

Electrical properties of $x\text{NiFe}_2\text{O}_4 + (1 - x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composites

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Abstract

The standard double sintering ceramic method was used to prepare the magnetoelectric (ME) composites with ferrite and ferroelectric phases. The crystalline phases of the sintered samples were studied by the X-ray diffraction technique. The dielectric parameter such as dielectric constant was determined as a function of frequency (in the range 100 Hz–1 MHz) and temperature (room temperature to 650 °C) at different test frequencies. The DC resistivity as a function of temperature and AC conductivity as a function of frequency were studied for different compositions. Effect of resistivity on ME voltage coefficient is explained.

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Keywords: XRD; DC resistivity; Dielectric constant; AC conductivity; ME effect

1. Introduction

Much interest has been recently created in magnetoelectric materials that generate electrical response (ME output) by application of external magnetic field (called ME_H effect) or magnetization by external electric field (called ME_E effect) [1]. In 1894, Curie pointed out the possibility of the polarization of the asymmetric molecular body under an external magnetic field. Subsequently in 1957, Landau and Lifshitz argued that the ME effect could principally exist in some magnetically ordered crystals [3]. The ME effect was observed for the first time in antiferromagnetic Cr_2O_3 in 1961 and later some single phase crystal families were discovered to have ME effect. However, these single phase materials show so weak a ME effect that they have not yet found any technological applications. Alternatively, piezoelectric/ferrite (e.g. $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$) composite ceramics have been found to exhibit a larger ME effect than that single phase materials which results from the coupling of magnetic–mechanical–electrical interactions [2].

The ME effect occurs as a product property between piezoelectric and piezomagnetic phases and is not observed in the individual component phases [4]. In order to obtain good ME

response first, no chemical reaction should occur between piezoelectric and piezomagnetic materials during the sintering process. Second, the resistivity of the magnetostrictive phase should be as high as possible to prevent the leakage of charges through low resistance path. Third, mechanical defects such as pores at the interface between the two phases should not exist in the composites for good mechanical coupling [5]. Important applications of these materials include magnetic electric sensors in radioelectronics, optoelectronics, microwave electronics and transducers in instrumentation [1].

Literature survey indicates that not much work on the physical properties of magnetoelectric composites has been done. The work available in literature is confined to the measurement of ME effect only. As the ME coefficient of composites largely depends on equilibrium between these two phases, it is necessary to study in detail the electrical behaviour and dielectric properties of these composites. The present paper reports studies on electrical properties such as DC resistivity, AC conductivity and dielectric constant of the present composites in order to understand the conduction mechanism and dielectric behaviour. The resistivity plays a vital role in getting good ME output as mentioned above.

Nickel ferrite is a well-known spinel magnetic material suited for high frequency applications in the telecommunication field due to its high resistivity and low eddy current losses. In addition, $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) has large figure of merit and superior dielectric and piezoelectric properties.

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2. Experimental

2.1. Preparation

The composites containing two individual phases viz. ferrite (NiFe_2O_4) and ferroelectric ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$) were prepared by standard double sintering ceramic method. The ferrite phase was prepared through solid-state reaction between AR grade NiO and Fe_2O_3 in appropriate molar proportions as starting materials. These basic oxides were mixed and ground in agate mortar for couple of hours and presintered at 900°C for 9 h. The ferroelectric phase was prepared following the same route by mixing AR grade BaCO_3 , SrCO_3 and TiO_2 in their appropriate molar proportions and presintering them at 1000°C for 10 h. The ME composites were prepared by mixing 15, 30 and 45 mol% of NiFe_2O_4 phase with 85, 70 and 55 mol% of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ phase, respectively. The composite mixtures were presintered at 1100°C for 11 h. The pellets having 3–4 mm thickness and 10 mm diameter were prepared using the hydraulic press. The pellets were sintered finally at 1200°C for 12 h to yield the final product.

2.2. Characterization

The samples were characterized by using X-ray diffractometer (Philips Model PW 1710) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Silver paste was applied on the surfaces of pellets for good ohmic contact. The DC resistivity was measured in the temperature range 300–800 K by two-probe method.

