J Mater Sci (2007) 42:5080–5084
DOI 10.1007/s10853-006-0594-6

Magnetoelectric and dielectric properties of $Ni_{0.5}Cu_{0.5}Fe_2O_4$–$Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME composites

C. M. Kanamadi · S. R. Kulkarni · K. K. Patankar · S. S. Chougule · S. J. Patil · B. K. Chougule

Received: 23 April 2005 / Accepted: 19 June 2006 / Published online: 22 February 2007

Abstract The (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME composites have been synthesized by a standard ceramic method. The presence of single phase in x = 0 and x = 1 as well as two phases in x = 0.15, 0.30 and 0.45 composites has been confirmed by XRD. The dielectric constant (ε') and dielectric loss (tan δ) have been studied as a function of temperature and frequency. These composite materials exhibit maximum dielectric constant with a variation of frequency and temperature. The composite 15% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 85% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ had the highest magnetoelectric voltage coefficient of 0.248 mV/cm Oe at room temperature among the studied composites.

Introduction

The magnetoelectric composites with electrostrictive and magnetostrictive materials are of interest as transducers, which transform the changes in a magnetic field into electric voltage and vice-versa [1]. It can be used as a Hall sensor for magnetic field measurement, or as an electric current measurement [2]. The combination of both ferroelectric and ferromagnetic materials in a single material is expected to show new properties such as magnetoelectric, magnetooptic [1, 3, 4] and other new coupling properties, due to the occurrence of coupling effects between the magnetization and electric polarization. However, there are only a few naturally occurring materials that can exhibit both spontaneous magnetization and electric polarization [5]. Numerous ME single-phase materials have been developed, but their ME effect is weak [6]. A much stronger ME effect could be realized in a composite of piezoelectric phase or magnetostrictive phase by using product properties. That is, under applied magnetic field, the mechanical deformation induced by magnetostriction and is mediated by mechanical stress and results in electric fields being induced due to piezoelectric effect [7, 8]. Various different methods have so far been used in the synthesis of such materials. Among these, the solid state reaction method has been widely employed and the properties of the resulting materials studied extensively. Sintered magnetoelectric composites have many advantages compared to in situ composites. The sintered composites are much easier and cheaper in fabrication than in situ composites. Moreover, molar ratio of phases, grain size of each phase and sintering temperature are easily controllable [2, 9].

$BaTiO_3$ and $PbZrTiO_3$ are the most suitable piezoelectric materials for ME composites because of their high piezoelectric coefficients [2, 9]. Hence, in the present study we have chosen $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ as the piezoelectric phase. The $Ni_{0.5}Cu_{0.5}Fe_2O_4$ is used as piezomagnetic phase because of their superior magnetostriction coefficient, magneto-mechanical coupling factor and high electrical resistivity [10].

C. M. Kanamadi (✉) · S. R. Kulkarni · K. K. Patankar · S. S. Chougule · S. J. Patil · B. K. Chougule
Composite Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India
e-mail: cm_kanamadi@yahoo.co.in

S. R. Kulkarni
e-mail: bkc_phy@unishivaji.ac.in

Experimental

The (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ composite materials were prepared by standard ceramic method. AR grade powders of NiO, CuO and Fe_2O_3 were used to prepare the ferrite phase. The ferroelectric phase viz. $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ was prepared by using AR grade $BaCO_3$, $PbCO_3$, TiO_2 and ZrO_2 powders. The individual phases were ground for couple of hours and mixed in required molar proportions. The ferrite phase ($Ni_{0.5}Cu_{0.5}Fe_2O_4$) and ferroelectric phase ($Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$) were presintered separately at 900 °C and 1000 °C for 12 h respectively. The composite mixture was again presintered at 1100 °C for 12 h. Pellets of the presintered powder were prepared by applying a pressure of 5–6 tonnes/inch^2 in a hydraulic press. The pellets were finally sintered at 1150 °C for 12 h. The X-ray diffraction patterns of the samples were taken on Philips X-ray Diffractometer (Model PW 1710) using CrKα radiation (λ = 2.2897 Å). The samples were coated with silver paste to ensure good ohmic contacts. The AC parameters such as capacitance (C) and dissipation factor (tan δ) of the samples were measured in the frequency range 100 Hz to 1 MHz using LCR meter bridge (Model HP 4284 A). The variation of dielectric constant and loss tangent with temperature was studied by recording these parameters at different frequencies. To realize ME signal in the composites, samples have to be poled electrically and magnetically. The electric poling was carried out by heating the samples at 200 °C and subsequently cooled to room temperature in an external field of about 2.5 kV/cm. The samples were poled magnetically by applying an external DC magnetic field of 6 kOe at room temperature. The experimental arrangement for measurement of ME output is described elsewhere [11, 12].

