Research Journal of Material Sciences ____ ISSN 2320–6055
Vol. **1(3),** 7-11, April **(2013)** *Res. J. Material Sci.*

Structural, Dielectric and Magnetic Study of $0.7(Pb_{0.85}La_{0.15}TiO_3)/0.3(Ni_{0.4}Zn_{0.6}Fe_2O_4)$ Composite

Parmar Kusum, Sharma Anshu, Bala Kanchan and Negi N.S.
Department of Physics, Himachal Pradesh University Shimla-05, INDIA

Available online at: www.isca.in
Received 13th October 2012, revised 27th December 2012, accepted 9th April 2013

Abstract

In the present study, $Pb_{0.85}La_{0.15}TiO_3$(PLT) and $Ni_{0.4}Zn_{0.6}Fe_2O_4$(NZF) materials were synthesized by using the Metallo - Organic Decomposition (MOD) chemical route, which were further used as basic materials for the preparation of $0.7(Pb_{0.85}La_{0.15}TiO_3)/0.3(Ni_{0.4}Zn_{0.6}Fe_2O_4)$ [PLT/NZF] composite. The structural analysis of individual phases PLT, NZF and PLT/NZF composite were carried out using X-ray diffraction study which confirms a tetragonal pervoskite structure for PLT phase, cubic spinel structure for NZF phase and no any secondary phases present in composite. The microstructure of composite was studied by using scanning electron microscope (SEM). The room temperature hysteresis measurement shows the low value of saturation magnetization (M_s) of PLT/NZF composite (~ 12emu/g) as compared to ferrite (NZF) phase (~37emu/g). The variation of dielectric constant and loss factor of composite with frequency was also studied. The variation of dielectric constant with temperature of PLT/NZF composite show diffuse phase transitions (DPT).

Keywords: Composite, MOD technique, XRD, SEM, Magnetic study, Dielectric study.

Introduction

The Magneto-electric (ME) composites mainly consist of two phases, ferrite (piezomagnetic) and ferroelectric (piezoelectric). Ferrites show piezomagnetic behavior due to their magnetostriction property in presence of ac magnetic field[1]. The cross mechanical coupling between ferrite and ferroelectric phases give rise to new materials with magnetoelectric (ME) property. The ME property of a composite is shown by the electric polarization on the application of magnetic field or magnetic polarization on the application of electric field[2,3]. ME composites have considerable prospective for applications in multifunctional devices like sensors, transducers, magneto-electric memory devices etc.[4]. A number of such composites exist between lead (Pb) based piezoelectric and magnetic constituents like Ni, Zn based ferrite[5-10]. In this work we have taken PLT as the piezoelectric phase and NZF as piezomagnetic phase. PLT and NZF materials are synthesized by metallo organic decomposition chemical route. MOD chemical route is mostly used to prepare thin film solution[11,12]. To the best of our knowledge, no reports are available in the literature on studies of MOD processed ferrite/ferroelectric composite materials. The advantages of this method include high solution stability, low processing temperature, and composition is easily controllable. Once the ferrite/ferroelectric composite synthesized, it is important to know if the intrinsic properties of the magnetic and ferroelectric phases maintained, without major changes of the interaction mechanisms between the two phases. The present work studies the structural, dielectric and magnetic behavior of PLT/ NZF composite.

Material and Methods

PLT and NZF phases of PLT/NZF composite were individually prepared by using MOD chemical route. For the synthesis of PLT, a stoichiometric amount Lead-2-ethylhexonate (with 20% extra lead was taken to compensate lead loss), Lanthanum-2-ethylhexonate and tetra- n-butyl orthotitanate solutions were mixed, heated at 80°C for 1 hr and 5-7 drops of polyethylene glycol (PEG) were added as surfactant. The mixed solution was then dried at 300°C to get powder. The dried powder was presintered at 650°C for 2 hrs. Similar steps were followed to prepare NZF by taking Nickel-2-ethylhexonate, Zinc-2-ethylhexonate and Iron-3-ethylhexonate as precursor solutions. The dried powder was presintered at 700°C for 3 hrs. PLT and NZF powder were mixed in 0.7:0.3 weight ratios. After uniform mixing the PLT/NZF composite was sintered at 750°C for 1hr. The pellets of 9mm diameter and ~1 to 1.2 mm thickness were formed and sintered at 950°C for 4 hrs for dielectric studies.

