International Symposium of Research Students on Materials Science and Engineering
December 20-22, 2004, Chennai, India
Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras

DIELECTRIC CHARACTERIZATION OF $CA_{0.1}SR_{0.9}R_{0.1}BI_{1.9}TA_2O_9$ (R=LA, ND, PR) CERAMICS

Rizwana[a] , G.S.Kumar[b] and P.Sarah[a]*
[a]CVR College of Engineering, Vastunagar, Mangalpalli (V), R R district 501 510, A.P, India
[b]Dept. Of Physics, Material research Lab., Osmania University, Hyderabad 500 007, A.P, India

ABSTRACT

Ceramic samples $Ca_{0.1}Sr_{0.9}R_{0.1}Bi_{1.9}Ta_2O_9$ with R=La, Nd, Pr are prepared by solid state double sintering route. These samples are examined by X-ray diffraction for phase identification and the lattice parameters are calculated from the data. Morphological characterization is done using scanning electron microscope. The compositional identification is done by Energy Dispersive Analysis by X-ray (EDAX). Dielectric studies include measurement of dielectric constant and loss as a function of temperature.

Keywords: Rare earth, XRD, SEM, EDAX and Dielectric.

1. INTRODUCTION

Many physical properties of materials may vary significantly with a subtle change of chemical composition through doping or substituting of desired impurities, although the change of physical properties may be due to completely different mechanisms and the doping level can vary substantially from material to material. This approach is applied in Bismuth layered structure ferroelectrics (BLSFs) so as to enhance the ferroelectric properties and improve the processing conditions. Recently, BLSF perovskite materials such as $Bi_4Ti_3O_{12}$ (BIT), $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2(Nb, Ta)_2O_9$ (SBTN) for FeRAM applications have attracted increasing attention in the research community because they are fatigue-free and lead-free.[1] These are excellent candidates for applications in data storage digital memory systems, in addition to many other important applications such as piezoelectrics, pyroelectrics and electro-optics for sensors and actuators.[2,3]

There have been many efforts reported recently in the open literature to enhance the properties of layered Perovskite ferroelectrics by the addition or substitution of alternative cations. Previous studies by the U. Chon et al.,[4] indicates that direction and magnitude of remanent polarization of highly c-axis oriented bismuth titanate (BIT)-based films are very susceptible to the substitution of trivalent rare-earth cations for bismuth. It is found that TiO_6 octahedra in the pseudo-perovskite blocks of BIT thin films show the shift of octahedron along the a axis, which is largely enhanced due to the substitution of lanthanides (e.g., La, Pr, Nd, Sm etc) for Bi in the pseudo-perovskite blocks. Thus one would expect to obtain fatigue-free characteristics by destabilizing the oxygen ions located at the Ti-O octahedron layer in BT films making it suitable for the realization of high density NVFRAM devices. These rare-earth cations meet the requirements of the ionic radius, the stable curie temperature and the phase stability of layered perovskites.[5]

In the present work, effect of rare earth doping on lattice parameters, microstructure and dielectric properties of $Ca_{0.1}Sr_{0.9}Bi_2Ta_2O_9$ (CSBT) is studied.

2. EXPERIMENT

Ceramic samples $Ca_{0.1}Sr_{0.9}R_{0.1}Bi_{1.9}Ta_2O_9$ (R=La, Nd, Pr) are prepared by solid state reaction sintering using starting materials $CaCO_3$, $SrCO_3$, La_2O_3, Nd_2O_3, Pr_2O_3, Bi_2O_3 and Ta_2O_5 (AR grade, 99.5% pure). The homogeneous powder is manually ground for 3 hrs and pre-sintered at 800°C for 2 hrs. Pellets are made using binder at uniaxial pressure 3 tonnes/cm^2 and finally sintered at 1200°C for 2 hours. The relative density of pellets is nearly 90%. X-ray diffraction data is collected on a Phillips X-ray diffractometer using Cu-K_α radiation. Scanning electron micrographs are taken from sample surfaces that are used for morphology determination. Samples are silver coated for measurements. Samples are poled with field 15KV/cm at 150°C for 30 min in a silicon oil bath prior to dielectric measurements. The dielectric measurements as a function of temperature are made using HP 4192A Impedance analyzer.