Results and discussion

Figure 1 shows XRD patterns of (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ (where x = 0.15 and 0.30) composite samples. All the peaks can be identified. The patterns show two sets of well defined

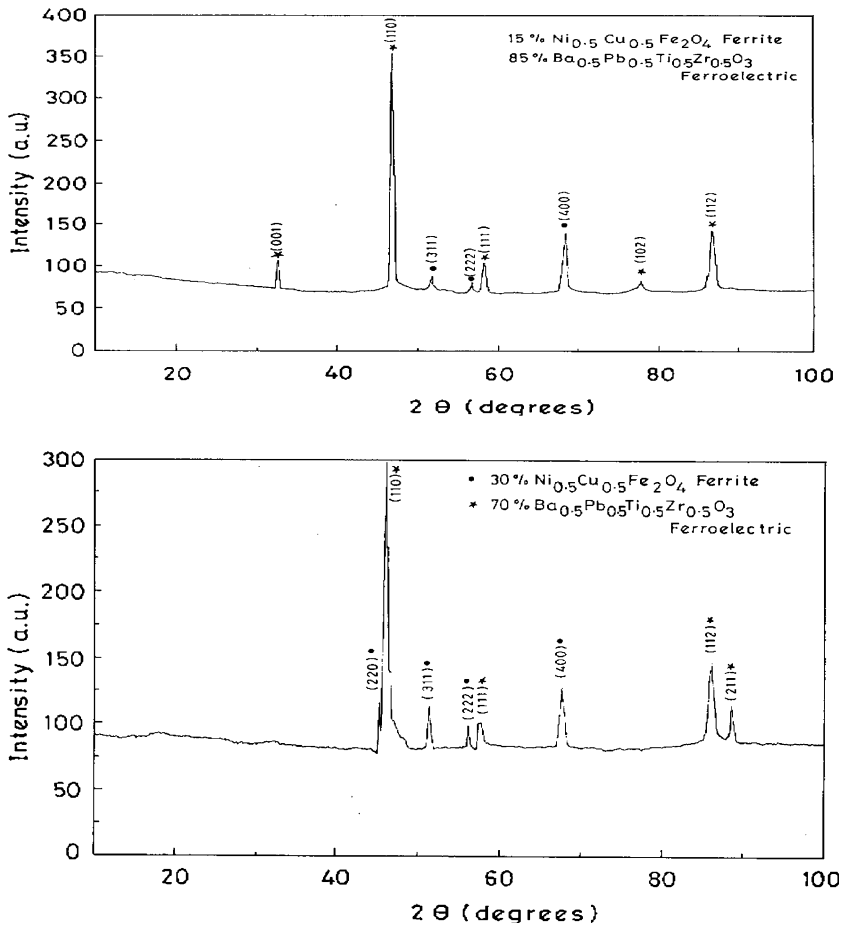

Fig. 1 XRD pattern of (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composites (x = 0.15 and 0.30)

peaks and there are no peaks corresponding to intermediate or additional phases apart from those of $Ni_{0.5}Cu_{0.5}Fe_2O_4$ and $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$. It is also clear from the figure that, no chemical reaction between ferrite and ferroelectric phases has taken place, which is the primary requirement for observance of the ME effect of a composite.