The crystallographic and microstructural properties of the ferrites were studied by X-ray diffraction (PANalytical X'Pert PRO diffractometer) with CuKα radiation and scanning electron microscope (SEM Quanta 250, FEI Make - USA) respectively. The compositional analyses of composite were performed using energy dispersive x-ray spectroscopy (EDXS). The magnetic properties were measured by using vibrating sample magnetometer VSM (Microsense, USA) at room temperature. The dielectric measurements were performed by using Wayn Kerr 6520 impedance analyser in the frequency range of 1 kHz to 1MHz and temperature range 150°C to 380°C.

Table-1
Lattice Parameters and Saturation magnetization values for PLT, NZF and composite

Compositions	Lattice Parameters		c/a	Saturation Magnetization Ms(emu/g)
	a(A°)	c(A°)		
PLT	3.94384	3.95498	1.00282	-
NZF	8.4087	-	-	37
PLT/ NZF	3.93432/ 8.4079	3.95044/ -	1.00409	12

Results and Discussion

The X-ray diffraction patterns of individual PLT, NZF phases and composite are shown in figure 1. All diffraction lines in XRD pattern reveal a tetragonal pervoskite structure for PLT phase and cubic spinel structure for NZF phase. XRD pattern of composite confirms no any secondary phase which reveals that individual phases (PLT, NZF) have not chemically reacted. The lattice parameters for ferroelectric PLT and ferrite NZF phase have been calculated and are given in table 1.

Scanning Electron Microscope (SEM) images of composite PLT/NZF, PLT and NZF powder sample sintered at 750°C, 650°C and 700°C are shown in figure 2(a-c). The SEM micrographs show the polycrystalline nature of microstructure with different grain sizes which are non-uniformly distributed throughout the sample surface. Energy dispersive x-ray spectroscopy (EDX) spectra of the PLT/NZF composite sintered at 750°C is shown in figure 3, which confirms the presence all the elements (Pb,La,Ti,Ni,Zn and Fe).

Hysteresis loops of composite PLT/NZF and NZF powder sintered at 750°C and 700°C are shown in figure 4. Both NZF ferrite and PLT/NZF composite show ferromagnetic character having small value of coercive field (H_c) and remanent magnetization (M_r) at room temperature (as shown in inset of figure -4). The saturation magnetization (M_s) value for NZF is ~ 37emu/g and for composite is ~ 12emu/g. It follows that magnetization of composite originates from the unbalanced anti parallel spins as in the pure NZF[13]. However, magnetic parameters (H_c, M_r and M_s) of composite have less value than for NZF which may be explained on the basis that some of ferrite grains are connected to ferroelectric grains which act as pores in the presence of applied magnetic field[14].

The variation of dielectric constant and loss factor (tanδ) of PLT, PLT/NZF composite and NZF pellets sintered at 950°C with frequency at room temperature are shown in figure 5(a-b) . At lower frequency region the value of dielectric constant decrease to minimum value and then remains constant afterwards at high frequencies. The dielectric dispersion at lower frequency is due to Maxwell-Wagner type interfacial polarization in agreement with Koop's phenomenological theory[15]. At higher frequencies, the dielectric constant remains constant due to electronic polarization. In electronic polarization, electric dipoles are unable to follow the fast variation of the applied alternating electric field resulting in low dielectric constant. The value of dielectric constant of PLT/NZF composite at room temperature lies between NZF and PLT phase. Similar type of decrease in dielectric constant with addition of ferrite to ferroelectric phase has reported by Lopatine et.al.[16] and Gelyasin and Laletin[17] in$NiCoFe_2O_4$ +$BaTiO_3$ composites and $NiCoFe_2O_4$ +PZT composites. The variation of loss factor (tanδ) with frequency shows the similar dispersion as that of dielectric constant with frequency.

The variation of dielectric constant of PLT, PLT/NZF composite pellets sintered at 950°C with temperature at fixed frequencies i.e. at 1 kHz, 10 kHz, 100 kHz and 500 kHz are shown in figure 6(a-b) . It has been observed that dielectric constant increases with the increase of temperature and attains the maxima. In PLT phase a sharp and well defined peak has been observed which corresponds to transition from ferroelectric to paraelectric phase whereas in PLT/NZF a broad peak has been observed which correspond to diffuse phase transition[18]. Diffuse phase transitions (DPT) of composite can be explain on the fact that ferroelectric grains are surrounded by non-ferroelectric (NZF)grains. It has been reported in literature [18, 16, 19] that in various ME composites the broadening of peak is one of the most important characteristic of a disorder perovskite structure with diffuse phase transition. The broadening of the transition has been attributed to disorder in the arrangement of cation on one or more crystallographic sites in the structure, leading to a microscopic heterogeneity in composites and thus in distribution of different localized Curie points.

