JOURNAL OF MATERIALS SCIENCE **37** (2002) 807–811

Dielectric and mechanical properties of PZN-PFN-BZN ternary system

M. JAIN, A. GARG, A. K. TRIPATHI, T. C. GOEL
Department of Physics, Indian Institute of Technology, Delhi, New Delhi 110016, India
E-mail: tcg@physics.iitd.ernet.in

The Ferroelectric relaxor ternary system 0.5PZN-(0.5 − x)PFN-xBZN was prepared using the columbite precursor method. The stability of the perovskite phase was studied as a function of BZN content in the system. It was observed that BZN is a good stabilizer of perovskite phase because of the high value of electronegativity difference between its cation and anion. It has also been observed that addition of BZN increases the dielectric maxima peak value and decrease the Curie temperature of the ceramics. The ternary composition 0.5PZN-0.425PFN-0.075BZN has been identified for MLCs applications. It has a T_c of around room temperature with a peak dielectric constant $\cong$6400 and tan $\delta \sim 0.05$. The mechanical properties of relaxor materials have also been studied and reported.

1. Introduction

Multilayer ceramic capacitors can be improved by either reducing the thickness of the dielectric layer or increasing the dielectric constant. There are certain limitations on reducing the dielectric thickness due to problems with fabrication processes and dielectric breakdown. Lead based relaxors, because of their high dielectric constant, are useful dielectrics for increasing the capacitance volumetric efficiency of multilayer ceramic capacitors. The relaxor materials of the form $Pb(B_1B_2)O_3$ usually show a high dielectric constant with a broad dielectric maxima [1–3] and are of particular interest in multilayer ceramic capacitors (MLCs) because of their large capacitance, compact design and high reliability. Also, these relaxors have a relatively low sintering temperature (~1100°C) as compared to traditionally used barium titanate based ceramic materials (~1300°C) [4–6] which facilitates the replacement of platinum electrodes by less expensive silver or silver palladium electrodes. Amongst the lead based relaxors, lead zinc niobate (hereafter designated as PZN) is a ferroelectric with the perovskite structure which exhibits a diffused phase transition. It has a rhombohedral structure at room temperature and undergoes a phase transition at ~140°C to the paraelectric cubic phase [7, 8]. It is, however very difficult to prepare pure perovskite phase for PZN ceramics [9–11]. A mixture of perovskite and pyrochlore phase is usually obtained. The presence of pyrochlore phase severely degrades the dielectric properties. It has been observed that PZN ceramics can be stabilized in pure perovskite phase by the addition of other perovskite materials, having cations with a high electronegativity difference and tolerance factor [12, 13]. Additives like $SrTiO_3$ (ST), $BaTiO_3$ (BT), $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN), $Pb(Fe_{1/2}Nb_{1/2})$ O_3 (PFN) and $PbTiO_3$ (PT) have been successfully used to stabilize PZN ceramics [14]. In the present study an attempt has been made to obtain PZN based relaxors in a pure perovskite phase. PFN and BZN, which are known to stabilise in a perovskite phase have been used to prepare PZN-PFN-BZN solid solution.

The applications of these ceramics involve electrical and thermal induced stresses as well as mechanical loads induced due to vibrations, which may result in mechanical failure. The study of the mechanical properties of relaxor ceramics has, however, received very little attention. The mechanical properties of these ceramics in addition to structural and dielectric properties have been studied and are reported in this paper.

2. Experimental procedure

The compositions selected for the present study are 0.5PZN-(0.5 − x)PFN-xBZN where x varies as 0,0.05, 0.075 and 0.1. All samples were prepared using a columbite precursor method [15]. Weighed amounts of ZnO and Nb_2O_5 were mixed and wet ball milled in propanol using Zirconia (ZrO_2) ball in a poly-propylene jar for 12 hours. The slurry was dried by heating it at 80°C on a hot plate with continuous stirring. The dried powder was crushed in an agate mortar pestle and calcined in a platinum crucible at 1000°C for 4 h. The columbite $ZnNb_2O_6$ (ZN) thus obtained was crushed and sieved. Similarly, columbite $Fe_2Nb_2O_8$ (FN) was prepared using the powders of Fe_2O_3 and Nb_2O_5. PZN-PFN was prepared by mixing appropriate amount of PbO with ZN and FN while BZN was prepared using $BaCO_3$ and precalcined ZN. 3 wt% excess PbO was added to the compositions for compensation of lead loss during calcination and sintering. The final ternary compositions were prepared by ball milling and calcining PZN-PFN and BZN powders at 900°C/2 h. The calcined powder was crushed, sieved and mixed with 4 wt% PVA binder to make samples. Pellets of 12 mmϕ and 2–3 mm thick were pressed using a uniaxial pressure of ~500 MPa. Binder removal was carried out by slowly heating the pellets to 600°C and holding there for 1 h which were subsequently sintered at 1150°C/2 h in a close set up using PZ + 10% PbO mixture to create lead rich atmosphere.