Figure 2 shows the frequency dependence of the dielectric constant (ε') at room temperature for the studied samples. It can be seen from the figure that the value of dielectric constant decreases continuously with increasing frequency. The decrease of dielectric constant with increase of frequency is a normal dielectric behaviour. This type of behaviour was also observed by us earlier [12, 13]. The dielectric dispersion can be explained on the basis of Koop's two layer model and Maxwell–Wagner polarization theory [14–16]. Since an assembly of space charge carriers in the inhomogeneous dielectric structure described requires finite time to line up their axes parallel to an alternating electric field, the dielectric constant naturally decreases, if the frequency of the reversal field increases [17]. The decrease in the values of both ε' as the frequency increases can be related to the electron exchange between the Fe^{2+} and Fe^{3+} ions which can not follow the alternation of the electric field beyond a certain critical frequency [18].

The temperature dependence of the dielectric constant (ε') for the composites is shown in Figs. 3, 4 and 5 for x = 0.15, 0.30 and 0.45 respectively. The dielectric constant increases with a rise in temperature up to the Curie temperature (T_c) and then it decreases. The two maxima are observed related to ferrite and ferroelectric Curie temperatures. The maximum value of ε' shifts towards higher temperature with increasing frequency. From the plot it is also seen that T_c shifts towards lower temperature side as the content of ferrite phase in the composite increases. This type of behaviour can be attributed to the presence of two types of charge carriers viz. electrons and holes [19]. Since the mobility of holes is smaller than that of electrons, it is expected that their contribution to polarization appears only at higher temperature causing the observed decrease [20]. The value of dielectric constant is found to be enhanced with increase in the content of ferrite in the composite (Figs. 4 and 5). This high value can be explained on the basis of the fact that it has maximum number of ferrous ions whose exchange $Fe^{2+} \leftrightarrow Fe^{3+}$ given rise to maximum dielectric polarization.

The variation of dielectric loss (tan δ) with temperature for x = 0.15 is shown in Fig. 6. The increase in

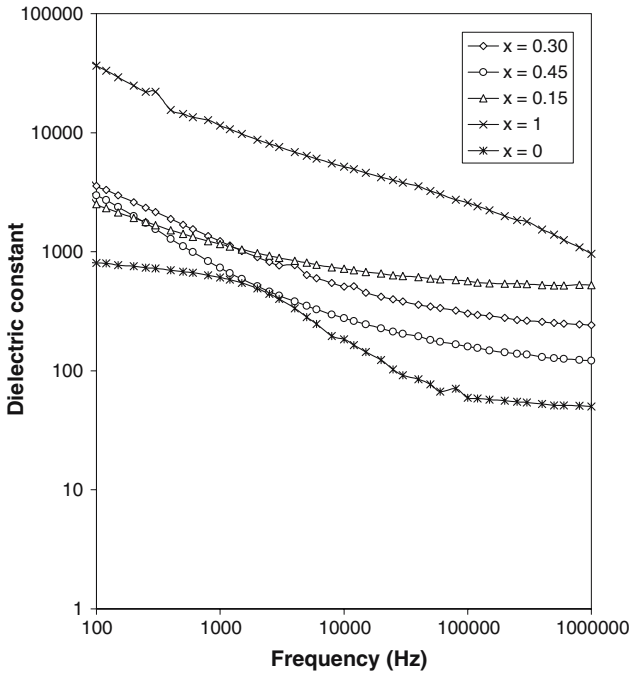

Fig. 2 Variation of dielectric constant with frequency for (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composites