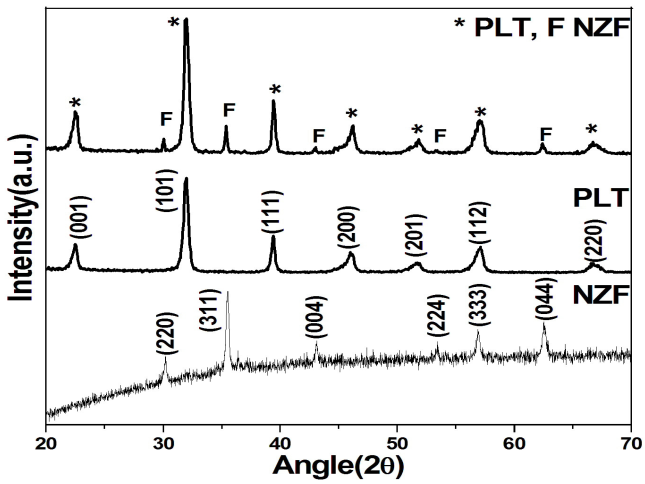

Figure-1
XRD pattern for PLT, NZF and PLT/NZF composite material sintered at 650° C 700° C, and 750° C

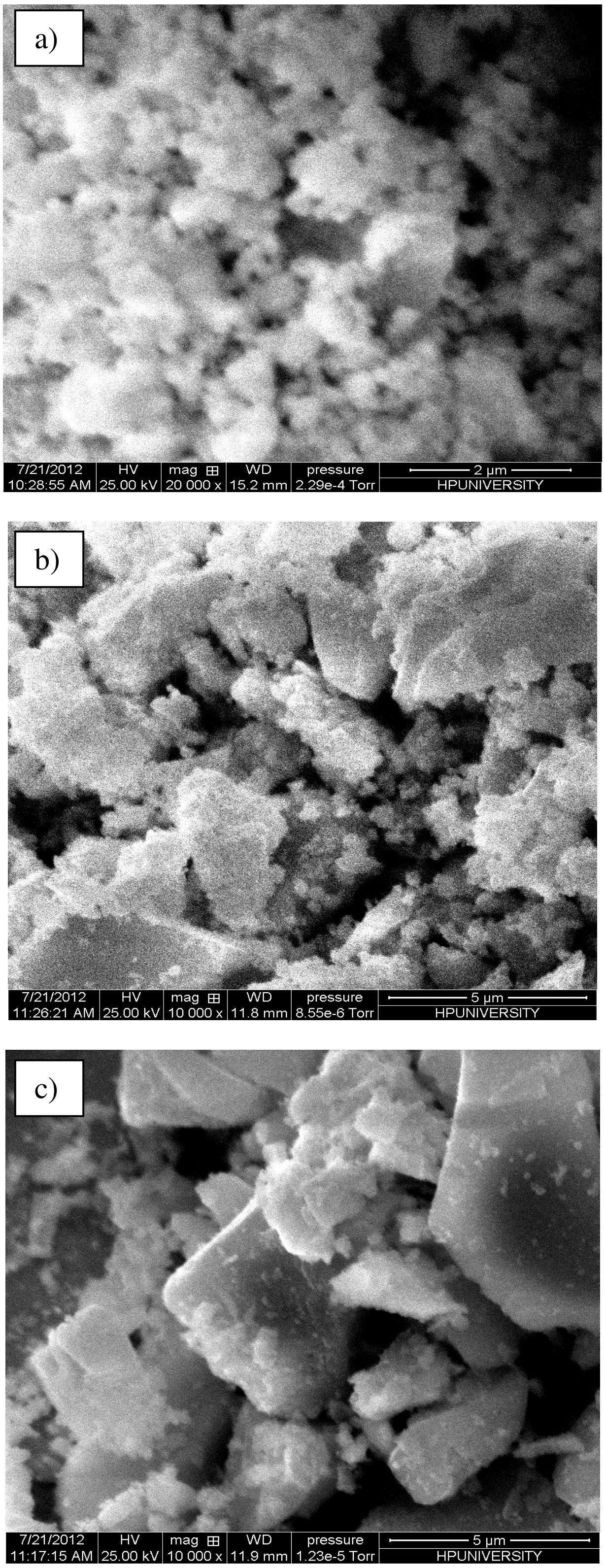

Figure-2
SEM images of a) PLT/NZF composite b) PLT and c) NZF powder sintered at 750° C, 650° C and 700° C

