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SHORT COMMUNICATION

Effect of Heating Rate on Electromechanical Properties of PNN–PZT Solid Solution

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ABSTRACT

Lead nickel niobate–lead zirconate titanate ($Pb(Ni_{1/3}Nb_{2/3})_{0.5}$ –$Pb(Zr_{0.15}Ti_{0.35}O_3)$, (PNN-PZT)) solid solution was synthesised by columbite process. Samples sintered at various heating rates for 4 h holding and their effect on electromechanical properties have been studied. When heating rate was 8 °C/min from room temperature to 900 °C and holding for 4 h at 1280 °C, highest relative permittivity and piezoelectric charge constant were observed, whereas heating rate of 3.5° C/ min and holding for 4 h at 1280 °C have shown inferior electromechanical properties and grain coarsening. The piezoelectric charge constant (d_{33}) ~612 *p*C/N and dielectric constant (e)~ 5950 observed in fast heating rate specimen as against to d_{33}~ 137 *p*C/N and e~4294. XRD result shows the formation of pyrochlore-free perovskite phase. Fine grains were observed for fast heating rate specimens.

Keywords: PNN-PZT, piezoelectric properties, and dielectric properties, piezoelectric ceramic materials, ceramic actuator material, electronic materials, perovskite

1. INTRODUCTION

With the advent of more intelligent electronic devices recently, the importance of ceramic actuator in the form of solid displacement element has continuously increased. There are many piezoelectric ceramics materials have been developed from binary system containing relaxor and normal ferroelectric materials, most studied materials with very high dielectric constant (a) $Pb\ (Mg_{1/3}\ Nb_{1/3})–PbTiO_3$ (PMN-PT), (b) $Pb\ (Zn_{1/3}\ Nb_{1/3})–PbTiO_3$ (PZN-PT), and (c) $Pb(Ni_{1/3}Nb_{2/3})–Pb(Zr,Ti)O_3$ (PNN-PZT) with high dielectric constant and piezoelectric constant[1-8]. Many researchers have studied PNN-PZT system. In 1974, Luff[8], *et al.* first studied ternary solid solution $Pb(Ni_{1/3}Nb_{2/3})$-PZ-PT and found excellent piezoelectric properties at the composition 0.5PNN-0.35PZ-0.15PT[8]. Robert[9], *et al.* studies the phase diagram for the 0.4 PNN-0.6 PZT and observed MPB was at 23 mol per cent PZ for 40 mol per cent PNN at room temperature and the MPB bends towards the region richer in zirconium as the temperature increases[9].

Another study by Vittayakorve[10] showed the phase structure and dielectric properties of PNN-PZT with variation of PZT and established the ferroelectric phase diagram between PZT and PNN[10]. A number of papers have been published related to the processing and piezoelectric properties. B-site precursor route is popular one for the synthesis of PNN-PZT and has shown superior electromechanical properties over the standard columbite route[11]. In the present work, $Pb(Ni_{1/3}Nb_{2/3})–Pb(Zr,Ti)O_3$ system has been synthesised by columbite method. The composition was selected from the work of Luff[8], *et al.* because of excellent piezoelectric properties[8]. The main purpose of the present study was to evaluate the effect of heating rate on dielectric and piezoelectric properties of PNN-PZT.

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2. EXPERIMENTAL

The basic composition used was $Pb(Ni_{1/3}Nb_{2/3})_{0.5}- Zr_{0.15}Ti_{0.35}O_3$, (PNN-PZT). To avoid the formation of the detrimental pyrochlore phase, the columbite method was used for the fabrication of the PNN-PZT ceramic samples. The stoichiometric amounts of AR-grade *NiO* and Nb_2O_5, were first ball-milled in distilled water using ZrO_2, media. The dried powder was then calcined at 1000 °C for 6 h in a closed alumina crucible. The second stage was the fabrication of perovskite PNN-PZT. *PbO*, *TiO*, and *ZrO*, were added to the previously synthesized $NiNb_2O_6$ (NN) precursor. The mixture was then ball-milled, dried, and calcined at 1100 °C for 4 h, to avoid the formation of pyrochlore the heating rate between 500 °C to 800 °C was kept fast. Calcination powder was milled for 24 h and then dried. This was followed by mixing of 10 Wt per cent of PVA as a binder in the calcined powder and the specimens (dia 14.25 mm and thickness 2.5 mm) were pressed using uniaxial press. Specimens were subsequently sintered in a *PbO*-rich atmosphere with different heating rates at 1280 °C for 4 h.