3. RESULTS AND DISCUSSION

The structural characterization is accomplished by X-ray Diffraction (XRD) studies. Figure 1 shows the XRD spectra of rare earth doped CSBT. It is clear that single phase layered perovskites are formed with no detectable secondary phase. The lattice parameters calculated from the XRD data are listed in the table 1. It can be seen from the table that the parameter values for Nd are less where as for Pr and La are more compared to CSBT.

The microstructure of the samples is observed using scanning electron microscope. SEM for rare earth doped CSBT are shown above. SEMs are taken on a freshly fractured surface of the pellet. The plate and needle like grains are observed possibly due to the anisotropic crystal structure on account of the anisotropic growth behaviour of such materials. The grains of La doped are smaller and are very close to each other compared to other rare earth doped materials. The grains of Nd doped are larger than the others.

Dielectric constant and loss are measured as a function of temperature at different frequencies. The curie temperature and peak dielectric constant does not change much with frequency. Figures 4(a) & 4(b) show dielectric constant and loss with temperature at 50KHz. Curie temperature and the dielectric constant strongly depend on the ionic radii, which in turn effects structural distortion. Usually in ferroelectrics, a strong bond is formed between the Bi ion of the bismuth-oxide layer and apex oxygen of the perovskite at the phase transition. When the ions of differing radii are doped, this short Bi-O bond shears the perovskite layer, causing rotations of the oxygen octahedra and thereby, has a profound influence on the observed ferroelectricity in such compounds.[6] There is a decrease in the phase transition temperature with rare earth doping. The transition temperatures for R=0, La, Pr, Nd are 372°C, 270°C, 254°C, 285°C respectively. The dielectric constant at transition temperature decrease with La (149) doping where as it increases with Nd (260) and Pr (252) doping. This may be due to the reason that ionic radii of La is smaller than Bi where as ionic radius of Nd and Pr is larger than Bi. The peak dielectric constant values of Nd and Pr doped CSBT slightly vary. The reason may be that ionic radius of Nd and Pr is almost same. The slight difference in these values may be because of their polarizabilities. It is also observed that with the doping of rare earths, peak at the phase transition is little diffused. Peak for the CSBT is sharp.

Dielectric loss does not change much with doping. In all the cases loss increases with temperature and there is a sudden increase in the loss at temperatures greater than 400°C. The reason may be due to the increase in the concentration of intrinsic charge carriers at such high temperatures.[7, 8]

4. CONCLUSIONS

It is observed that the lattice parameter values increase from Nd to La. The grains become smaller from Nd to La. The presence of rare earths in the composition is confirmed from EDAX. Curie temperature decreases with rare earth doping. Dielectric constant at the phase transition increases from La to Nd. The properties of Pr are intermediate between La and Nd.

ACKNOWLEDGEMENT

The authors thank Prof S. V. Suryanarayana, Prof T Bhimasankaram Dept. of physics, Osmania University and GSI, Hyderabad for extending their lab facilities to us. We thank DRDO, New Delhi for the financial assistance.

REFERENCES

1. P de Araujo C A , Cuchiaro J D, Mcmillan L D, Scott M C and Scott J F, "Fatigue-Free Ferroelectric capacitors with Platinum Electrodes", Nature (London) 374 (1995) 627.
2. Lines M E and Glass A M, Principles and Applications of ferroelectrics and Related Materials ,Clarendon press, Oxford, 1977.
3. Scott J F and De Araujo C A, Science, 246 (1989) 1400.
4. Chon U, Jang H M, Lee S H and Yi G C, J. Mater. Res. 16 (2001) 3124.
5. Wolfe R W and Newnham R E, J. Electrochem. Soc. 116 (1969) 832.
6. Newnham R E, Wolfe R W and Dorrain J F, Mater. Res. Bull. 6 (1971) 1029.
7. Naoto Hirosaki, Tadshi Sekiya, Rong-Jun Xie, Yoshio Akimune, Kazuo Matsuo and Tatsuo Sugiyama, Appl. Phys. Lett. 80 (2002) 835-837.
8. Rizwana, G S Kumar and P Sarah, Indian J Phys, communicated, 2004.