X-ray diffraction (XRD) of the sintered pellets was carried out using Rigaku diffractometer. The percentage of perovskite phase was calculated using the following equation:

$$\%\text{perov} = \frac{100 \times \text{Iperov}}{\text{Iperov} + \text{Ipyro}}$$

where Iperov and Ipyro are the intensities of the 100% peaks of the respective phases.

The sintered density of the samples was obtained using Archimede's principle. The samples were electroded using air-dry silver paste for electrical measurements. The Dielectric constant and loss tangent were determined as a function of temperature and frequency using a Hewlett-Packard impedance analyzer (HP 4192A).

The Fracture toughness (K_{IC}) of the samples was measured on mirror polished pellets using an indentation technique [16]. For this, samples were polished to a mirror finish using 3 and 1 μm diamond paste successively. These were then cleaned using acetone and indented in a Vicker's Microhardness Tester (Leitz Model2002, Germany) at 10 N load. 6–8 indentations were carried out on each sample. The K_{IC} was obtained using the formula [17].

$$K_{\text{IC}} = 0.0726\ PC^{-3/2}$$

where, P is the load in Newton and $2C$ is the total crack length.

The hardness was obtained at 4.9 N using the formula [18]

$$H_{\text{v}} = 0.47P/a^2$$

where, P is the load in Newtons and, a, is half the average diagonal length.

3. Results and discussion

3.1. Structural study (X-ray diffraction, sintered density and SEM studies)

Fig. 1a–d shows the X-ray diffractograms of sintered samples of composition 0.5PZN-(0.5 − x)PFN- xBZN for different values of x. The ternary system shows the presence of pyrochlore phase along with perovskite phase for $x = 0$ and $x = 0.05$. The ceramic stabilises in the pure perovskite phase when the molar ratio of BZN is increased further ($x = 0.075/0.1$). Variation in the perovskite phase with BZN content as evaluated from XRD is shown in Fig. 2. This increase in perovskite phase with an increasing amount of BZN may be due to the higher value of tolerance factor, which is due to absence of lead and the electronegativity difference in BZN ceramics as compared to PFN [19].

The variation of sintered density with the variation in moles of BZN in the system is shown in Fig. 3.

