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Low temperature sintering and high piezoelectric properties of strontium doped PNZT–PNN ceramics processed via the columbite route

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Abstract

This study investigated the influence of strontium doping on both the sintering behavior and the piezoelectric properties of PNZT–PNN ceramics. The piezoelectric ceramics was produced by solid state reaction between metallic oxides, strontium carbonates ($SrCO_3$) and oxides precursors. $NiNb_2O_6$ precursors were mixed with the oxides to avoid the large-scale formation of pyrochlore phases during the sintering process and to favor the formation of the perovskite structure. Sintering experiments were accomplished between 900 °C and 1100 °C for PNZT–PNN with 0–4 mol% strontium. Dilatometer curves indicated that the densification of these samples occurs by 850 °C and the electromechanical characterization showed that strontium doping enhances the soft piezoelectric properties of the PZT–PNN ceramics.

Consequently, a sintering temperature of 900 °C is sufficient to obtain doped PZT–PNN tablets with 99% of the theoretical density and excellent soft piezoelectric properties ($\varepsilon_r > 4000$; $K_p > 60$; $d_{33} > 1000$ pm/V). This makes those ceramics suitable for the construction of high efficiency actuators with low sintering temperature. The low Curie temperature is the only drawback of this material for some applications such as engine fuel injection.

Keywords: PZT; PNN; Strontium doping; Columbite route; Low temperature sintering; High piezoelectric properties

Lead nickel niobate–lead zirconate titanate perovskite solid solutions have been intensively studied for their attractive soft ferroelectric properties of interest for actuator applications. However, the high sintering temperature needed to obtain dense and pyrochlore-free material is the main obstacle for the production of multilayer actuators with low-cost electrodes. Hence, the goal of the presented study is to reduce the sintering temperature of PNN–PZT.

The pyrochlore phases are formed by the reaction of lead oxide and niobium oxide between 650 °C and 900 °C[1] during thermal treatment.

The use of $NiNb_2O_6$ precursors, generally known as the "columbite route", makes it possible to reduce the formation of pyrochlore phase and then obtain dense and pyrochlore-free piezoceramics with sintering at 1200 °C.[2]

Some authors attempt to reduce the sintering temperature of PZT–PNN by introducing doping oxides creating a low temperature eutectic melt.[3–6] However, a glass phase generally remains at the grain boundaries and penalizes the soft piezoelectric properties of the ceramics.

The present study investigates the effect of strontium carbonate doping on the solid state reactions, densification process and electromechanical properties of powders and ceramics with the formula $Pb_{0.9775-X}\ Nd_{0.015}\ Sr_X\ [(Zr_{1-Y}Ti_Y)_{0.674}\ (Ni_{1/3}Nb_{2/3})_{0.326}]O_3$. The PNZT–PNN powders were prepared following a columbite route process and the doping rate X was varied from 0 to 4 mol%.

1. Experimental procedure

The oxides (PbO, Nd_2O_3, NiO), precursors ($Zr_{1-Y}Ti_YO_2$, $NiNb_2O_6$) and $SrCO_3$ were weighted with 3.0 mol% excess of both lead and nickel oxides and then ball milled in water with ZrO_2 cylinders as grinding media in a PET jar for 18 h. The powder obtained was calcined at 750 °C for 2 h at a heating rate of 3.3 K min^{-1} and ball milled under the same conditions as the first milling process. The average particle size after the first milling was 1.1 μm and 0.8 μm after the second milling

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(measured using a Mastersizer S-Malvern Instruments Ltd.). In order to identify the particle size effect on the sintering behaviour, the recipes were also prepared using high energy milling (HEM) process. The average particle size of these powders was 0.5 μm.

Pressed disc shapes of calcined powder were debinded and then sintered in a PbO saturated alumina crucible at a heating rate of 3 K min^{-1} and a sintering temperature maintained for 2 h. Samples of all recipes were sintered every 50 K between 900 °C and 1250 °C.

After silver electrode deposition by means of a PVD process, the relative permittivity (ε_r) of the samples was obtained by measuring the capacitance at 25 °C. The coupling factor k_p was determined at 25 °C using an HP 4194A impedance analyzer. The large signal piezoelectric constant d_{33} (under 1 kV) at 25 °C was determined from S–E hysteresis loop measurement using a SIEMENS Transient Recorder B3143. The Curie temperature was found by monitoring the capacitance measurement on heated samples.

