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Modification of mechanical properties in PMNT 90:10 by substitution with La

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Abstract

Modern actuator systems require highly specialised, tailored electroceramic compositions, in order to realise their full potential. These modifications include many mechanical modifications, such as density adjustment, transparency, and grain size refinement. The work reported here describes a very simple method by which the Young's modulus in the system $Pb(Mg_{1/3}Nb_{2/3})O_3$ can be accurately controlled, by substitution with low La concentrations onto the Pb site; substitution of 1 at% La raises the Young's modulus from 98.6 to 116 MPa in the composition $Pb(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}O_3$. This may be used to raise significantly the resonant frequency of an actuating system. La doping was also shown to increase the porosity, from 0.4 to 2.8%.

Keywords: Actuators; Elastic modulus; Ferroelectric properties; Mechanical properties; $Pb(Mg,Nb)O_3$; Perovskites; PMNT

1. Introduction

Lead magnesium niobate [PMN, $Pb(Mg_{1/3}Nb_{2/3})O_3$] was prepared initially in the late 1950s.[1] Considerable literature exists on the production, crystal chemistry and dielectric properties of the polycrystalline form,[2–9] and within single crystals.[10] It has become a very important dielectric due to both a high relative permittivity and a broad maximum around the Curie point (occurring at about −15°C), being used in many applications, such as high performance capacitors. If a solid solution is generated with lead titanate ($PbTiO_3$), with a Curie point of 490°C, the system PMNT [$Pb(Mg_{1/3}Nb_{2/3})_{100-x}Ti_xO_3$] is generated, whereby the Curie point can be tailored to suit a desired operating temperature. If x is set to 10 (PMNT 90:10), the resultant electroceramic displays a very strong electrostrictive effect around room temperature, and a peak permittivity of up to 35,000. Such materials have many uses as piezoelectric replacements due to a very low dielectric loss, such as in high frequency applications (>100 kHz).

La-doped materials are important, not least due to interesting optical properties.[11] The effect of La substitution into either PMN or PMNT has been studied with respect to ordering, i.e. the 1:1 ordering of Mg^{2+} and Nb^{5+} has been attributed to the high electrostatic field created by the substitution of La^{3+} onto a Pb^{2+} site[12–15]. The objective of this work is to explore the mechanical effects of La on PMNT 90:10.

2. Experimental

Compositions were determined such that the PLMNT was prepared by substitution, rather than addition according to the generic formula $Pb_{(1-3x/2)}La_x(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}O$, with $x=0$, 0.001, 0.005 and 0.01. No excess lead was used. The precursors were milled in acetone (using a high energy attrition mill), dried and calcined at 800°C for 4 h. The material was prepared using a two-stage columbite process.[16,17] The calcined powder was subsequently milled with 1 wt% Glascol, and dried to provide a powder with an average primary particle size of 0.2 μm. Pellets (green diameter 50 mm) were uniaxially pressed at 100 MPa, using a hardened steel die set. The binder/lubricant was burnt-out by heating up to 500°C at 25°C h^{-1}, and the pellets were sintered at a range of temperatures for 2 h, with a heating and cooling rate of 300°C h^{-1}, in order to find their

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optimum sintering temperatures. The pellets were fired in sealed alumina crucibles, in order to minimise lead loss.

The sintered pellets were lapped and sawn, subjected to XRD analyses, and the density calculated by the geometrical method. These samples were subsequently lapped and optically polished to 200 μm, then sawn into beams for four point bend (FPB) and resonant analyses, in order to determine Young's Moduli. Ten samples were prepared of each composition for FPB, in order to generate a reasonable statistical analysis. SEM was conducted on gold coated fracture surfaces.

Mechanical experiments were conducted using conventional compressive/tensile testing apparatus (Instron), in conjunction with a high sensitivity 10 N load cell, and an optical displacement transducer. The test configuration is shown in Fig. 1. The displacement at the centre of the beam was solved from the movement of the upper load points trigonometrically. This true displacement was used in conjunction with the measured force to calculate the Young's modulus, employing standard bending moment theory. The differential stress between the surface and the centre of the beam was calculated.

The Young's modulus was determined electromechanically using an impedance analyser (Hewlett-Packard HP4194A) in conjunction with a DC bias, in order to determine the resonant frequency.