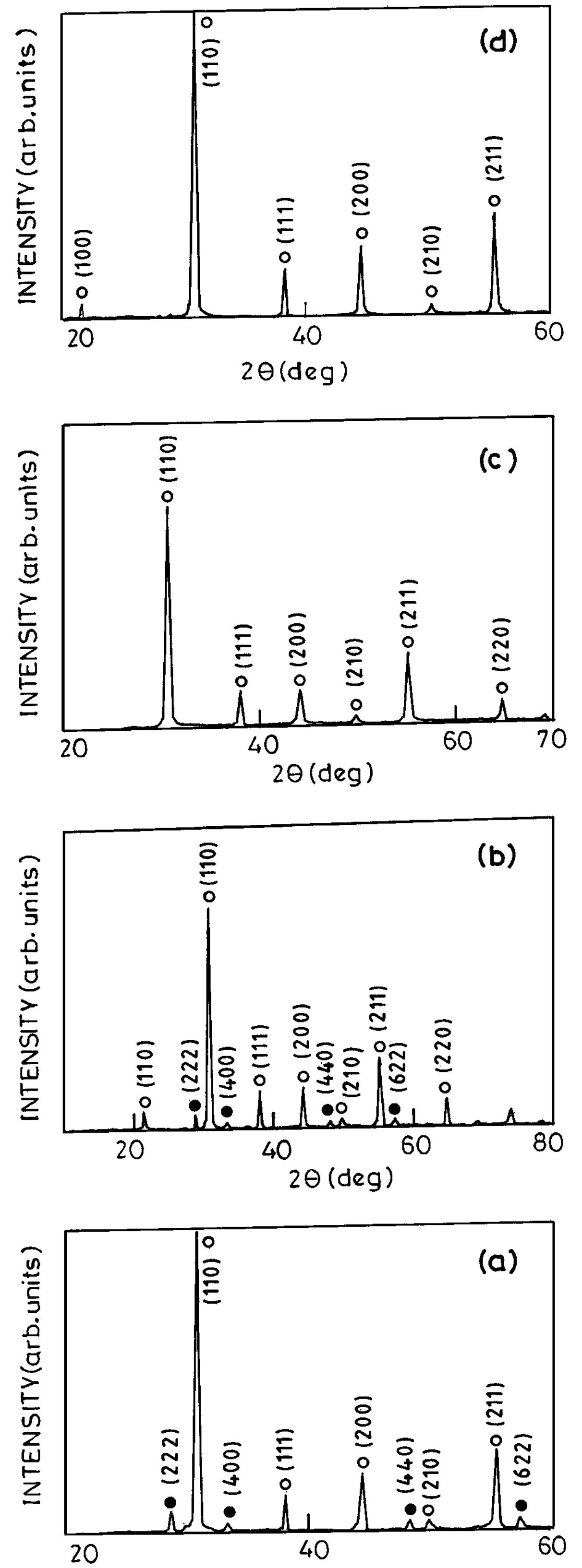

Figure 1 XRD of 0.5PZN-(0.5 − x)PFN-x BZN samples (a) $x = 0.0$ (b) $x = 0.05$ (c) $x = 0.075$ (d) $x = 0.1$.

It is observed that the sintered density decreases with increasing BZN content in the samples. In the PZN-PFN-BZN ternary solid solution, PFN has the lowest sintering temperature (~950°C) and may act as flux. Therefore, the decrease in low sintering temperature PFN content in the sample will lead to a decrease in the sintered density. The SEM of these ceramics shows

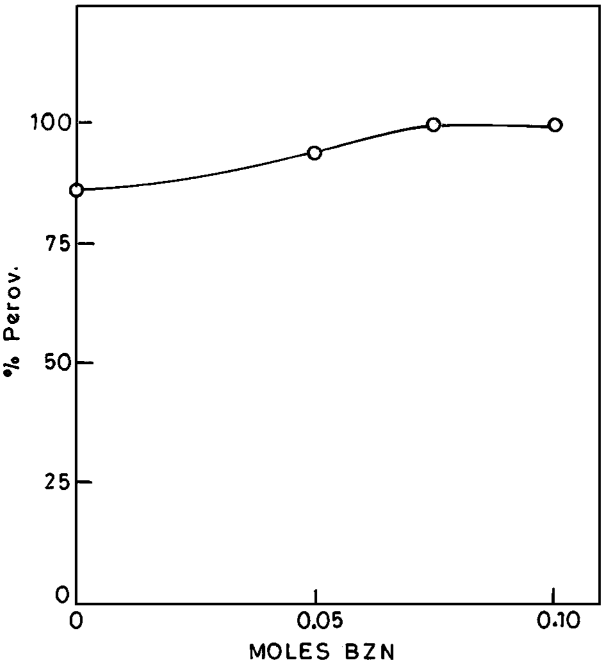

Figure 2 Variation of perovskite phase percentage in the ceramic with BZN content.

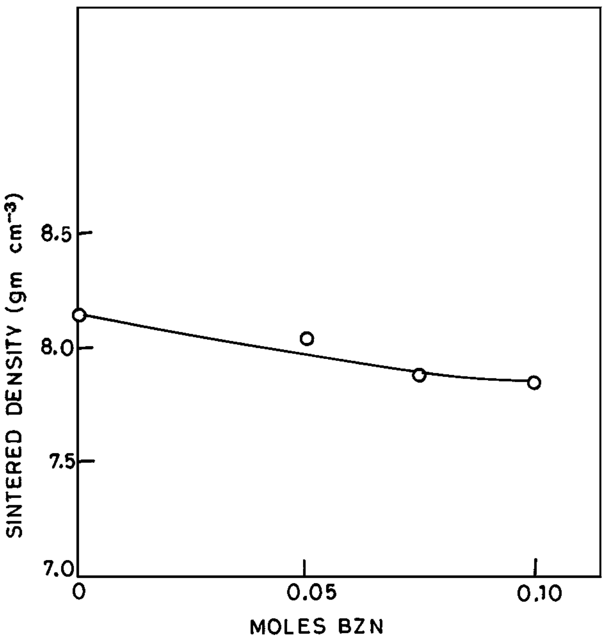

Figure 3 Variation of sintered density with BZN content.

no significant variation in the grain size with changing BZN content.