In order to study the solid state reactions phenomenon, samples of uncalcined powder were heated up in an alumina crucible at a heating rate of 3 K min^{-1} and maintained for 3 min at the maximum temperature before cooling at a rate of 7 K min^{-1}. Samples of all recipes were sintered every 50 K between 600 °C and 900 °C. The different phases were observed by X-ray diffraction (Siemens Diffractometer D500) using the Cu Kα radiation. Phase identification was carried out using the EVA database.

Dilatometer measurements were performed with a Netzsch dilatometer (model M1351) and a heating rate of 1 K min^{-1} up to 1250 °C under air atmosphere. The powder samples were previously isostatically pressed at 3000 bar.

2. Results

2.1. Calcined powder and sintering

Pure perovskite phase was obtained after calcination of the oxides-precursors mixture at 750 °C for 2 h (Fig. 1A) for the 4 mol% Sr doped PNZT–PNN recipe. Powders with lower doping concentrations contain both perovskite and pyrochlore phases and the lower the doping concentration, the more pyrochlore appears on the XRD diagram. The recipe without Sr doping also exhibits a significant quantity of lead oxide.

After sintering at 900 °C for 2 h, all samples are free of pyrochlore phase and recipes containing more than 1 mol% of strontium exhibit a pure perovskite phase diagram (Fig. 1B). For 0 mol% and 1 mol% of Sr doping, the diagram shows an unknown second phase whose peaks are close to several lead oxide structure diffraction patterns, but with different relative intensities. After sintering at 1000 °C or 1100 °C for 2 h, all samples showed the same pure perovskite structure as the 4 mol% Sr at 900 °C.

The dilatometer sintering curves (Fig. 2A) show a smaller shrinkage than the effective one of discs sintered in an alumina crucible in a kiln (Fig. 2B); we assume the 2 h sintering plateau to be responsible of this difference. More interesting is the sintering behavior of the undoped powder: the dilatometer curves show

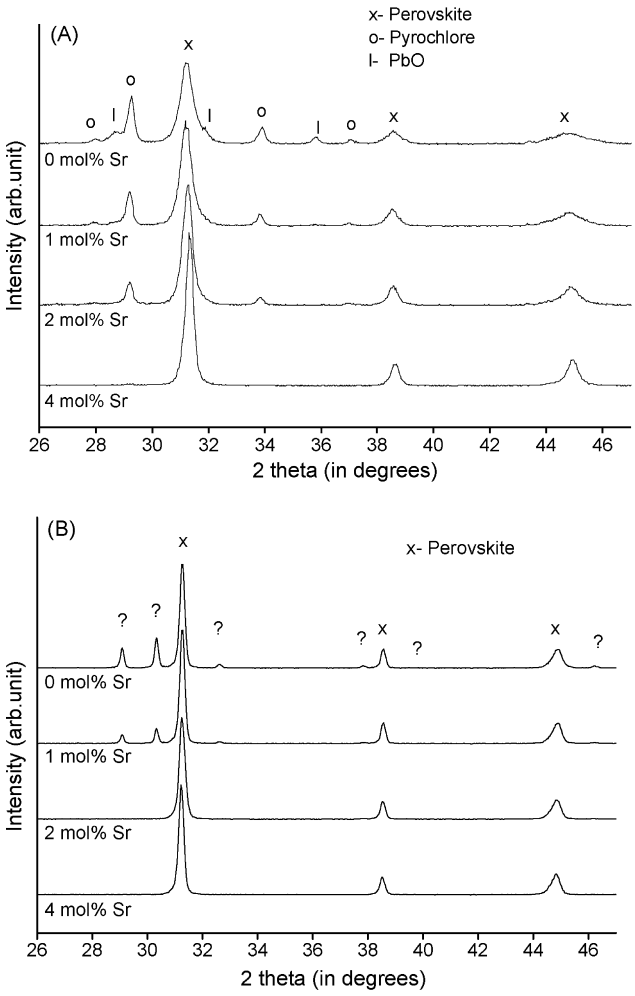

Fig. 1. XRD patterns of Sr-doped PNZT–PNN (A) powders calcined for 2 h at 750 °C and (B) discs sintered for 2 h at 900 °C. The "?" correspond to an unknown phase.

an abrupt densification after a small expansion slope at 800 °C and a higher shrinkage than the Sr-doped powders. On the other hand, the sintering experiments show this powder to densify less than the doped powders. The dilatometer curve is characteristic of a liquid phase formation and the abrupt contraction of the partially molten sample under the pushrod pressure. Without any pressure, this liquid phase does not help the densification and crystallizes at the grain surface when the sample is cooled. It should correspond to the unknown phase observed for samples sintered at 900 °C (Fig. 1B). The high energy milled (HEM) powder doped with 2 mol% Sr exhibits a sharper densification process than the ball milled one (Fig. 2).