The dielectric constant was studied as a function of frequency (100 Hz–1 MHz) and as a function of temperature at test frequencies using LCR meter bridge (Model HP 4284 A). The AC conductivity of the samples was determined from the dielectric parameters using the relation

$$\sigma_{\text{AC}} = \omega \epsilon \epsilon_0 \tan \delta \quad (1)$$

where ϵ_0 is the permittivity of the free space, ω the angular frequency and $\tan \delta$ is the loss tangent.

3. Results and discussion

3.1. XRD analysis

The XRD patterns for the composites with $x=0.15$, 0.30 and 0.45 are shown in Fig. 1. The peaks in the XRD patterns were identified to be characteristics of both $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and NiFe_2O_4 phases. The NiFe_2O_4 ferrite phase exhibits a cubic spinel structure with lattice parameter $a = 8.33 \text{ \AA}$. The ferroelectric phase $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ shows a tetragonal perovskite structure with lattice parameters $a = 3.98 \text{ \AA}$ and $c = 3.99 \text{ \AA}$. The lattice parameters match fairly well with the lattice parameters of the

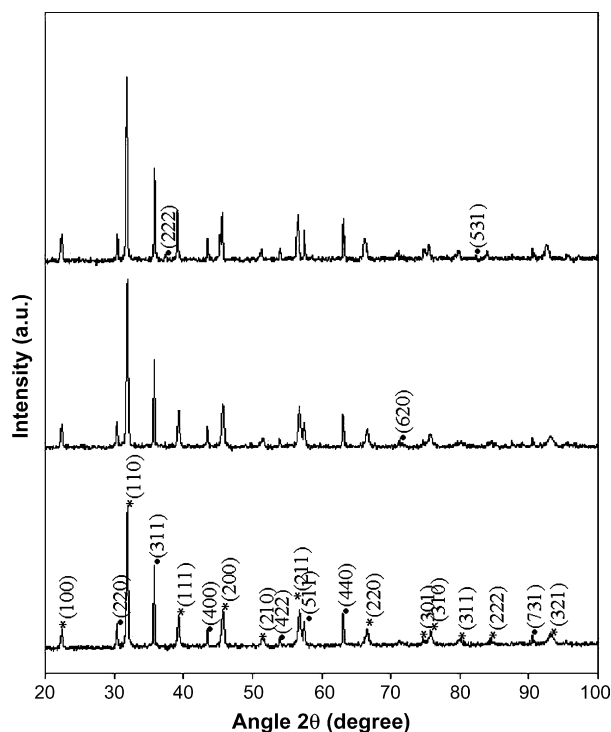


Fig. 1. XRD patterns of $x\text{NiFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composites.

components when present as single phase materials. A comparison between the XRD patterns of composites reveals that the intensity of ferrite peaks increases with increasing percentage of ferrite in the composites. The number of peaks of ferrite phase also increase with increasing ferrite content. The lattice parameters for all the compositions are given in Table 1.

3.2. Electrical resistivity

Electrical resistivity is an important property as far as the ME composites are concerned. The study of electrical resistivity produces valuable information regarding the behaviour of free and localized electric charge carriers in the samples. The variation of DC resistivity with temperature is shown in Fig. 2. There are two regions of conductivity. The presence of first region observed at

Table 1
Data on electric and dielectric properties of $x\text{NiFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ME composites

| Composition x | Lattice parameters | | | $\rho_{\text{RT}} (\times 10^9 \Omega \text{ cm})$ | Dielectric constant at T_c | T_c ($^\circ\text{C}$) | $(dE/dH)_H$ ($\mu\text{V}/\text{cm Oe}$) |
|-----------------|--------------------|----------------------|-------|--|------------------------------|----------------------------|--|
| | Ferrite phase | Ferroelectric phase | c/a | | | | |
| 0 | – | $a=3.97$ $c=3.97$ | 1.00 | 4.4 | – | – | – |
| 0.15 | $a=8.33$ | $a=3.96$ $c=3.98$ | 1.00 | 1 | 7358 | 605 | 380 |
| 0.30 | $a=8.32$ | $a=3.96$ $c=3.98$ | 1.00 | 0.78 | 4870 | 595 | 343 |
| 0.45 | $a=8.33$ | $a=3.96$ $c=3.97$ | 1.00 | 0.56 | 3796 | 590 | 293 |
| 1 | $a=8.33$ | – | – | 0.03 | – | – | – |