3.2. Dielectric properties

Fig. 4 shows the typical temperature variation of the dielectric constant at different frequencies for the PZN-PFN-BZN system. It exhibits a broad dielectric constant maximum and exhibits relaxor behavior. A typical temperature dependence of the dissipation factor (tan δ) at various frequencies is shown in Fig. 5. The dissipation factor is found to be practically independent of BZN content in the ferroelectric region. The temperature dependence of dielectric constant (at 1 kHZ) for different BZN contents has been plotted in Fig. 6. It is observed that the dielectric constant maxima is around $\sim$6400 for all compositions except for $x = 0.1$, where it is significantly higher ($\sim$8400), though its transition temperature is below 0°C.

The transition temperature of the ferroelectric should not be below room temperature for practical applications. The Room temperature value of dielectric constant in composition with $x = 0.075$ is very high $\sim$6400

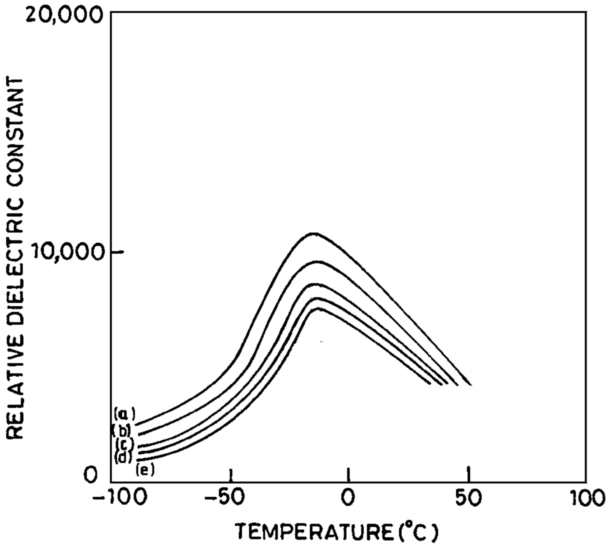

Figure 4 Variation of dielectric constant with temperature for 0.5PZN-0.425 PFN-0.075BZN sample at (a) 100 Hz (b) 1 kHz (c) 10 kHz (d) 1 MHz.

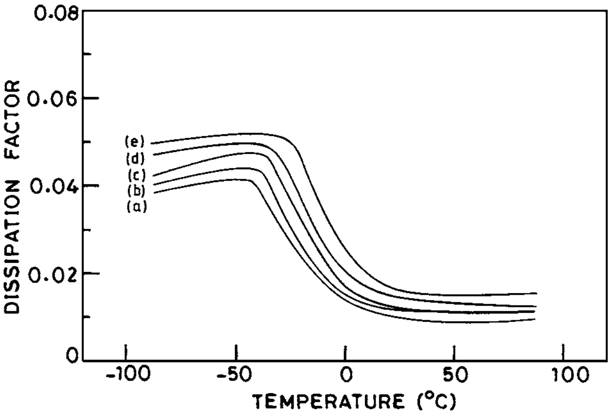

Figure 5 Variation of dissipation factor with temperature for 0.5PZN-0.425 PFN-0.075BZN sample at (a) 100 Hz (b) 1 kHz (c) 10 kHz (d) 1 MHz.