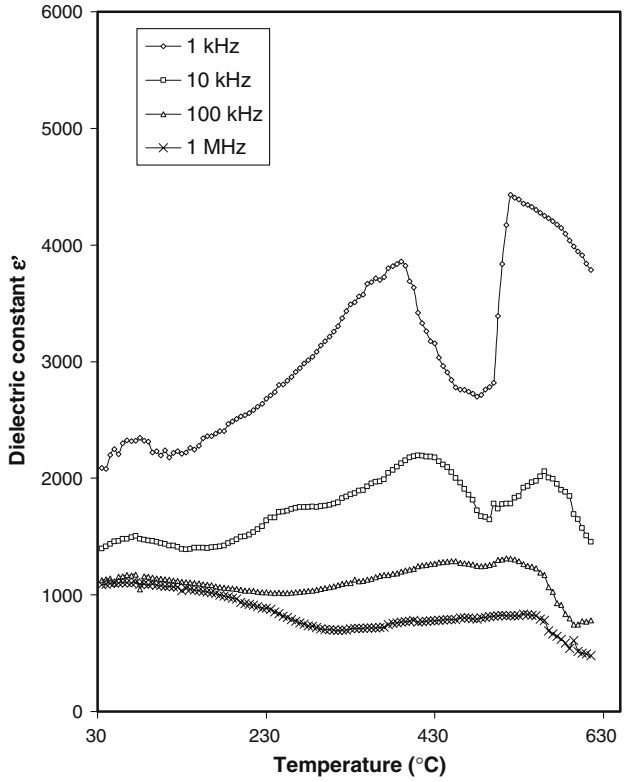

Fig. 3 Variation of dielectric constant with temperature for 15% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 85% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composite

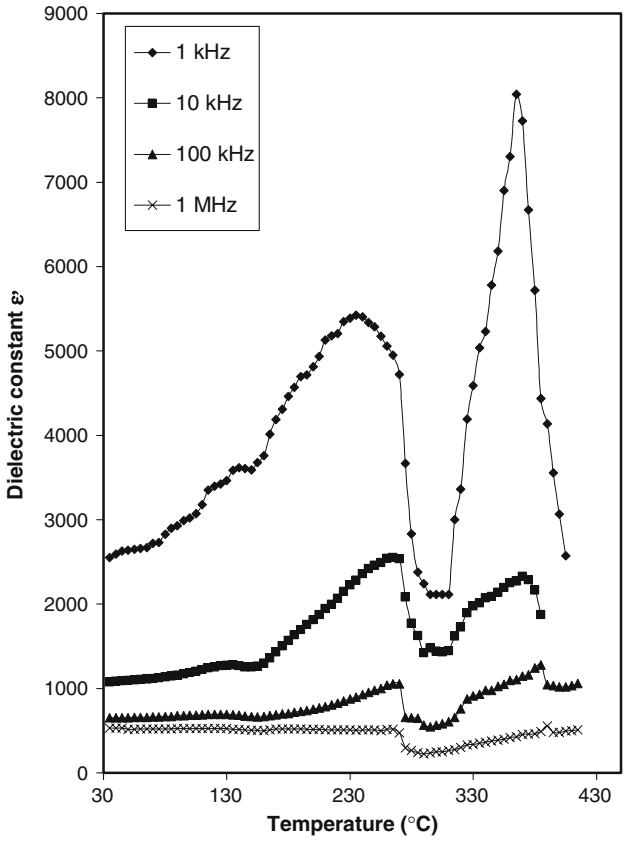

Fig. 4 Variation of dielectric constant with temperature for 30% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 70% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composite

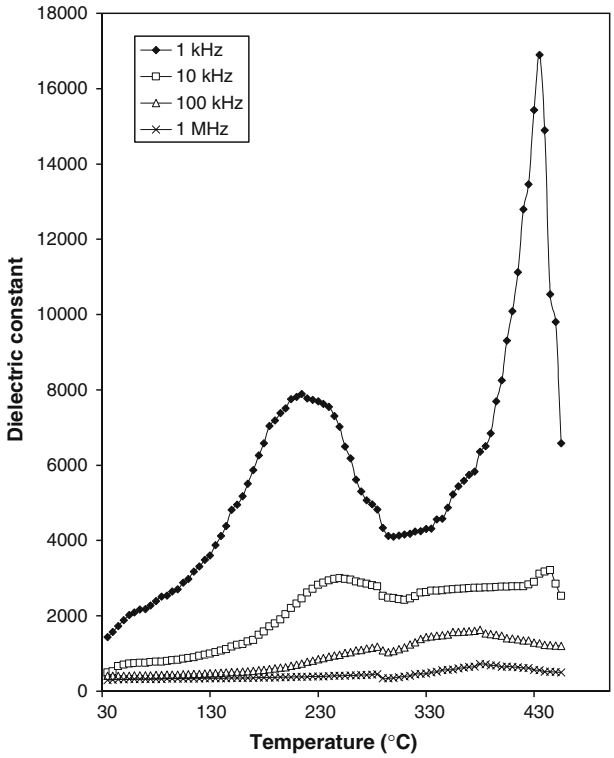

Fig. 5 Variation of dielectric constant with temperature for 45% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 55% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composite

loss tangent with increasing temperature ensures the semiconducting nature or thermally activated mechanism of conduction in the samples.

