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Effect of Sintering Temperature on Structural and Piezoelectric Properties of PNN-PZT Ceramics

Sandeep Mahajan, O.P. Thakur, and Chandra Prakash

Solid State Physics Laboratory, Delhi-110 054

ABSTRACT

Sintering temperatures affect the structural and piezoelectric properties of $PbNi_{1/3}Nb_{2/3}$-$PbZrO_3$-$PbTiO_3$ system considerably; therefore the effect has been studied on mechano-chemically processed powder. This process involves activating mixed oxides of PbO, NiO, Nb_2O_5, ZrO_2 and TiO_2, and in the present study, calcination steps at an intermediate temperatures were skipped which are usually required in conventional solid state reaction methods and chemical routes. Single-phase formation was confirmed from XRD patterns which shows rhombohedral structure at higher sintering temperature. Investigations of the microstructure indicate almost linear increase in grain size from 0.98 m to 2.56 m when the sintering temperature was varied from 1050 °C to 1150 °C. A high value of planar coupling factor (k_p) = 67 per cent and piezoelectric charge coefficient (d 33 ~ 750 pm/V; (as determined from strain versus electric field curve at low field) were obtained for the ceramic specimens sintered at 1100 °C. The maximum strain was observed ~ 0.21 per cent at 40 kV/cm applied field for the sample sintered at 1100 °C for 4 h.

Keywords: PNN-PZT ceramics, piezoelectric properties, dielectric properties, sintering temperature, piezoelectric ceremics, piezoelectric materials, mechanical activation, perovskite phase

1. INTRODUCTION

Piezoelectric materials have attracted much interest, both from fundamental and applied aspects, such as multilayer ceramic actuator, transducer, sensor and actuator applications. In recent years, several compositions were investigated, the most interesting ones are $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$[1-4].

The PNN-PZT system was first studied in detail by Buyanova[2,5], *et al*. in 1965 and reported the morphotropic phase boundary (MPB) of the system. After that, Luff[2], *et al*. investigated the piezoelectric properties and observed that the highest value obtained at 0.5 PNN-0.35 PT-0.15 PZ. This pseudo-ternary solid solution is a promising candidate for piezoelectric microactuators due to its better piezoelectric properties and excellent response characteristics of strain[2]. Therefore, new multilayered piezoelectric devices were developed and utilised for newly developed electronic components such as inkjet printer heads, piezoelectric transformers, and various sensors.

Silver and palladium alloys are generally used as inner electrodes for multilayered piezoelectric ceramics[6,7]. However, the piezo ceramics prepared using the conventional method require a high sintering temperature (> 1200 °C) that decrease the reliability of the multilayered piezoelectrics and their compositions

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are difficult to control because of *PbO* vaporisation at such high sintering temperatures. Therefore, lower temperature sintering is an important technique for suppressing compositional fluctuation and improving the piezoelectric properties, reliability, and reproducibility of these ceramics.

In general, the sintering temperature of a ceramic is lowered by the incorporation of low-melting point additives[8,9]. However, one has to compromise with the partial degradation of electrical properties. Recently, a breakthrough was made in synthesising *PbO*-based relaxor ferroelectrics and piezoelectrics[10,11], where the formation of desired perovskite phase in constituent oxides was triggered by mechanical activation. This is in contrast to the traditional calcination at one or more elevated temperatures.

They also observed that the precursor phases, which are always involved in the temperature-driven solid-state reaction as a result of the interfacial reactions, do not occur in the activated oxide mixtures prior to the perovskite phase. This led them to believe that the formation mechanisms of perovskite triggered by mechanical activation are different from those in the thermally activated solid-state reactions. It is possible to achieve fine particle via this process, which in turn helps in reduction of sintering temperature. The aim was to reduce sintering temperature without degrading the properties of the materials, and if possible, to enhance the properties by sintering at lower temperatures.

To meet these objectives, adoption of mechanical activation process has been proposed to lower the sintering temperature. In most of the study, columbite route was adopted to prepare pyrochlore-free single phase in this system. However in the present study, all the starting chemicals were mixed and single phase was successfully synthesised directly without calcinations steps. In this study, the structural and piezoelectric properties of the PNN-PZT ceramics have been examined at different sintering temperatures.