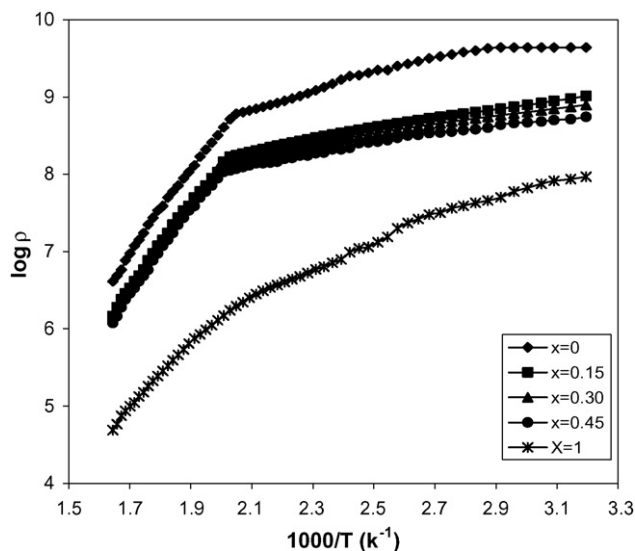


Fig. 2. Variation of DC resistivity with temperature for $x\text{NiFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

lower temperatures is due to impurities and is attributed to the ordered ferroelectric phase and the second region that occurs at higher temperatures which is due to polaron hopping may be attributed to disordered paraelectric state [6]. With increase in temperature resistivity goes on decreasing. The rate of decrease is slow up to the transition temperature and thereafter it decreases rapidly later on showing the semiconducting nature of the samples. The decrease in resistivity with increase in temperature is due to the increase in the thermally activated drift mobility of charge carriers according to the hopping conduction mechanism. In such a hopping process, the carrier mobility is temperature dependant and is characterized by activation energy [7]. The activation energy values are given in Table 1. The resistivity of the composites is found to decrease with increase in ferrite content mainly because when the ferrite particles disperse in the composite to make the chain with ferroelectric grains the electrical resistivity of the composites is reduced significantly because of the low resistivity of the ferrites [5].

3.3. Dielectric properties

3.3.1. Frequency dependence

The variation of dielectric constant as a function of frequency for the composites is shown in Fig. 3. The dielectric constant decreases with increase in frequency and remains constant at higher frequencies. The decrease is rapid at lower frequencies showing dispersion in the lower frequency region. The dielectric dispersion observed at lower frequencies is attributed to the interfacial polarization due to the two mediums that have different permittivities and conductivities. When an electric field is applied to the composites, space charge provided by the ferrite phase is accumulated at the interface of the two phases. The high dielectric constant observed at lower frequencies is not usually intrinsic but is rather associated with a heterogeneous conduction in the multiphase structure of the composites [8]. It is attributed to different types of polarizations (electronic,

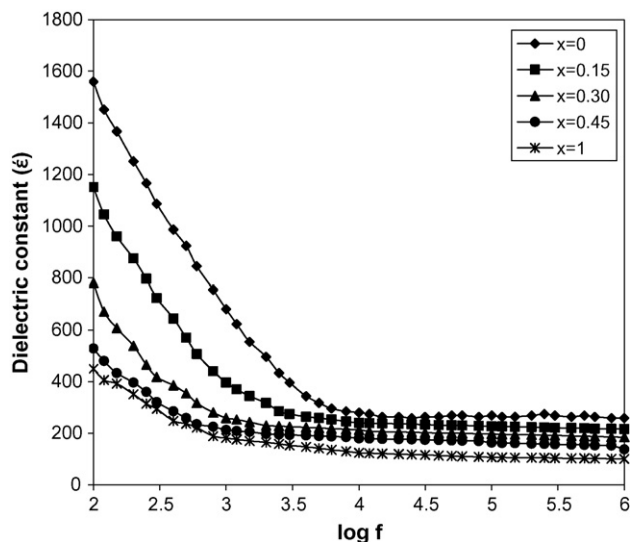


Fig. 3. Variation of dielectric constant with frequency for $x\text{NiFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

atomic, interfacial, ionic, etc.). At higher frequencies it arises due to the electronic polarization [9]. In case of composites, the high value of dielectric constant is ascribed to the fact that ferroelectric regions are surrounded by non-ferroelectric (ferrite) regions similar to the case relaxor ferroelectrics [10], this gives rise to interfacial polarization. From the figure it is also observed that the dielectric constant decreases with increase in ferrite content, which is due to lower dielectric constant of ferrite as compared to the ferroelectric phase.