The characterization of the sintered discs shows that Sr doping favors the densification and the soft piezoelectric properties of PNZT–PNN ceramics (Table 1) but decreases the Curie temperature. Sintering at 900 °C allows the production of ceramics with d_{33} above 1100 pm/V (large signal).

2.2. Mixed oxide powder

Three main phases are detected in samples treated between 600 °C and 850 °C (Fig. 3): a perovskite phase, a pyrochlore

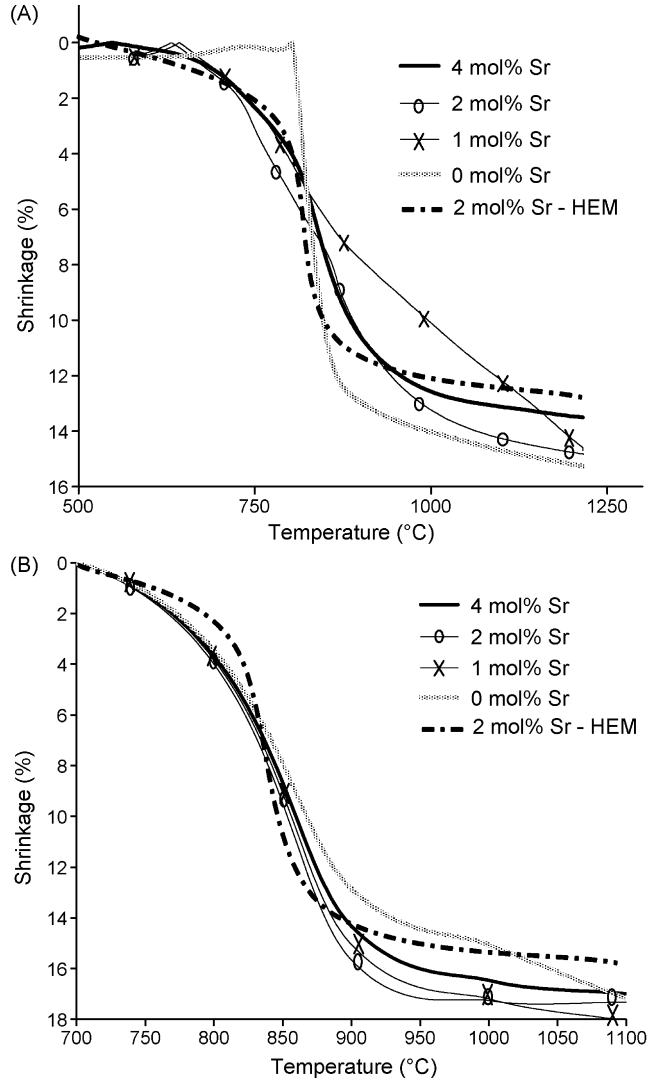

Fig. 2. Shrinkage curves of Sr-doped PNZT–PNN powder compact measured (A) in a dilatometer with isostatic pressed samples and (B) with axially pressed discs after 2 h sintering in a PbO saturated alumina crucible.