2. EXPERIMENTAL PROCEDURE

Oxide powders of *PbO*, Nb_2O_5, *NiO*, ZrO_2 and TiO_2 were used as raw materials with the nominal composition of $Pb[(Ni_{1/3}Nb_{2/3})_{0.50}\text{-}(Zr_{0.32}Ti_{0.68})_{0.50}]O_3$. Excess *PbO* (2 mol %) was taken to compensate the lead loss during sintering at the elevated temperature. For mechano-chemical process, 50 g of the powder was placed in a tungsten carbide-coated jar with 80 zirconia balls (high density and high purity) of dia 10 mm and subjected to dry grinding, using a planetary ball mill at 800 rpm for 20 min only. The synthesised powders were pressed into disks of 10 mm dia and then sintered in air for 4 h at temperatures 950 °C, 1050 °C, 1100 °C and 1150 °C in closed alumina crucible configuration with a small amount of equimolar ratio of *PbO* and ZrO_2 as a lead source powder. XRD patterns were recorded using Philips diffractometer (model P.W-3020) using *Cu-K* radiation. Microstructural study for the fractured surface of all the samples was carried out using SEM (Leo 1430, Japan).

For electrical measurements, both the sides of sintered and polished pellets were sputtered by gold serving as the electrode using sputter coater (Desk II TSC cold sputter unit). Hysteresis loops were recorded using automated P-E loop tracer (M/s AR Imagetronics, India) at 50 Hz based on modified Sawyer-Tower circuit. The remnant polarisation (*Pr*) and coercive field (*Ec*) were determined from the hysteresis loops. Poling of thin slices was done by applying dc field of 20 kV/cm at 120 °C for 30 min. The planar electro-mechanical coupling coefficient, k_p was determined from resonance-antiresonance peak frequencies measured by impedance analyser (Agilent 4294A).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of PNN-PZT samples sintered at different temperatures. A full stabilisation of perovskite phase was achieved for the whole sintering temperature range studied and the formed phase seems to be a mixture of rhombohedral and tetragonal phases, which is also expected from the ternary phase diagram for the PNN-PZT system[12]. Figure 2 shows the variation of sintered density as a function of sintering temperature for PNN-PZT system. Maximum density was observed for the sample sintered at 1100 °C for 4 h. However, the sintered density decreased slightly with higher sintering temperature that may be due to the loss of lead.

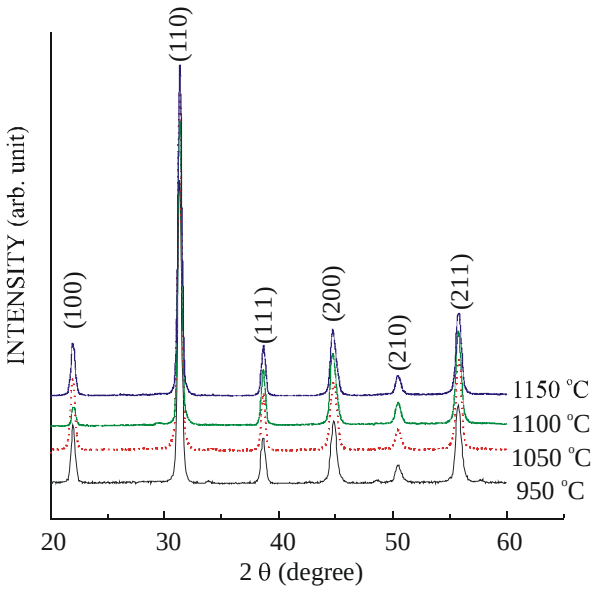


Figure 1. XRD patterns with different sintering temperatures for PNN-PZT system.

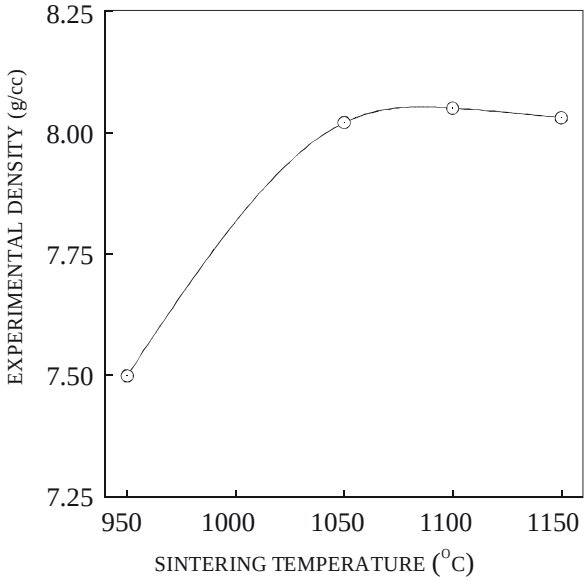
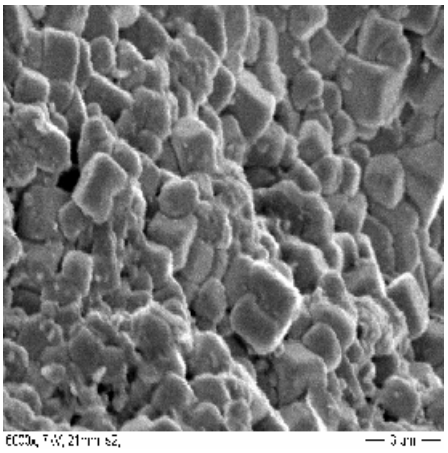