Table 1. Lattice parameters values for La, Pr, Nd doped CSBT.

Sample	a (Å)	b (Å)	c (Å)	V (Å)
R=0	5.4938	5.5055	24.9981	756.0914
R=Nd	5.4833	5.5001	24.9793	753.3405
R=Pr	5.5115	5.5313	25.0661	764.1572
R=La	5.5275	5.5445	25.1367	770.3688

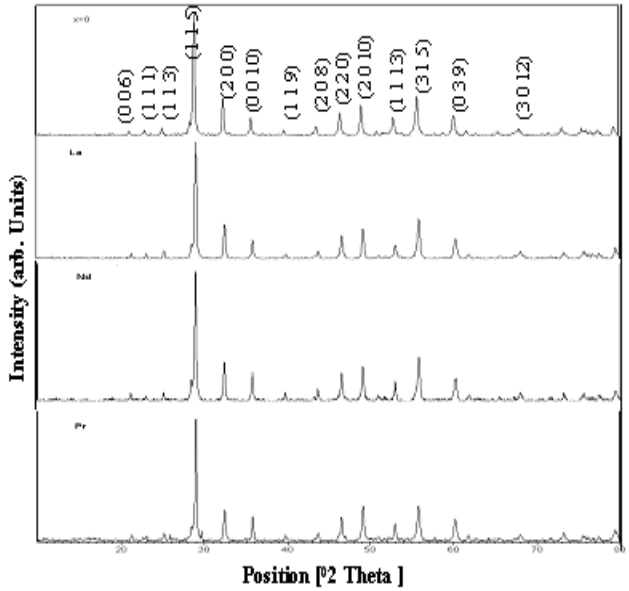


Figure 1. X-ray diffraction pattern of La, Pr, Nd doped CSBT samples.

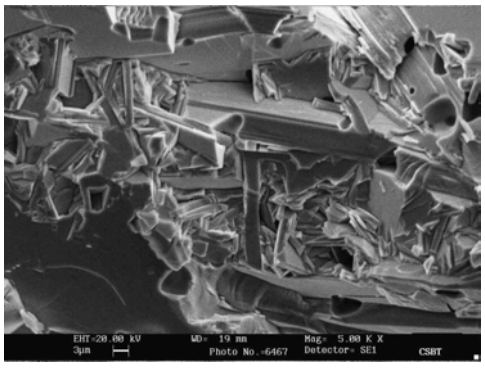


Figure 2(a)

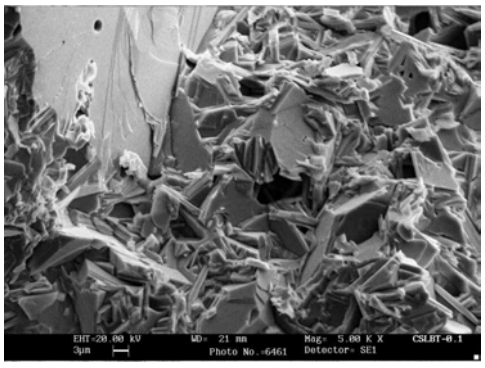
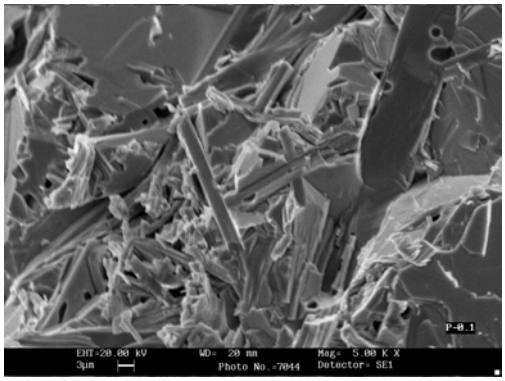


Figure 2(b)