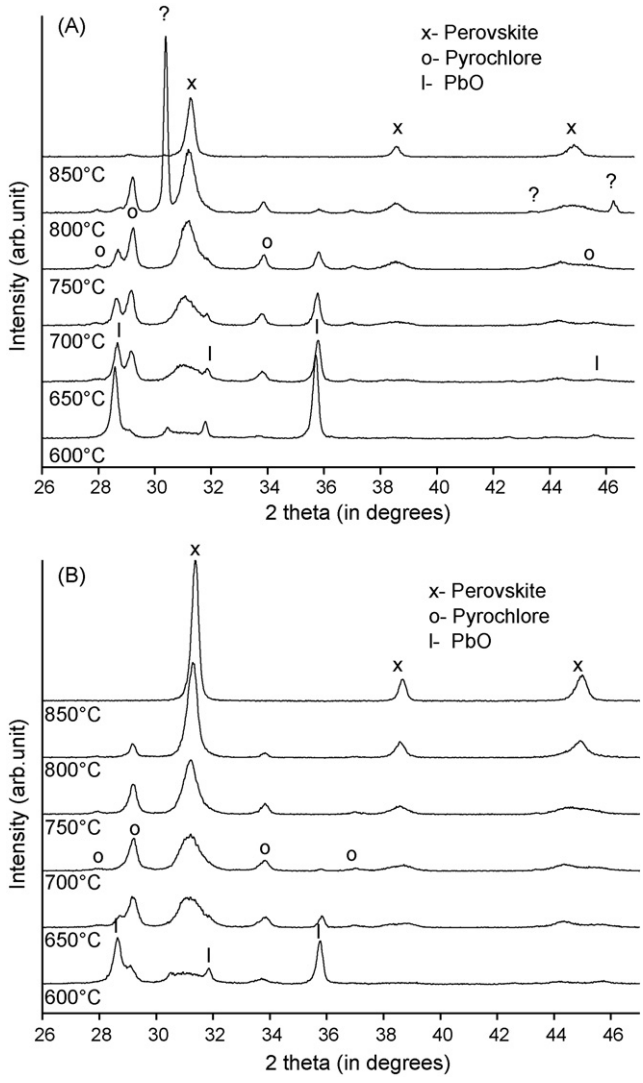

Fig. 3. XRD patterns of mixed oxide powders of the (A) PNZT–PNN recipe doped with (B) 2 mol% of Sr, calcined for 3 min at the given temperature. The "?" correspond to an unknown phase.

phase with compositions close to $Pb_3Nb_4O_{13}$ and lead oxide PbO (whose main peak has often been attributed to the pyrochlore phase). In order to calculate the amount of each phase present in the powder samples, the equation proposed by Swart and Shrout[2] was modified to take account of the coexistence of lead in three phases:

$$\%\text{Pyrochlore} = \frac{I(\text{pyro})}{I(\text{perov}) + I(\text{pyro}) + I(\text{pbO})} \times 100 \qquad (1)$$

where I(perov) refers to the intensity of the $\{1\,1\,0\}$ peak of the perovskite phase, I(pyro) refers to the $\{2\,2\,2\}$ peak of the pyrochlore phase and I(PbO) refers to the $\{1\,0\,0\}$ peak of the PbO phase (the amount of PbO was calculated using the same equation).

For the undoped PNZT–PNN powder, the pyrochlore phase forms mainly between 600 °C and 650 °C and remains stable up to 800 °C (Fig. 4) whereas it appears and disappears at lower temperatures and in higher amounts as the rate of Sr doping increases. Concomitantly, the PbO amount decreases at 600 °C and its disappearance occurs at lower temperature for higher doping rates.

Table 1
Density and piezoelectric properties of discs sintered at 900 °C and 1000 °C for 2 h

	900°C / 2h					1000°C / 2h				
[Sr] doping	density	ε_r	k_p	d_{33} (pm.V^{-1})	T_{Curie} (°C)	density	ε_r	k_p	d_{33} (pm.V^{-1})	T_{Curie} (°C)
0 mol% Sr	6,88	1843	0,24	537	170	7,67	3497	0,59	863	172
1 mol% Sr	7,63	3655	0,65	905	164	7,75	3949	0,68	962	165
2 mol% Sr	7,78	4282	0,64	1011	154	7,88	4671	0,66	1068	154
4 mol% Sr	7,85	5373	0,58	1120	129	7,91	5738	0,61	1190	131