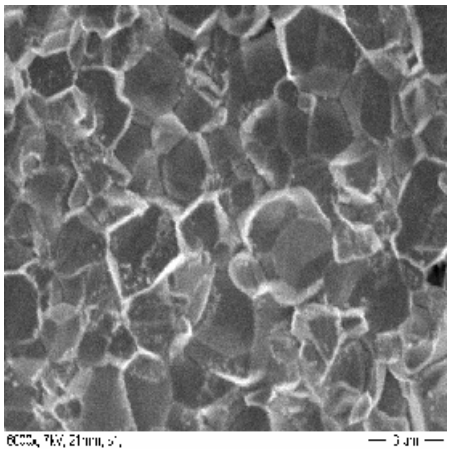
Figure 2. Variation of experimental density with sintering temperature.

The microstructures for the PNN-PZT system sintered at 1050 °C, 1100 °C, and 1150 °C are shown in Fig. 3. It is clear that the grain size is strongly influenced by the sintering temperature, which increased from ~0.98 m to 2.56 m and it is shown that grain size ~1.84 m gives better piezo properties.

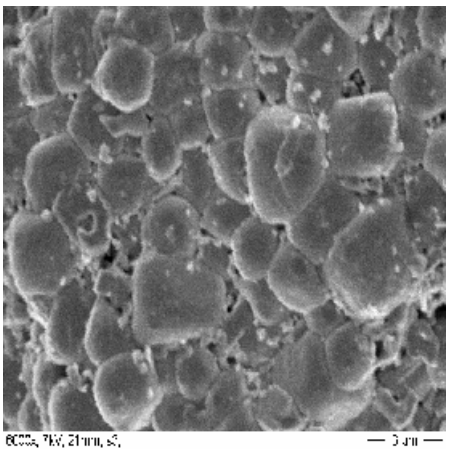
Effect of sintering temperature on grain size is shown in Fig. 4 and it is seen that as the sintering temperature was increased, grain size increased almost linearly. Figure 5 shows a typical hysteresis loops with an applied field of 5-6 kV/cm at different sintering temperatures. The saturation polarisation



(a)



(b)



(c)

Figure 3. SEM for PNN-PZT composition sintered at: (a) 1050 °C, (b) 1100 °C, and (c) 1150 °C.

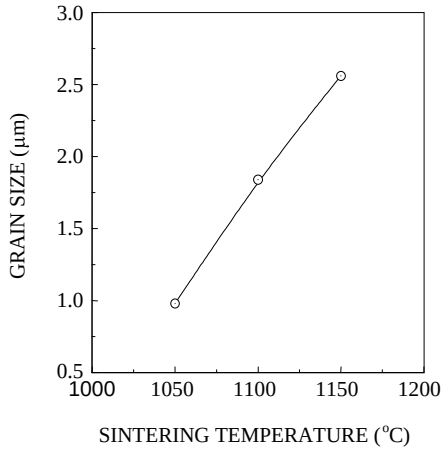


Figure 4 Variation of grain size with different sintering temperatures.

(P_{sat}), remnant polarisation (Pr) and coercive field (Ec) were 33 C/cm^2, 23 C/cm^2, and 2.6 kV/cm, respectively. The electromechanical coupling factor of the radial mode vibration (k_p) as a function of sintering temperature is calculated and it was observed that sample with 1100 °C gave maximum value of k_p (67 %).

In general for a high extrinsic strain, two facts are important: (i) lattice distortion, and (ii) domain activity. At low tetragonal phase content, the domain activity is very high but the lattice distortion is too low for obtaining a high extrinsic strain of the material. Higher domain activity is due to a decrease of the lattice distortion with increasing relaxor content. The lower lattice distortion explains also the lower Ec of PNN-PZT in comparison to those of normal PZTs, which allows domain switching at lower electrical or mechanical stresses. The piezoelectric strain was measured for the PNN-PZT ceramics sintered at different temperatures, and is included in Fig. 6.