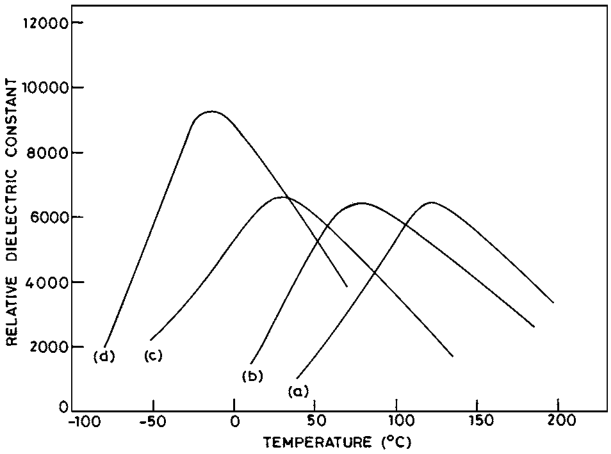

Figure 6 Variation of dielectric constant (1 kHz) with temperature for 0.5PZN-$(0.5 - x)$PFN-x BZN ceramics (a) $x = 0.0$ (b) $x = 0.05$ (c) $x = 0.075$ (d) $x = 0.1$.

with a dissipation factor ~0.05. Therefore this composition seems to be a potential capacitor material as its T_c is also ~30°C.

The dielectric constant in the ferroelectric ceramics depends on various factors like composition, perovskite phase content and the grain size of the sample [20]. As mentioned earlier increasing the amount of BZN in the ceramic leads to an increase in perovskite phase and porosity, whereas there is no significant variation in grain size. So it appears that the major contributor to the increase in dielectric maxima in the PZN-PFN-BZN ternary system is the stabilization of perovskite phase with BZN.

3.3. Mechanical properties

Fig. 7 shows the variation of fracture toughness (K_{IC}) of 0.5PZN-$(0.5-x)$PFN-xBZN ceramics with varying BZN content. As can be observed from the figure, K_{IC} decreases with an increasing amount of BZN in the samples. We believe that the decreasing Curie temperature with addition of BZN is the main contributor to this decrease in fracture toughness in our samples. Cook *et al.* [21] showed that K_{IC} decreases monotonically with temperature through the Curie point. Phonkar *et al.* [22] recognized that the increased toughness of barium titanate in the tetragonal state is due to interaction of cracks with 90° domains in the structure. These domains switch their direction under the stress field of a crack and give rise to energy adsorption leading to an increase in toughness. In our samples also domain switching due to the stresses at the crack tip seems to be mainly responsible for their toughness behaviour. Decreasing the Curie temperature with the addition of BZN leads to a lowering of K_{IC} as less energy is required and absorbed during domain switching. The variation of Vicker's hardness with the BZN content in PZN-PFN-BZN system is shown in Fig. 8. The hardness also decreases with the BZN content. There seems to be a closer correlation of hardness with sintered density. The increasing porosity at the grain boundary leads to a reduced grain boundary strength, which leads to a lowered hardness. The correlation of hardness with density has also been observed earlier [23].

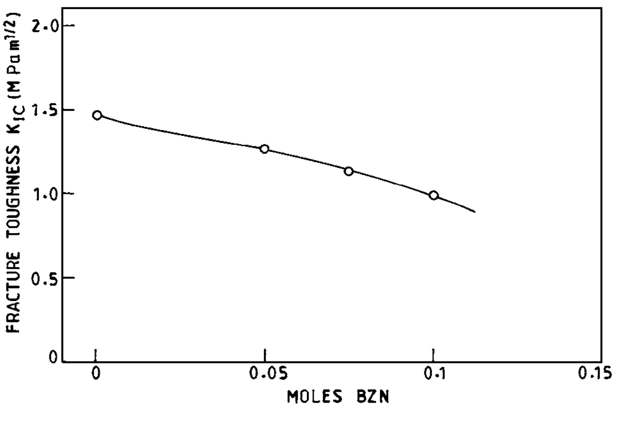

Figure 7 Variation of fracture toughness (K_{IC}) with BZN.

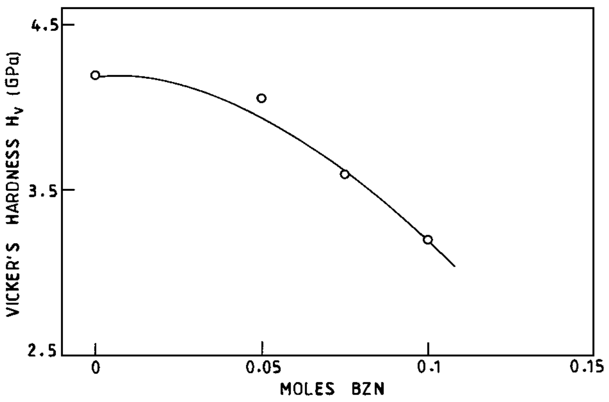

Figure 8 Variation of Vicker's hardness (H_v) with BZN.