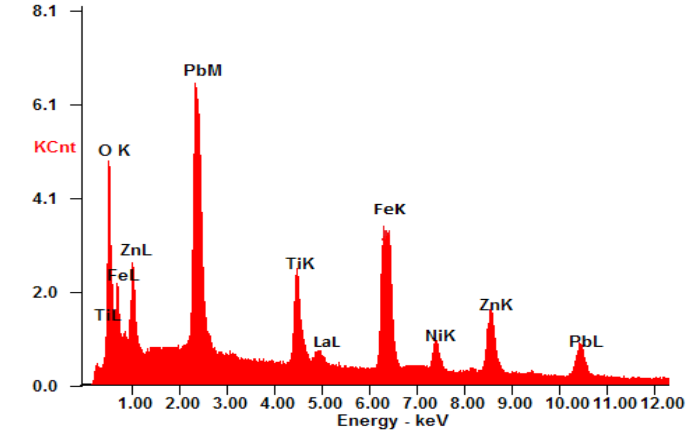

Figure-3
EDX spectra of PLT/NZF composite

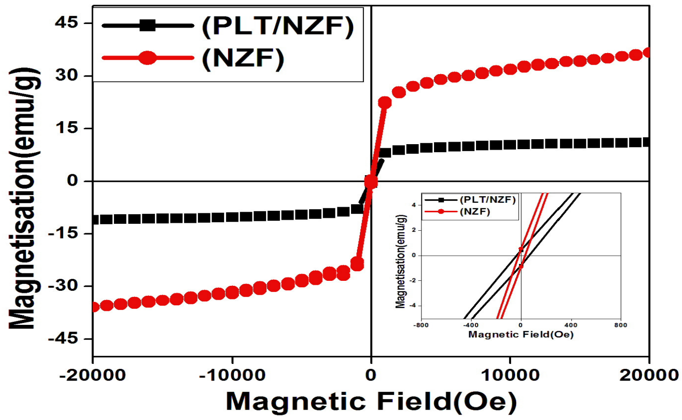

Figure-4
Hysteresis loop for NZF, PLT/NZF composite powder sintered at 700°C, 750°C

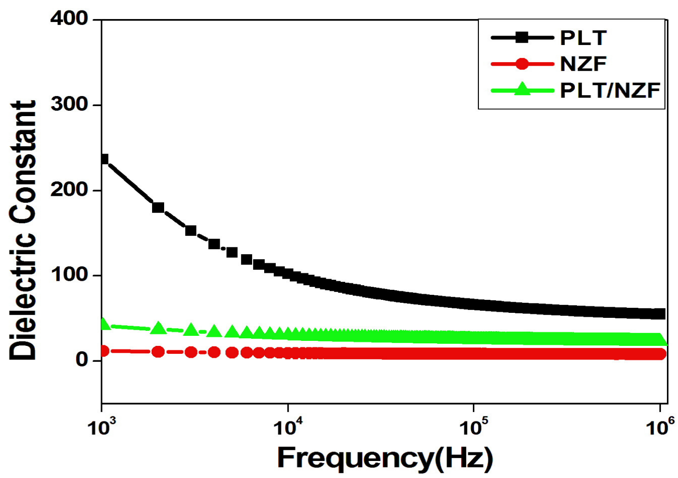

FIGURE-5
Dielectric Constant Vs frequency plot for PLT, NZF and PLT/NZF composite