3.3.2. Temperature dependence

Figs. 4–6 show the variation of dielectric constant of the composites with temperature at four different frequencies (viz. 1 kHz, 10 kHz, 100 kHz and 1 MHz). For all the composites, dielectric constant is found to increase with increase in temperature, reaches a maximum value at Curie temperature and follows

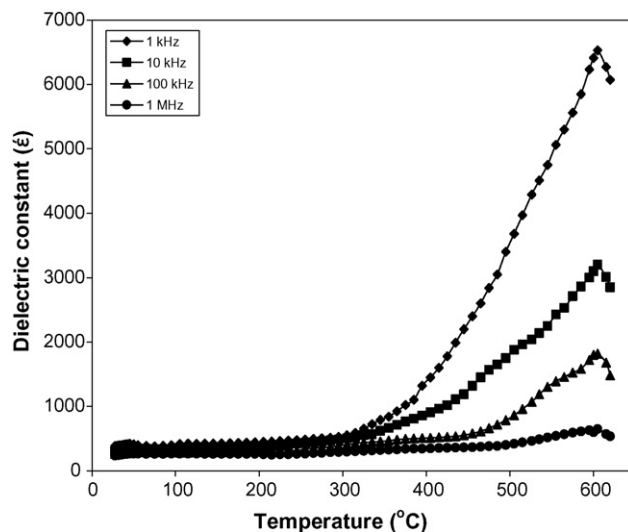


Fig. 4. Variation of dielectric constant with temperature for 15% $\text{NiFe}_2\text{O}_4 + 85\% \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

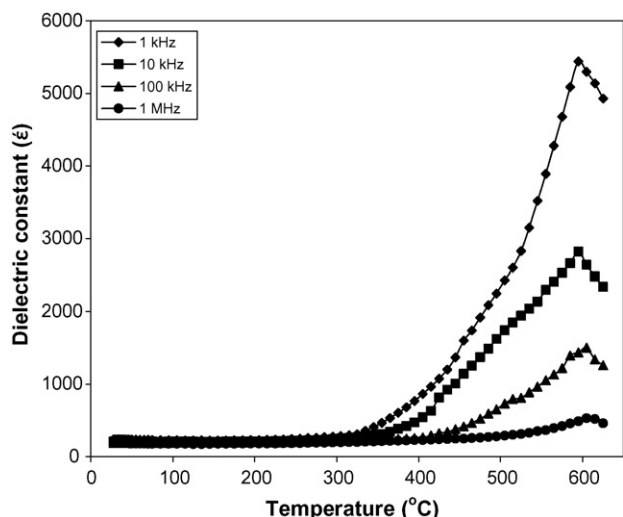


Fig. 5. Variation of dielectric constant with temperature for 30% NiFe_2O_4 + 70% $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

a decreasing trend indicating the phase transition. As the temperature increases AC electrical conductivity increases due to increase in drift mobility of thermally activated electrons. As a result dielectric polarization increases causing an increase in dielectric constant and loss tangent with temperature. The huge increase in dielectric constant near transition temperature (T_c) can be explained by the temperature dependant characteristics of domain wall motion. At lower temperature it is difficult for the domains to move so that the extrinsic contribution of domain walls to the dielectric response is small. At temperatures above T_c the ferroelectric phase has been translated to the paraelectric phase wherein all the domains disappear causing decrease in dielectric constant [11]. The Curie temperature is found to decrease with increase in ferrite content. This is because the electric field induced magnetic phase transition depends on the strength of interaction between electric and magnetic ordering, which in turn depends on the molar ratio of the phases [12]. The