4. Conclusion

The ternary composition 0.5PZN-0.425PFN-0.075BZN has been identified as the potential material for MLCs devices. The value of dielectric constant (~6400) and loss tangent (~0.05) are comparable to other PZN based relaxors [24, 25]. It has small temperature variation of dielectric constant around room temperature. The mechanical properties of the relaxor are also reasonable.

References

1. A. A. BEREZHNOI, V. N. BUKHMAN, L. T. KUDINOVA and I. E. MYL'NIKOVA, *Soviet Phys. Solid State* **10**(1) (1968) 192.
2. N. P. KHUCHUA, V. F. BOVA and I. E. MYL'NIKOVA, *ibid.* **10**(1) (1968) 194.
3. G. A. SMOLENSKII, N. N. KRAINIK, A. A. BEREZHNOI and I. E. MYL'NIKOVA, **10**(9) (1969) 2105.
4. J. N. HERBERT, "Electrocomponent Science Monographs," vol. 6: Ceramic Dielectrics and Capacitors (NY, 1985).
5. S. G. KANG, H. KIM, K. TAKAHASHI and M. TSUKIOKA, *Jpn. J. Appl. Phys* **33** (1994) 5407.
6. M. YONESAWA, *Ferroelectrics* **68** (1986) 181.
7. Y. YOKOMIZO, T. TAKAHASHI and S. NOMURA, *J. Phys. Soc. Jpn* **28**(5) (1970) 1278.
8. J. KUWATA, K. UCHINO and S. NOMURA, *Ferroelectrics* **22** (1979) 863.
9. *Idem., Jpn. J. Appl. Phys* **21**(8) (1982) 1298.
10. T. R. SHROUT and A. HALLIYAL, *Am. Ceram. Soc. Bull* **66** (1987) 704.
11. Y. MATSUNO, H. SASAKI, S. HAYAKAWA, F. KANAMURA and M. KOZUMI, *J. Phys. Soc. Jpn.* **28** (1970) 410.
12. S. L. SWARTZ and T. R. SHROUT, *Mater. Res. Bull* **17** (1982) 1245.
13. J. R. BELSICK, A. HALLIYAL, U. KUMAR and R. E. NEWNHAM, *Am. Ceram. Soc. Bull* **66** (1987) 664.
14. A. HALLIYAL, U. KUMAR, R. E. NEWNHAM and L. E. CROSS, *J. Amer. Ceram. Soc* **70** (1987) 119.
15. U. KUMAR, L. E. CROSS and A. HALLIYAL, *ibid.* **75** (1992) 2155.
16. T. R. SHOURT and A. HALLIYAL, *Am. Ceram. Soc. Bull* **66** (4) (1987) 704.
17. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 533.
18. G. EVANS and E. A. CHARLES, *ibid.* **59** (1976) 371.
19. J. M. LONGO, P. M. RACCAH and J. B. GOODENOUGH, *Mater. Res. Bull* **4** (1969) 191.
20. O. FURUKAWA, Y. YAMASHITA, M. HARATA, T. TAKAHASHI and K. INAGAKI, *Jpn. J. Appl. Phys.* **24** (1985) 96.
21. R. F. COOK, S. W. FREIMAN, B. R. LAMAE and R. C. POHANKAR, *Ferroelectrics* **50** (1983) 267.

22. R. C. POHANKAR, R. W. RICE and WALKER, *J. Amer. Ceram. Soc.* **59** (1976) 71.
23. A. GARG and T. C. GOEL, *Mater. Sci. and Engg.* B **60** (1999) 128.
24. M. V. RADHIKA RAO, A. M. UMARJI, Y. KUMAR, K. K. JAIN and E. S. RAJGOPAL, *J. Mater. Sci. Lett.* **16** (1997) 122.
25. S. G. KANG, H. KIM, K. TAKAHASHI and M. TSUKIOKA, *Jpn. J. Appl. Phys.* **33** (1994) 5407.

Received 13 October 2000
and accepted 16 October 2001