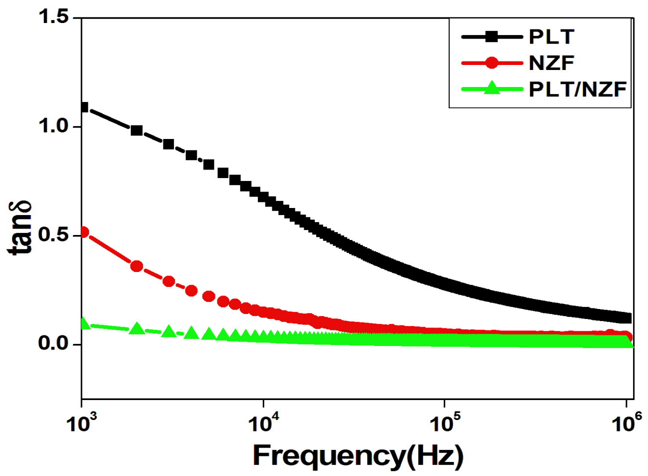

Figure-5
Loss factor tanδ Vs frequency plot for PLT, NZF and PLT/NZF composite

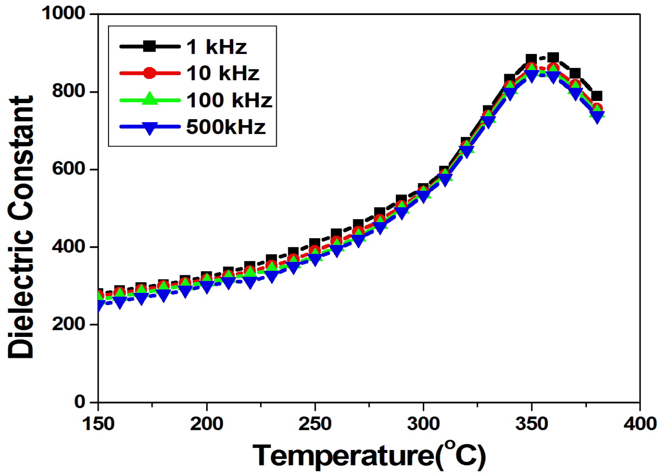

Figure-6
Dielectric Constant Vs Temperature plot for PLT

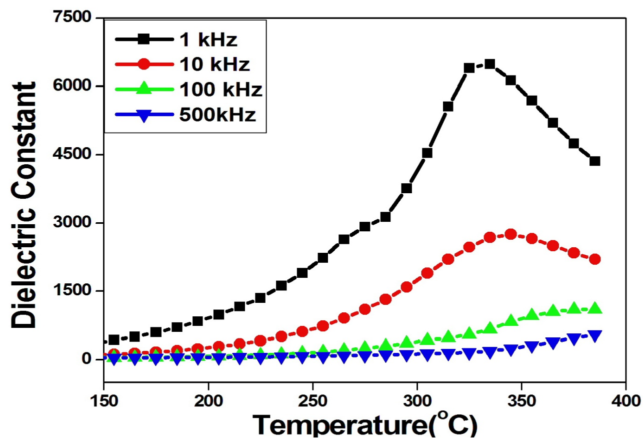

Figure-6
Dielectric Constant Vs Temperature plot for PLT/NZF composite

Conclusion

PLT/NZF composites have been synthesised by chemical route. XRD confirms the coexistence of both phases (PLT and NZF) in PLT/NZF composite. XRD pattern reveals tetragonal perovskite structure for PLT and cubic spinel structure for ferrite phase. The MH curve of Composite shows ferromagnetic character at room temperature. Both dielectric constant and loss factor of composite show dispersion in the lower frequency region. The variation of dielectric constant of composite with temperature shows a broad peak, which indicates the diffuse phase transition from ferroelectric to paraelectric phase. Maxwell-Wagner relaxation at the interface of the ferroelectric and ferromagnetic phases plays important role particularly at low frequencies and higher temperatures. The dielectric and magnetic studies suggest PLT/NZF composite as an important multiferroic composite for further magneto-electric investigations. In order to study the ferroelectric and ferromagnetic domain interaction in the composite further investigations are necessary.

Acknowledgments

One of authors (Kusum Parmar) would like to thank UGC(BSR) for awarding fellowship.