The densities of the sintered bodies were measured by the Archimedes method. The crystal structure of the sintered specimens were analysed using XRD, (Philips-X, pert Pro). The microstructures of chemically etched samples were studied using a SEM (Geol-JSM 6360). For electromechanical characterisation, sintered samples were polished with diar-thickness ration ~ 10:1. Then silver electrodes were screen-printed and cured at 600 °C. The capacitance at room temperature was measured using LCR meter (HP-4262A) at 1 kHz. Dielectric constant was computed using spacemen dimensions and the permittivity. The specimens for d_{33} measurements were poled in silicon oil bath at 80 °C for 20 min at 3 kV/ mm. All electromechanical measurements were performed after 30 days of poling. Mechanical quality factor (Q_m) and coupling factor (K_p) were calculated based on anti-resonance frequency (f_a) and resonance frequency (f_r), using standard formulas. The d_{33} was measured by Berlincourt Piezo CPDT 3330 d_{33} meter. Resonance, anti-resonance frequencies, and impedance were measured using impedance analyzer (HP 4192A).

3. RESULTS AND DISCUSSION

PNN-PZT is basically solid solution of relaxor ferroelectric PNN and normal ferroelectric PZT. It should give high permittivity (property of a relaxor material) and high piezoelectric charge constant (property of a normal ferroelectric material).

X-ray analysis indicated the existence of single-phase columbite, $NiNb_2O_6$ (NN) JC-PDF No 31-0906 (Fig.1). Figure 2 is the XRD of PNN-PZT that shows the existence of pyrochlore-free perovskite phase. Figure 3 depicts the variation of dielectric permittivity (ε) and piezoelectric charge constant (d_{33}) with heating rate in the temperature interval 25 °C to 900 °C. It was observed that the

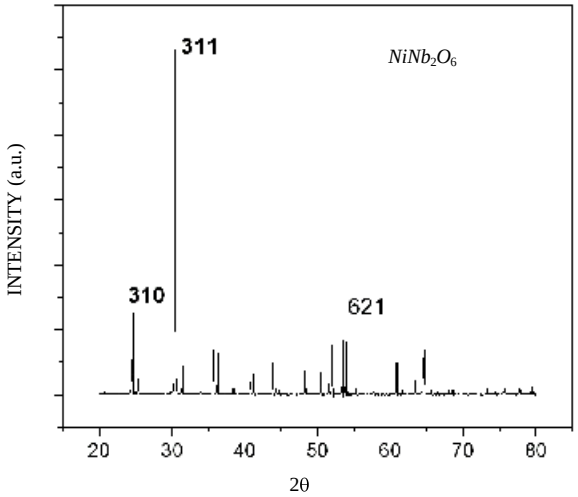


Figure 1. XRD pattern of calcined NN ($NiNb_2O_6$).

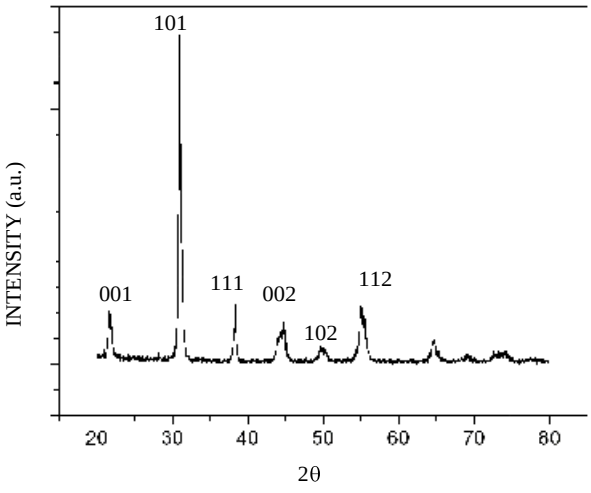


Figure 2. XRD pattern of calcined PNN-PZT.