3. Results and discussion

3.1. Density

The maximum density of the four studied compositions are shown in Fig. 2. All samples were sintered at 1075 °C for 2 h; raising the sintering temperature further provided no further increase in density. All samples were seen to contain no pyrochlore, within the measurable limits of XRD. A general decrease in density can be seen from the figure. This may be a result of a reducing A site (Pb/La) occupancy, and less efficient liquid phase sintering. The theoretical density of PMNT 90:10 is approximately 8.15 Mg m^{-3}, as determined from XRD measurements; the addition of such small concentrations of La does not change this value. The percentage of theoretical density, therefore, changes from 99.6% for no La to 97.2% for 1 at% La. Further materials will be synthesised with excess lead, in an attempt to retain the high density of the undoped composition.

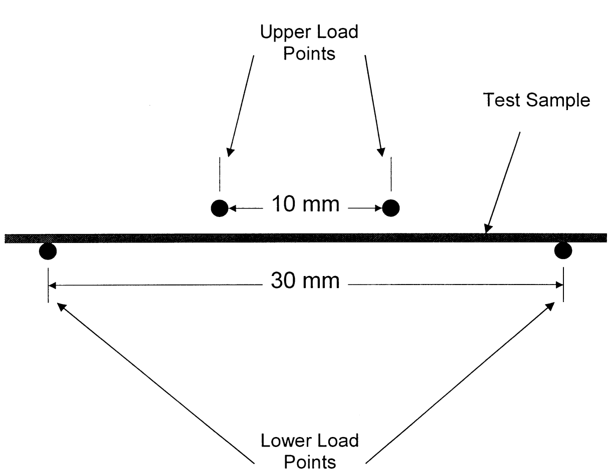

Fig. 1. Four-point bend test sample and load point configuration.

3.2. Microstructure

Examples of the microstructures of the 0.1 and 1.0 at% La-doped PMNT 90:10 sintered compacts are shown in Figs. 3 and 4, respectively. La does not refine the grain size using the concentrations studied, but the microstructures do show a slight increase in porosity, verifying the evidence presented from density measurements. The grain size for 0, 0.1, 0.5 and 1.0 at% doped

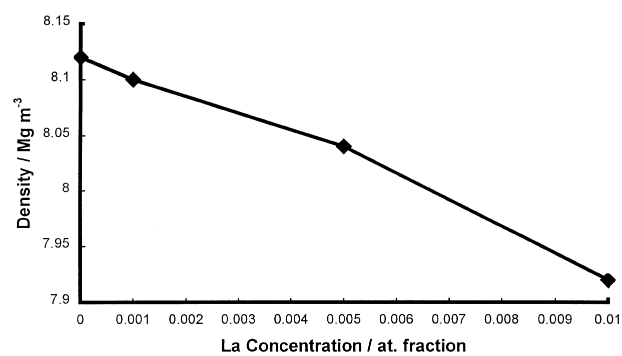

Fig. 2. Density vs. La concentration in PMNT 90:10.

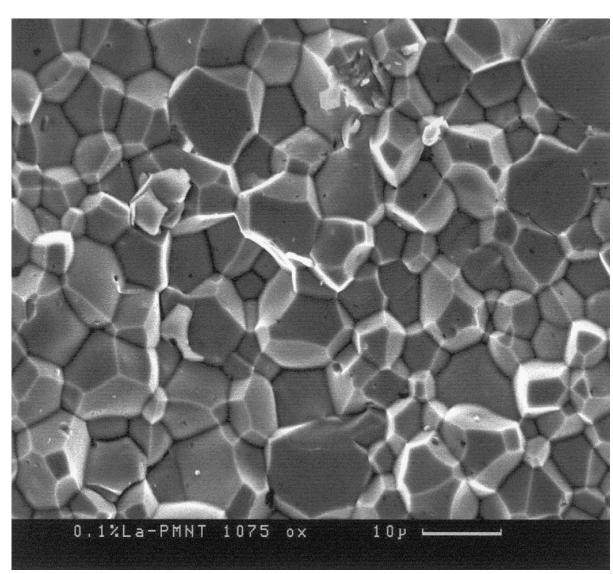

Fig. 3. Microstructure of 0.1%La-PMNT sintered at 1075°C for 2 h.

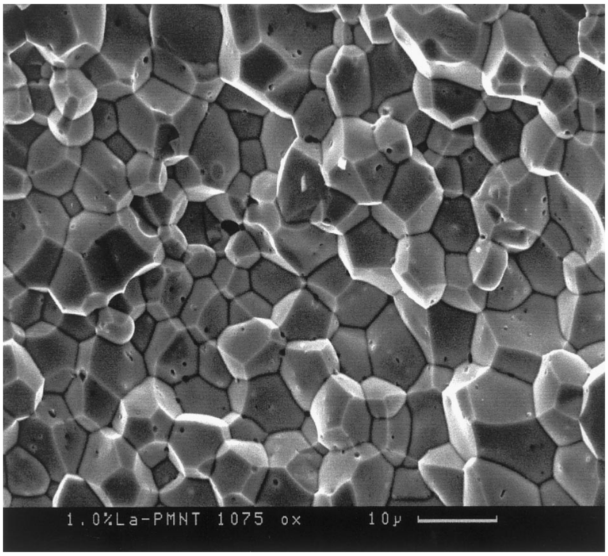

Fig. 4. Microstructure of 1.0%La-PMNT sintered at 1075°C for 2 h.