The maximum value of strain ~ 0.21 per cent was obtained for the sample at 40 kV/cm field sintered at 1100 °C which may be due to optimum ratio of lattice distortion and domain activity. However, the detailed investigation of XRD patterns need to be done to quantify the ratio of tetragonal and rhombohedral phases. Low magnitude of strain up to 1050 °C sintering temperature was observed due to poor crystallisation of ferroelectric phase and

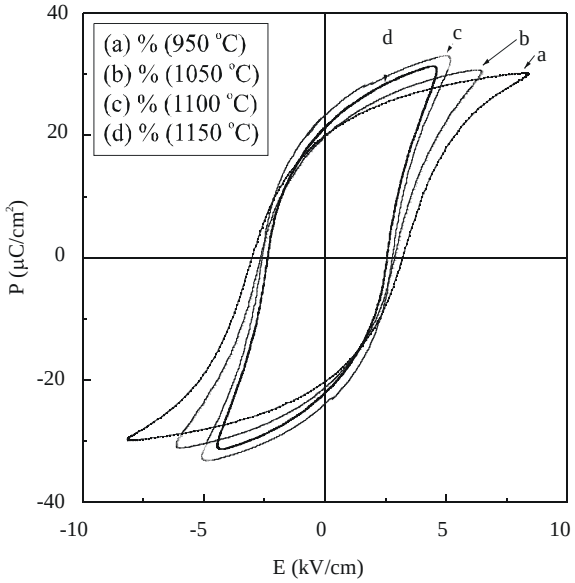


Figure 5. P-E hysteresis loops for PNN-PZT system with different sintering temperatures.

trace amount of unidentified second phase present that is also evidenced from XRD pattern. The hysteresis loss in S-E loop becomes smaller with higher sintering temperature and starts increasing at 1150°C owing to lead loss. The value of longitudinal piezoelectric constant (d_{33}) determined from the slope of strain versus electric field plot (low applied field region, up to ~ 10 kV/cm) shows value ~750 pm/V.

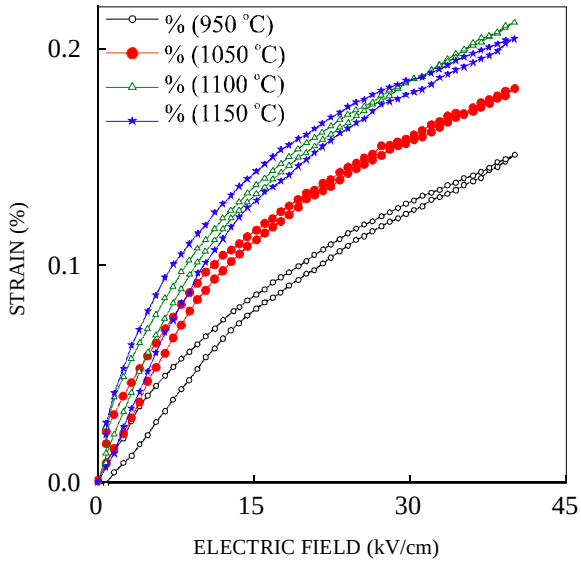


Figure 6. Strain versus electric field loops for PNN-PZT system sintered at 950 °C, 1050 °C, 1100 °C, and 1150 °C.

4. CONCLUSION

Approximately 98 per cent of theoretical density was achieved by sintering the ceramics at 1100 °C for 4 h by mechano-chemical synthesis and the grain size was found to be ~1.84 m. It could be possible to get pyrochlore-free perovskite phase without involving calcination steps and columbite precursor. Large value of electro-mechanical coupling coefficient, (k_p ~ 67 %) was observed for the specimen sintered at 1100 °C with d_{33} value of 750 pm/V. The higher value of strain (0.21%) was also achieved for the sample sintered at 1100 °C for 4 h. All these promising properties are suitable for sensor and actuator applications.

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REFERENCES

1. Berlincourt, D. Piezoelectric ceramics: Characteristics and applications. *J. Acoust. Soc. Am.*, 1981, **6**, 70-77.

2. Luff, D.; Lane, R.; Brown, K.R. & Marshallsay, H. J. Ferroelectric ceramics with high pyroelectric properties. *J. Br. Ceramic Soc.*, 1974, **73**, 251-64.