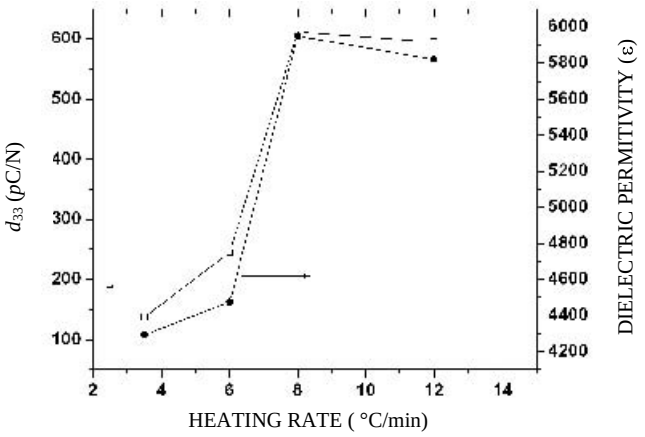
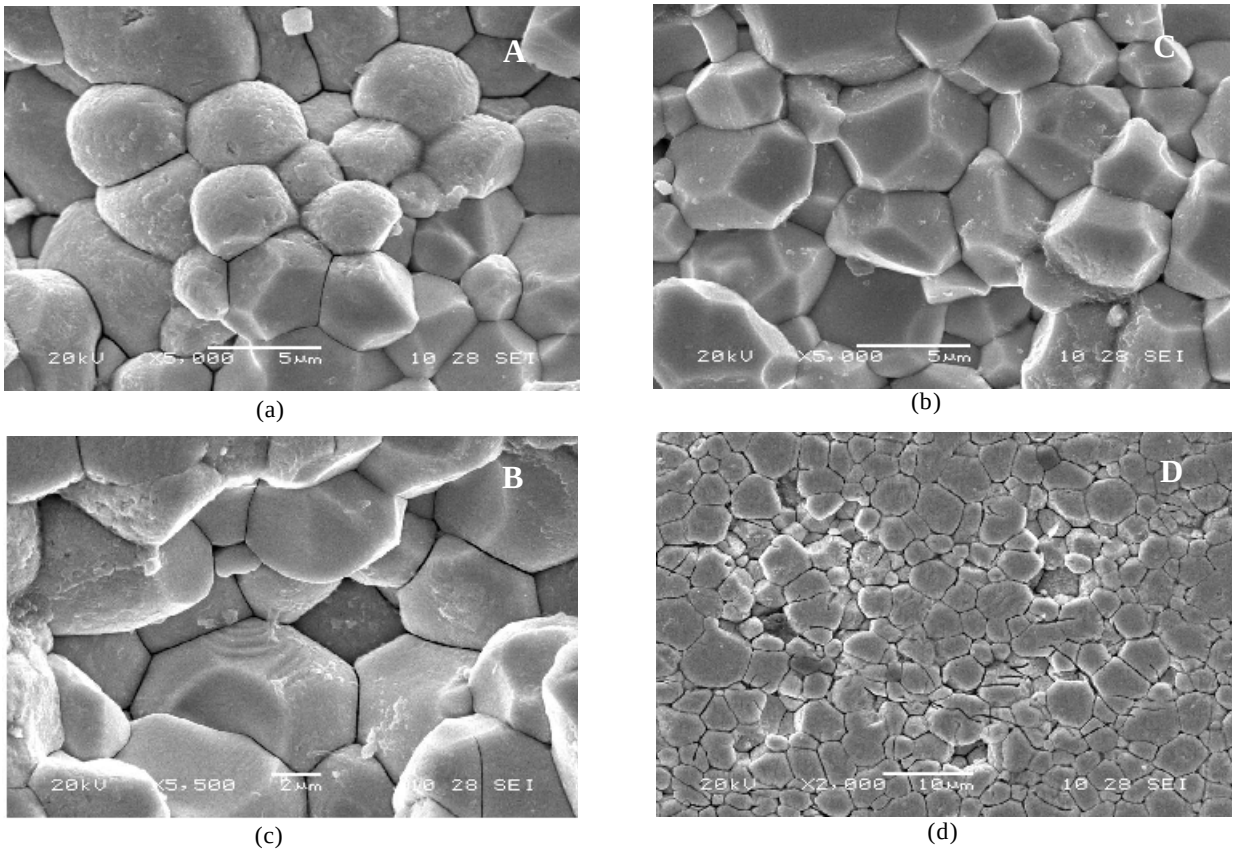


Figure 3. Variation of dielectric constant and piezoelectric charge constant with heating rate.

fast heating rate gives high ε and d_{33}. It is well-established that detrimental pyrochlore formation occurs in the temperature range 400 °C to 900 °C. The slow heating rates 3.5 °C/min and 6 °C/min lead to lead loss due to prolonged heating cycle and formation of pyrochlore structure which may deteriorate the piezoelectric and dielectric properties as observed in Fig. 3. It was also observed that dynamic heating between temperature intervals 400 °C to 900 °C helped in improving the piezoelectric and dielectric properties because it minimise the chances of formation of pyrochlore phase. Scanning electron micrographs showed the average grain size 4.5 μ for heating rate 12 °C/min for holding time of 4 h (Fig. 4). Dielectric and piezoelectric constants were highest for heating rate of 8 °C/min. Slower heating rates revealed the grain coarsening and lower of electromechanical properties (Table 1). Densities of the sintered samples were observed between 7.8 g/cc to 8 g/cc.

Table 1. Effect of heating rate on Q_m, Z_m, and K_p

	Heating rate (°C/min)			
	14	**8**	**6**	**3.5**
Q_m	65	73	60	80
Z_m	18	17	60	120
K_p	0.59	0.54	0.3	0.31



(a) (b) (c) (d)

Figure 4. SEM of polished and chemically etched surfaces of the specimens sintered at 1280 °C for 4 h: Heating rate (a) 14 °C/min, (b) 8 °C/min, (c) 6 °C/min, and (d) 3.5 °C/min.

4. CONCLUSION

In this study, dialectic and piezoelectric properties were measured for the system $Pb(Ni_{1/3}Nb_{2/3})_{0.5}$–$Zr_{0.15}Ti_{0.35}O_3$ with varying heating rates. It was observed that fast heating rate of 8 °C/min gives the highest ε = 5950 and d_{33} = 612 *p*C/N and lower impedance and Q_m at resonance frequency. This composition is suitable material for ceramic actuator applications.

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