Figure 7 shows the magnetoelectric voltage coefficient as a function of the D.C. magnetic field. From the plot it is clear that the ME output goes on increasing with increase in magnetic field and decreases afterwards. This ME coupling is achieved by electromechanical conversion in the piezoelectric phase and magneto-mechanical conversion in the magnetostrictive phase by stress transfer through the interface between the two phases. In the present study, it is demonstrated that the magnetostriction increases with the D.C. magnetic field and it saturates at a certain field. Therefore the ME voltage coefficient (dE/dH) decreases with further increase in field. It is reported that in spinels, the magnetostrictive coefficient reaches saturation at a certain value of magnetic field [3]. In the present composites, beyond 1400 Oe, the magnetostriction and the strain produced would also produce a constant electric field in piezoelectric phase forcing dE/dH to decrease with increasing magnetic field. It was also seen that as the percentage of ferrite in the composite increases the value of dE/dH decreases. This is due to low resistivity of ferrite phase as compared to that of ferroelectric phase, which offers a leakage path for the charges developed across the piezoelectric phase [21]. The composite 15% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 85% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ had the highest magnetoelectric voltage coefficient of 0.248 mV/cm Oe at room temperature among the studied composites.

Conclusions

The XRD patterns of the composites reveal the presence of both ferrite and ferroelectric phases. The intensity and number of ferrite peaks are observed to increase with increasing ferrite content in the composite. The tetragonality of the ferroelectric samples varies from 1.01 to 1.04. Since these composites have high dielectric constant ($\acute{\varepsilon}_{max}$ = 16891 for 45% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 55% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ composite) they turn out to be the best candidates for charge storage devices. Before measuring ME output, the samples were poled electrically by applying electric field of 2.5 kV/cm and magnetically by applying DC magnetic field of 6 kOe. The maximum magnetoelectric conversion factor is found to be 0.248 mV/cm Oe for 15% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 85% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$

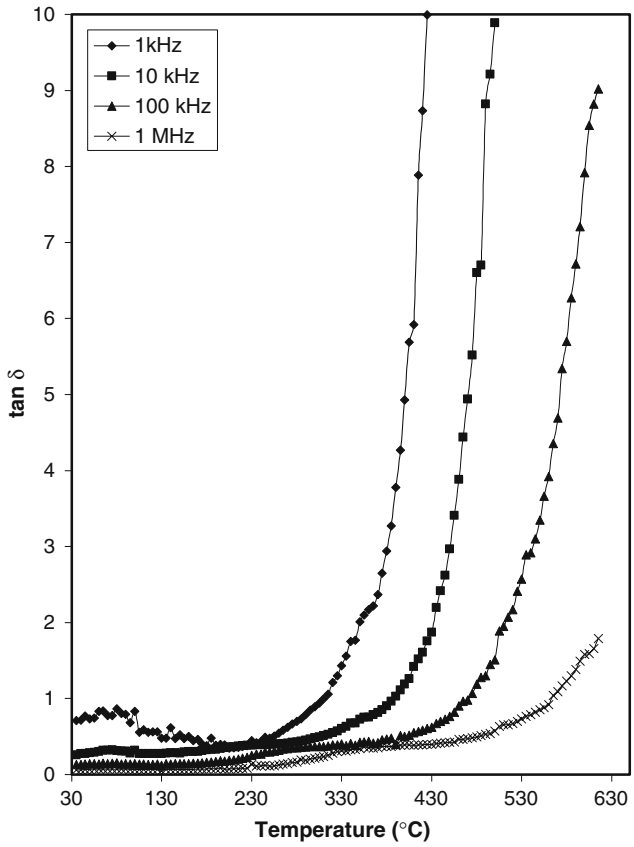

Fig. 6 Variation of dielectric loss with temperature for 15% $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + 85% $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composite