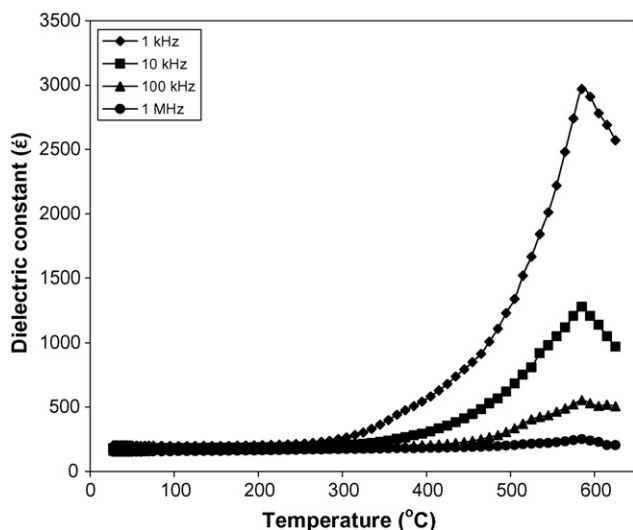


Fig. 6. Variation of dielectric constant with temperature for 45% NiFe_2O_4 + 55% $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

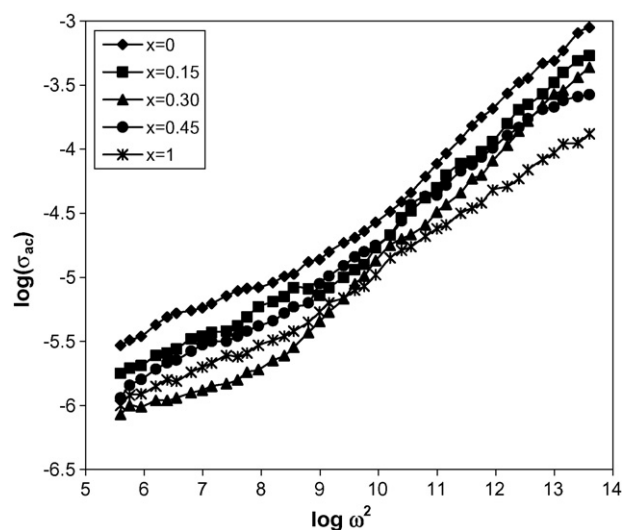


Fig. 7. Variation of AC conductivity with frequency for $x\text{NiFe}_2\text{O}_4$ + $(1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

decrease in dielectric constant is also attributed to the doping effect of ferrite addition in these composites. It is reported that difference in behaviour of permittivity as a function composition is a result of superposition of two effects, modification of the piezoelectric material with ferrite components and change in grain size of piezoelectric materials. Also the increase of ferrite content has a result of decrease in polarization efficiency leading to increased conductivity [13].

3.4. AC conductivity

To understand the conduction mechanism, AC conductivity was calculated. Fig. 7 shows the variation of $\log(\sigma_{AC} - \sigma_{DC})$ with $\log \omega^2$. The plots are almost linear indicating that the conductivity increases with increase in frequency. It is well known that there are two types of polarons viz. small polarons and large polarons. In the small polaron model the conductivity increases linearly with increase in frequency while in case of large polarons the conductivity decreases with increase in frequency [14]. For the present composites the plots indicate small polaron type of conduction. It has been also shown that for ionic solids the concept of small polaron is valid. This is in agreement with results reported earlier [15].

3.5. Effect of resistivity on ME effect

The ME effect of the ferrite–ferroelectric composite is known as product property of the composites. It is achieved from the interaction between different properties of the two phases in the composites [16]. Hence, the magnitude of ME effect is dependant on the compositions of the composite materials. The values of ME voltage coefficients are given in Table 1. Fig. 8 shows the variation of electrical resistivity and ME coefficient with the ferroelectric content. As the ferroelectric content increases both the resistivity and ME coefficient of the composites increase. This is due to the high resistivity of ferroelectric phase. The composite containing 85% of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ shows higher ME voltage