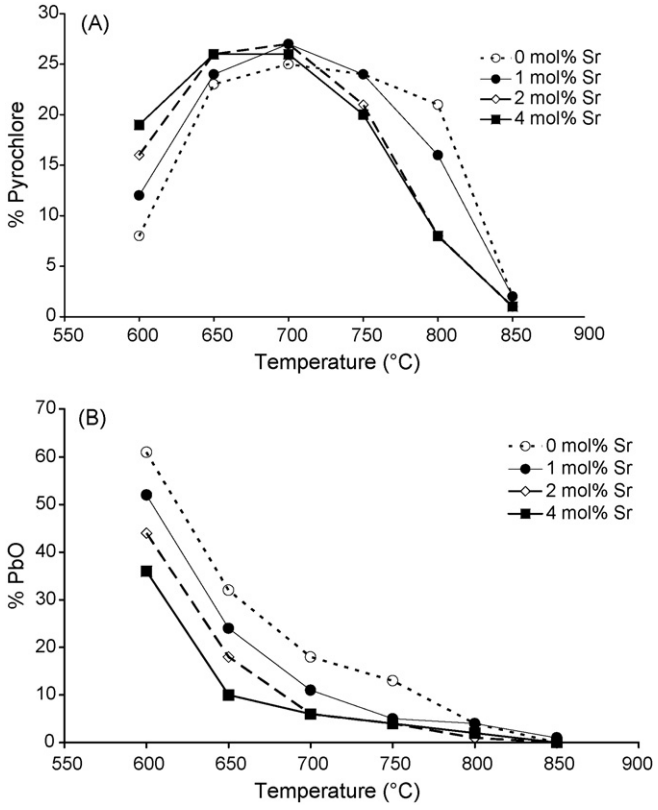

Fig. 4. Amount of (A) pyrochlore phase and (B) PbO present in the Sr-doped PNZT–PNN powders calcined for 3 min at the given temperature.

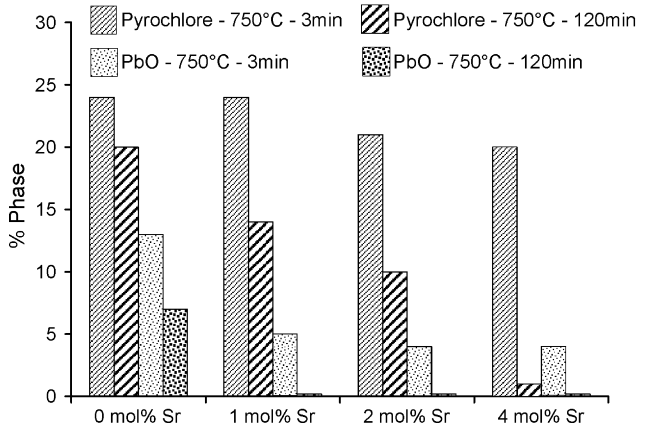

Fig. 5. Amount of pyrochlore phase and PbO present in the Sr-doped PNZT–PNN powder at the beginning (3 min) and at the end (120 min) of the calcination process at 750 °C.

The unknown phase (800 °C for the mixed oxide powder and 900 °C for the calcined ones) has been identified as lead oxide (with low incidence angle XRF) which melts and then textures at the surface of the powder particles as it cools.

3. Discussion

A comparison (Fig. 5) of the phases amounts between the beginning (Fig. 3, 750 °C) and the end of calcination at 750 °C (Fig. 1A) shows that the Sr doping rate increases the efficiency of the calcination process in eliminating the pyrochlore and PbO phases.

Strontium doping favors the consumption of lead oxide at low temperature by reducing the temperatures of both pyrochlore formation and pyrochlore conversion into perovskite. The later reaction consumes lead oxide and nickel oxide. This doping effect could be related to the ability of Sr^{2+} to build a perovskite lattice with oxides of lead, nickel or niobium at low temperature.[7,8]

In the undoped samples, a large amount of these oxides is present above 800 °C, and their evaporation penalizes the perovskite formation by modifying the reaction equilibrium.

For sintered samples, the belated and thus penalized solid state reaction between PbO, NiO and pyrochlore hinders the homogeneity and densification of ceramics without Sr doping; whereas samples containing more than 1 mol% Sr exhibit a pure perovskite structure and a high-density after sintering at 900 °C. The similar sintering curves for the "2 mol% Sr" and "2 mol% Sr –HEM" samples indicates that the implied phenomenon are largely thermally and a few mechanically activated.

The linear decrease trend of T_{Curie} between 0 mol% and 4 mol% doping proves that Sr^{2+} is built into the perovskite lattice. Sr^{2+} substitutes Pb^{2+}, favors the perovskite structure due to its lower electronegativity, and then induces a lower amount of pyrochlore phase in the samples. At low temperature, the higher densification of the doped samples favors the grain growth (radius growth from about 1 μm for "0 mol% Sr" to about 2.5 μm for "2 mol% Sr", at 950 °C) and then the ability of domains to switch.

The elimination of the pyrochlore phase, combined with the grain size increase, induces an enhancement of the soft piezoelectric properties of the PNZT–PNN ceramic samples.

4. Conclusion

This study shows that Sr-doped PNZT–PNN can be sintered at 900 °C and exhibit as high ferroelectric properties as the undoped one sintered at 1200 °C. The Sr-doping favors the formation of perovskite at low temperatures and then enables the densification process of a pure perovskite material to take place at a lower temperature than for the undoped ceramics. This makes those ceramics suitable for the construction of high efficiency actuators with low sintering temperature. The low Curie temperature is the only drawback of this material for some applications such as engine fuel injection.

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