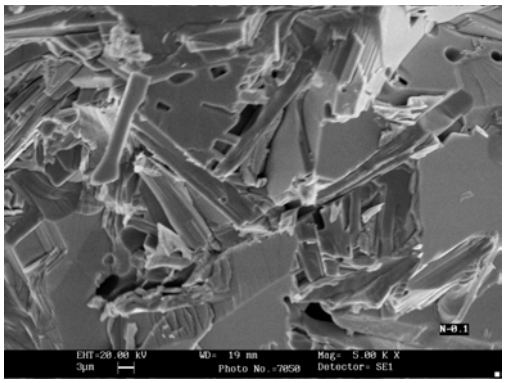


Figure 2(c) Figure 2(d)

Figure 2(a) SEM for CSBT
Figure 2(b) SEM for La doped CSBT
Figure 2(c) SEM for Pr doped CSBT
Figure 2(d) SEM for Nd doped CSBT

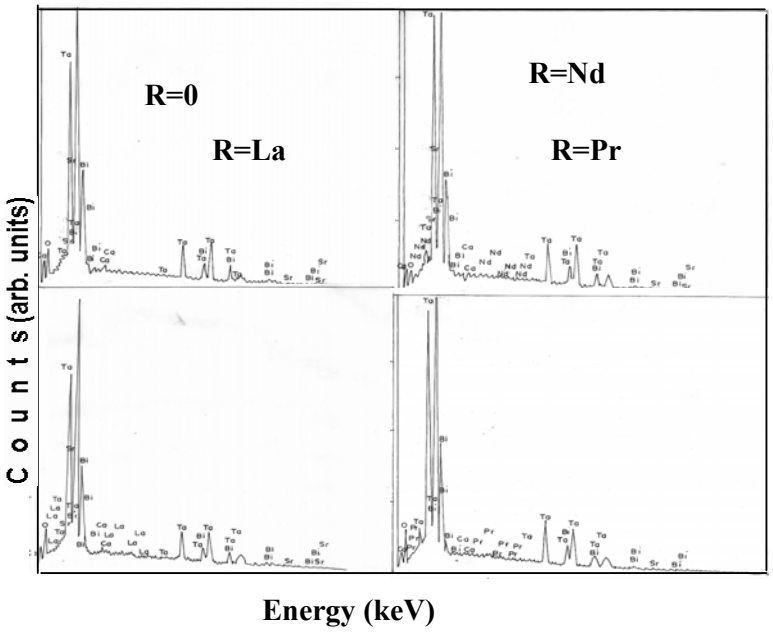
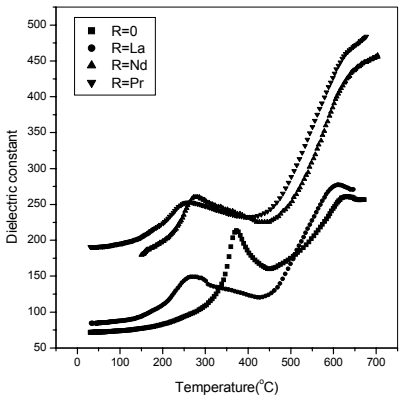


Figure 3

Figure 3 EDAX surface elemental composition spectra for La, Nd, Pr doped CSBT.
The surface composition of the rare earth doped CSBT is confirmed on the basis of Energy Dispersive Analysis by X-ray (EDAX). It showed the presence of the doped rare earths.



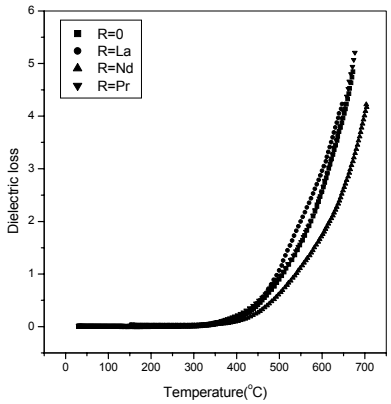


Figure 4(a) Figure 4(b)

Figure 4(a) Variation of dielectric constant of La, Pr, Nd doped CSBT with temperature at 50KHz.
Figure 4(b) Variation of dielectric loss of La, Pr, Nd doped CSBT with temperature at 50KHz.