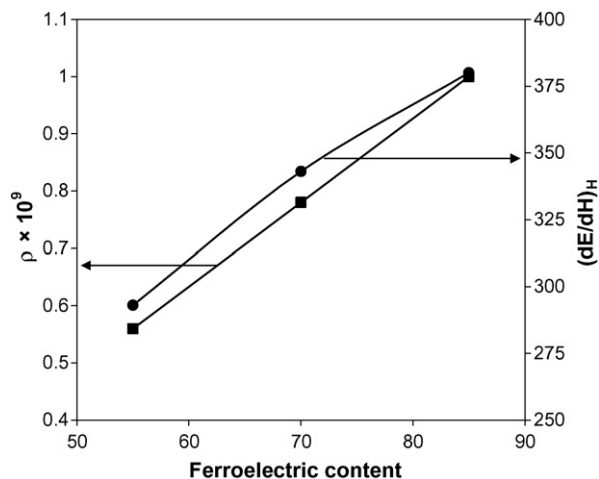


Fig. 8. Variation of DC resistivity and ME voltage coefficient with ferroelectric content for $x\text{NiFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ composite.

coefficient than others. The magnetostriction of the composites is small at these levels of BST that leads to decrease in dE/dH as predicted theoretically [16].

4. Conclusions

The ME composites containing ferrite and ferroelectric phases were prepared by standard conventional ceramic method. The X-ray characterization of materials reveals the presence of ferrite and ferroelectric phases. The samples show negative temperature coefficient of resistivity showing semiconducting nature. The decrease in dielectric constant with frequency shows the dielectric dispersion at low frequency regions. The dielec-

tric constant increases with increasing temperature and starts decreasing after passing through the transition temperature indicating phase transition from ferroelectric state to paraelectric state. The conductivity of the samples increases with increasing frequency that shows conduction due to small polaron hopping. Both the electrical resistivity and ME voltage coefficient are found to increase with increase in ferroelectric content.

References

- [1] C.W. Nan, L. Liu, N. Cai, J. Zhai, Y. Ye, Y.H. Lin, Appl. Phys. Lett. 81 (2002) 20.
- [2] J. Zhai, N. Cai, Z. Shi, Y. Lin, C.W. Nan, Appl. Phys. 95 (2004) 10.
- [3] P. Curie, J. Phys. 3 (1894) 393.
- [4] S.Q. Ren, L.Q. Wang, S.H. Song, F. Li, J. Mater. Sci. 40 (2005) 4375–4378.
- [5] J. Ryu, S. Priya, K. Uchino, H. Kim, Electroceramics 8 (2002) 107–119.
- [6] R.P. Mahajan, K.K. Patankar, A.N. Patil, S.C. Choudhari, A.K. Ghatage, S.A. Patil, Indian J. Eng. Mater. Sci. 7 (2000) 203–211.
- [7] J.Y. Zhai, N. Cai, L. Liu, Y.H. Lin, C.W. Nan, Mater. Sci. Eng. B 99 (2003) 329–331.
- [8] K.K. Patankar, S.S. Joshi, B.K. Chougule, Phys. Lett. A 346 (2005) 337–341.
- [9] S.L. Kadam, K.K. Patankar, C.M. Kanamadi, B.K. Chougule, Mater. Res. Bull. 39 (2004) 2265–2272.
- [10] S. Upadhyay, D. Kumar, O. Prakash, Bull. Mater. Sci. 19 (1996) 513.
- [11] X. Feng, Y. Xi, J. Appl. Phys. 92 (2002) 5.
- [12] S.L. Kadam, K.K. Patankar, V.L. Mathe, M.B. Kothale, R.B. Kale, B.K. Chougule, Mater. Chem. Phys. 78 (2003) 684–690.
- [13] D. Pandey, N. Singh, S.K. Mishra, Indian J. Pure Appl. Phys. 32 (1994) 616–623.
- [14] K.K. Patankar, S.S. Joshi, B.K. Chougule, Phys. Lett. A 346 (2005) 337–341.
- [15] J. Appel, F. Seitz, D. Thurnbull, H. Ehrenreich, Solid State Phys. 21 (1968) 193.
- [16] J.Y. Zhai, N. Cai, L. Liu, Y.H. Lin, C.W. Nan, Mater. Sci. Eng. B 99 (2003) 329–331.