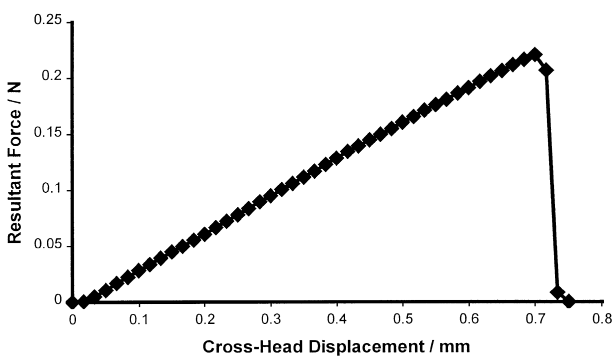

Fig. 5. Force/displacement data from four point bend analysis.

compositions is very close to 10 μm in all cases. An increase in sintering temperature, however, was shown to have a remarkable effect on the average grain size.

3.3. Four-point bend analysis

Fig. 5 shows a displacement/force profile obtained from a four-point bend mechanical test. The Young's modulus was determined using the linear region of the plot; non-linearities occur prior to fracture, as the sample bends and the linear mechanical equations become inaccurate.

Fig. 6 shows the variation of Young's modulus with La concentration. The effect is profound; doping with 1 at% La increases the Young's modulus from approx. 99 to 116 GPa, an increase of 17%. This increase must arise from the lanthanum stiffening the lattice, even at such low concentrations; it has been shown by other authors the acute effect La has on dielectric and electromechanical properties.

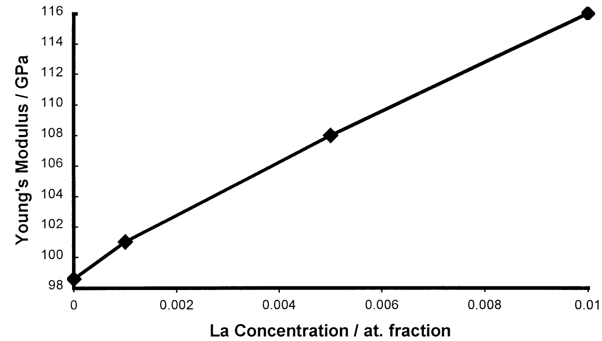

Fig. 6. Young's modulus vs. concentration for La-PMNT 90:10.

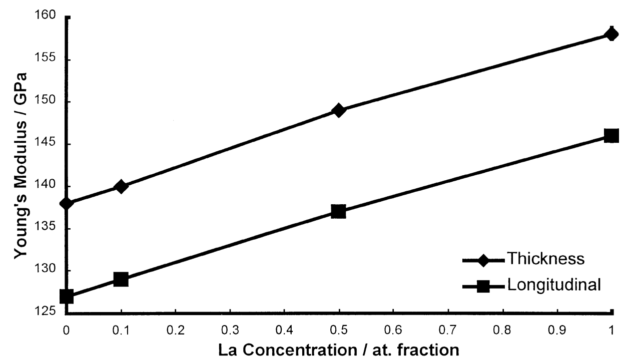

Fig. 7. Young's modulus as measured using impedance analysis.

3.4. Resonant analysis

The Young's modulus was calculated from the resonant frequency of the sample under a DC bias field, and the material density. It was found that different values were obtained from thickness and longitudinal measurements. The Young's moduli, obtained from each measurement did, however, rise with increasing dopant concentration, with a trend very similar to the mechanical testing technique (Fig. 7).

The effect of sample orientation on the measured value of the Young's modulus makes the impedance analysis technique quite unreliable for providing absolute values. For the comparison presented in Fig. 7, care was taken to make all samples with the same dimensions. The drive field appears to alter the measured value significantly. It is difficult to use the same drive field in all directions where the dimensions are very different, such as in thin wafers, because considerable electrical noise may result.

4. Conclusion

Doping with very low concentrations of La into PMNT 90:10 alters the Young's modulus considerably. This has many implications, because the composition, as well as the sample dimensions can now be used to adjust the resonant frequency. This allows a base material to work at a high operating frequency.

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