Polarization vs. electric field (P–E) loop for all samples (**B**) Magnetization vs. magnetic field (M–H) curves for all samples.

## Conclusion

Composites synthesized by conventional solid state method were characterized by x-ray diffraction technique and coexistence of both phases (ferroelectric and ferrite) was confirmed. Decrease in ferroelectric Curie temperature ($T_c$) and increase in room temperature dielectric constant with increase in La content was observed for all the composite samples. The room temperature dielectric loss of composite samples decreases as La content in ferroelectric phase increases. All the samples show ferroelectric hysteresis loops as well as ferromagnetic hysteresis loops.

**Reference**
1. Suchetelene, J. Van; *Philips Res. Rept.* **1972**, 27, 28.
2. Van Run, M.J.G.; Terrel, D.R.; Scholing, J.H.; *J. Mater. Sci.* **1974**, 9, 1710.
3. Lopatin, S.; Lopatin, I.; Lisvevskaya, I.; *Ferroelectrics* **1994,** 162, 63.
4. Layek, S.; Verma, H. C.; *Adv. Mater. Lett.* **2012,** 3, 533.
   **DOI:** 10.5185/amlett.2012.icnano.242
5. Layek, S.; Bag, S.K.; Verma, H. C.; *Adv. Mater. Lett.* **2013,** 4, 26.
   **DOI:** 10.5185/amlett.2013.icnano.289
6. Suryanarayana, S.V.; *Bull. Mater. Sci.* **1994,** 17, 1259.
7. Bracke, L.P.M.; Van Vliet, R.G.; *Int. J. Electron.* **198,** 51,225.
8. Zhao, K.; Chen, K.; Daj, Y.R.; Wan, T.G.; Zhu, J.S.; *Appl. Phys. Lett.* **2005,** 87, 162901.

**DOI:** 10.1063/1.2099545

9. Rani, R.; Kumar, P.; Singh, S.; Juneja, J.K.; Raina, K.K.; Kotnala, R.K.; Prakash ,C.; *Int. Ferroelectrics* **2010,** 122,38.
**DOI:** 10.1080/10584587.2010.504398

10. Jaffe, B.; Cook, W.; Jaffe, H.; *Piezoelectric Ceramics*, Academic Press, London, 1971.

11. Kumar, P.; Singh, S.; Juneja, J.K.; Prakash, C.; Raina, K.K.; *Mater. Chem. Phys*. **2011,** 125, 660.
**DOI:** 10.1016/j.matchemphys.2010.10.001

12. Dobal, P.S.; Dixit, A.; Katiyar, R.S.; Garcia, D.; Guo, R.; Bhalla, A.S.; *Ferro. Lett*., **2002,** 29, 1.
**DOI:** 10.1080/07315170214359

13. Islam, R.A.; Viehland, D.; Priya, S.; *J. Mater. Sci*. **2008,** 43, 1497.
**DOI:** 10.1007/s10853-007-2386-z

14. Ryu, J.; Carazo, A.V.; Uchino, K.; Kim, H.E.; *J. Electoceram*. **2001,** 7,17.

15. Bammannavar, B.K.; Naik, L.R.; *J. Magn. Magn. Mater*. **2012***,* 324, 944.
**DOI:** 10.1016/j.jmmm.2011.09.016

16. Wang, Z.; Schiferl, D.; Zhao, Y.; O'Neill, H.St.C.; *J. Phys. Chem. Solids* **2003,** 64, 2517.
**DOI:** 10.1016/j.jpcs.2003.08.005

17. Van Uitert, L.G.; *J. Chem. Phys*. **1956,** 24, 306.

18. Boomgaard, J.V.D.; Born, R.A.J.; *J. Mater. Sci*. **1978**, 13, 1538.

19. Prasad, K.; Chaudhary, R.N.P.; Chaudhary, S.N.; Sati, R.; *Bull. Mater. Sci*. **1996,** 19, 505.

20. Jiang, X.P.; Zeng, M.; Chan, H.L.W.; *Mater. Sci. Eng. A* **2006,** 438, 198.
**DOI:** 10.1016/j.msea.2006.02.109

21. Mukherjee, A.; Victor, P.; Parui, J.; *J. Appl. Phys*. **2007,** 101, 034106.
**DOI:** 10.1063/1.2433717

22. Fawzi, A.S.; Sheikh, A.D.; Mathe, V.L.; *Phys*. B **2010,** 405, 340.
**DOI:** 10.1016/j.physb.2009.08.090

23. Hennings, D.; Schell, H.; Simon, G.; *J. Am. Ceram. Soc*. **1982,** 65, 539.
**DOI:** 10.1111/j.1151-2916.1982.tb10778.x

24. Babu, S.N.; Suryanarayana, S.V.; Bhimasankaram, T.; *J. Alloys Compd*. **2009,** 473, 418.
**DOI :** 10.1016/j.jallcom.2008.05.097