3. Zhu, X.H.; Xu, J. & Meng, Z.Y. Dielectric and piezoelectric properties of $Pb(Ni_{1/3}Nb_{2/3})\ O_3$ - $PbTiO_3$-$PbZrO_3$ ceramics modified with bismuth and zinc substitutions. *J. Mater. Sci.*, 1997, **32**, 4275-281.

4. Alberta, E.; Bhalla, A.S. & Takenaka, T. The piezoelectric, elastic and dielectric constants for ceramics in the solid solution: (x)$[PbZrO_3]$-(1-x-z) $Pb\ (Zn_{1/3}Nb_{2/3})O_3$- (z) $PbTiO_3$. *Ferroelectrics,* 1996, **188**, 109-12.

5. Buyanova, E.A.; Strelets, P.L.; Serova, I.A. Isupov, V.A. Ferroelectric properties of $PbTiO_3$-$PbZrO_3$-$PbNi_{1/3}Nb_{2/3}O_3$ solid solutions. *Bull. Acad. Sci., USSR Phys. Ser.*, 1965, **29**, 1877-881

6. Wang, S.F. & Huebner, W. Interactions of *Ag*/*Pd* electrodes with fluxes used in multilayer dielectrics. *J. Am. Ceram. Soc.*, 1992, **75**, 2339-352.

7. Wang, S.F.; Huebner, W.; Pepin, J. & Dougherty, J. Silver-palladium thick film conductors. *J. Am. Ceram. Soc.*, 1994, **77**, 3049-053.

8. Hayashi, T.; Inoue, T. & Akiyama, Y. Low-temperature sintering of PZT powders coated with $Pb_5Ge_3O_{11}$ by sol-gel method. *J. Eu. Ceram. Soc.*, 1999, **19**, 999-1003

9. Chu, S. & Hsich, C. Dopping effect on the piezoelectric properties of low-temperature sintered PZT-based ceramics. *J. Mater. Sci. Lett.*, 1999, **18**, 1295-299.

10. Wang, J.; Dong, M.W.; Ng,W.B. & Xue, J.M. Mechano-chemical synthesis of 0.9 $Pb(Mg_{1/3}Nb_{2/3})O_{3-0.1}$ $PbTiO_3$ from mixed oxides. *Advanced Materials,* 1998, **11**, 210-15.

11. Koch, C.C. Synthesis of nanostructured materials by mechanical milling: problems and opportunities. *Nanostructured Materials*, 1997, **9**, 13-19.

12. Torsten, B.; Wanda, W.; Erling, R.; Annette, P.; Marija, K. & Barbara, M. New piezoceramic PZT-PNN material for medical diagnostics applications. *J. Eu. Ceram. Soc.*, 2001, **21**, 1469-472.

Contributors

Mr Sandeep Mahajan obtained his MSc and MPhil (Physics) both from the Devi Ahilya University, Indore, in 2003 and 2004, respectively. He joined DRDO at the Solid State Physics Laboratory (SSPL), Delhi, in 2004 as Junior Research Fellow and currently working as Senior Research Fellow, in the Electroceramics Group. His areas of research include: Synthesis and characterisation of ferroelectric, piezoelectric, and pyroelectric materials.

Dr O.P. Thakur obtained his PhD in ferroelectric glass-ceramics from the Institute of Technology, Banaras Hindu University, Varanasi, in 1998 and joined SSPL in 1995. Presently, he is working as Scientist D. He had been awarded *Dr K.S. Krishnan Research Fellowship* by Dept of Atomic Energy, Govt of India during his PhD. He has more than 50 research papers in reputed journals and also filed two patents. He was postdoctoral Research Associate at the University of Sheffield, UK during 2005-06 and worked on order-disorder perovskites. His main areas of research are: Glass ceramics, impedance spectroscopy, ferroelectric, piezoelectric, pyroelectric and microwave dielectric materials and devices.

Dr Chandra Prakash obtained his PhD from the University of Delhi in 1986 on ferrite materials. He joined DRDO in 1985 as Scientist B at the SSPL, Delhi. Presently, he is Scientist F. He has been co-recipient of *DRDO Technology Awards* for 1988, 1995, and 2002. He was on deputation to Materials Research Laboratory, PennState University during 1994-95 and worked on advanced ceramic materials. His areas of interests are: Electroceramic materials and devices. He has more than 110 papers published in reputed journals.