References

1. Srinivasan G., Rasmussen E.T. and Hayes R. Magnetoelectric effects in ferrite-lead zirconate titanate layered composites: The influence of zinc substituition in ferrite, *Physical Review B,* **67,** 014418 **(2003)**

2. Fiebig M., Revival of the magnetoelectric effect, *J Phys D: Appl Phys*, **38(3),** R123–R152 **(2005)**

3. Nan C.W., Bichurin M.I., Dong S.X., Viehland D. and Srinivasan G., Multiferroic Magnetoelectric Composites:Historical Perspective, Status, and Future Directions. *J. Appl. Phys.* **103** 031101**(2008)**

4. Groessinger R., Duong G.V., Baques d Bueno, Magnetoelectric materials—New materials for applications, *Int J Appl Electromag Mech*, **25(1)** 3–11 **(2007)**

5. Fawzi Abdul Samee, Effect of sintering temperature on structural, electrical, magnetic hysteresis and magnetoelectric effect on (x) $Ni_{0.7}Zn_{0.3}Fe_2O_4$ + (1-x) PLZT composite by Co-precipitation method, *Advances in Applied Science Research,* **2(5)** 577-589 **(2011)**

6. Fawzi Abdul Samee, Sheikh A.D., Mathe V.L. Composition dependent electrical, dielectric, magnetic and magnetoelectricproperties of (x)Co0.5Zn0.5Fe2O4 + (1−x)PLZT composites, *J.Alloys Compd.,* **493** 601–608 **(2010)**

7. Ryu J., Carazo A.V., Uchino K., and Kim H.E., Piezoelectric and magnetoelectric properties of lead zirconate titanate/Niferrite particulate composites, *Journal* *of Electroceramics*, **7,** 17–24 **(2001)**

8. Zhai J., Cai N., Shi Z., Lin Y. and Nan C.W., Magnetic-dielectric propertiesofNiFe2O4/PZT particulatecomposites, *Journal of PhysicsD*, **37,** 823–827 **(2004)**

9. Kulkarni S.R., Kanamadi C.M. and Chougule B.K., Magnetic and dielectric properties of Ni0.8Co0.1Cu0.1Fe2O4+PZT composites, *Journal of Physics and Chemistry of Solids* **67** 1607–1611**(2006)**

10. Adnan Islam Rashed and Shaahank Priya, Effect of piezoelectric grain size on magnetoelectric coefficient of $Pb(Zr_{0.52}Ti_{0.48})O_3–Ni_{0.8}Zn_{0.2}Fe_2O_4$ particulate composites, *J. Mater, Sci.,* **43** 3560**(2008)**

11. Zhang D.Z., Zheng X.J., X.Xu et. al., Ferro-piezoelectric properties of $0.94(Na_{0.5}Bi_{0.5})TiO_3–0.06BaTiO_3$ thin film prepared by metal–organic decomposition, *J. Alloys Compd.,* **504** 129-133 **(2010)**

12. Kumar acharya Susant, Lee Sang-Kwon, Ahn Byung-Guk et.al. Ferroelectric and piezoelectric properties of lead –free $BaTiO_3$ doped $Na_{0.5}Bi_{0.5}TiO_3$ thin film from matal-organic solution deposition, *J. Alloys Compd.,* **540,** 204-209 **(2012)**

13. Albuquerqne A.S., Ardission J.D. and Maccdo W.A.A., *J. Appl. Phys.,* **87**, 4352-4357 **(2000)**

14. Chao Xiaolian, Yang Zupei, Dong Mingyuan, Zhang Yi, Piezoelectric, dielectric and magnetic properties of (1–x)Pb[Zr, Ti, $(Mg_{1/2}W_{1/2})$, $(Ni_{1/3}Nb_{2/3})]O_3+x$(Ni, Co, Cu)FeO_4 composites, *J.Magn. Magn. Mater.,* **323** 2012-2016 **(2011)**

15. Koops C.G., On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies, *Physical Review,* **83** 121–124 **(1951)**

16. Lopatine S., Lopatina I. and Lisnevskaya I.V., Magnetoelectric PZT/ferrite composite material, *Ferroelectrics*, **162** 63–68 **(1994)**

17. Gelyasin A.E. and Laletin V.M., Properties of Barium titanate ceramics with Nickel ferrite addition, *Izvestija AkademiiNauk SSSR*, **24** 2067–2069**(1988)**

18. Patankar K.K. et. al. Dielectric behaviour and magnetoelectric effect in CuFe2O4-Ba0.8Pb0.2TiO3 composites, *Materials Chemistryand Physics,* **72,** 23–29**(2001)**

19. Cross L.E., Relaxor ferroelectrics, *Ferroelectrics*, **76** 241–267 **(1987)**