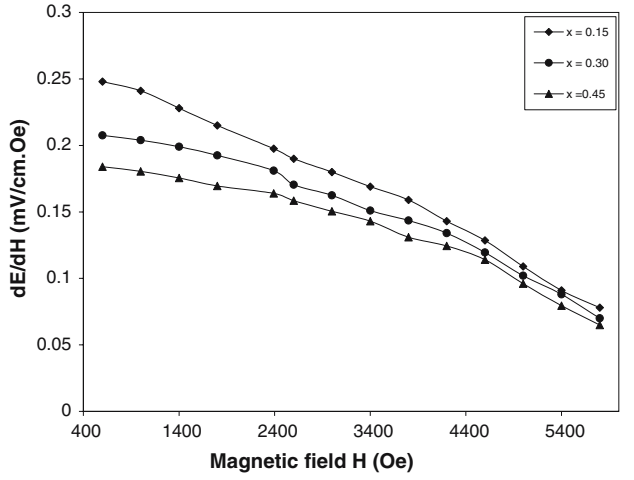

Fig. 7 Variation of magnetoelectric conversion factor with magnetic field for (x) $Ni_{0.5}Cu_{0.5}Fe_2O_4$ + (1–x) $Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ ME Composites

composite. These materials can be used as a Hall sensor for magnetic field measurement as well as electric current measurement.

Acknowledgements The authors are thankful to Dr. Y.D. Kolekar for fruitful discussions. The work was carried out under UGC-DRS II phase program.

References

1. Van Suchetelen J (1972) Philips Res Rep 27:28
2. Ryu Jungho, Vazquez Carazo Alfredo, Uchino Kenji, kim Hyoun-Ee (2001) J Electroceram 7:17
3. Suryanarayana SV (1994) Bull Mater Sci 17(7):1259
4. Kanai T, Ohkoshi SI, Nakasima A, Walanabe T, Hashimoto K (2001) Adv Mater 13:487
5. Hill NA (2000) J Phys Chem B 104:6694
6. Astrov DN (1961) Sovt Phys JETP 13:729
7. Harshe G, Dougherty JP, Newnham RE (1993) Int J Appl Electromagn Mater 4:161
8. Nan C-W (1994) Phys Rev B 50:6082
9. Qi X, Zhou J, Yue Z, Gul Z, Li L, Buddhudu S (2004) Adv Func Mater 14(9):920
10. Lupieko TG, Lopatina SS, Kozyrev IV, Zvyagintsev BI (1994) Inorg Mater 30:1353
11. Kadam SL, Patankar KK, Kanamadi CM, Chougule BK (2004) Mater Res Bull 39:2265
12. Kadam SL, Kanamadi CM, Patankar KK, Chougule BK (2005) Mater Lett 59:215
13. Patankar KK, Kadam SL, Mathe VL, Kanamadi CM, Kothavale VP, Chougule BK (2003) Brit Ceram Trans 102(1):19
14. Koops CG (1951) Phys Rev B 83:121
15. Maxwell JC (1973) Electricity and magnetism. Oxford University Press, London
16. Wagner KW (1993) Ann Physik 40:817
17. Parvatheeswara Rao B, Rao KH, Trinadh K, Calfun OF, (2004) J Optoel Adv Mater 6(3):951
18. Murthy VR, Sobhanadri J (1976) Phys Stat Sol A 36:K 133
19. El kony D, Saatan SA, Abo El Ata AM (2000) Egypt J Sol 23(1):137
20. Mathe VL, Patankar KK, Kothale MB, Kulkarni SB, Joshi PB, Patil SA (2002) Pramana – J Phys 58(5&6):1105
21. Kanamadi CM, Pujari LB, Chougule BK (2005) J Magn Magn Mater 295:139