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Cobalt-Doping of Lead Magnesium Niobium Titanate: Chemical Control of Dielectric Properties

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Abstract

An investigation has been carried out into the acceptor-doping of lead magnesium niobate titanate (PMNT), $0{\cdot}95\{Pb(Mg_{1/3}Nb_{2/3})O_3\}-0{\cdot}05\ PbTiO_3$*, through the introduction of cobalt ions. These are added by co-reaction of PMNT powder with CoO and PbO in a single-stage reaction to sintered ceramics. The technique is found to enhance the sinterability of PMNT in less oxidising* CO_2 *atmospheres. Furthermore, the dielectric response of the Co-doped ceramics depends on the sintering atmosphere employed. In air, a transition from relaxor to normal ferroelectric properties takes place upon addition of cobalt. However, in* CO_2*, relaxor properties persist at all levels of cobalt-substitution. This difference in behaviour is attributed to varying oxidation states of the cobalt ions, it being proposed that that air-sintered samples consist of a mixture of* Co^{2+} *and* Co^{3+} *ions. In* CO_2*-sintered samples, by comparison, the cobalt ions exist only in the +2 oxidation state. The relevance to the formation of dipoles, and to an understanding of relaxor ferroelectric ceramics is brought out, comparing the observed behaviour with that of PMNT doped with manganese. © 1998 Elsevier Science Limited. All rights reserved*

Zusammenfassung

Eine Untersuchung zum Akzeptor-Dotieren von Blei-Magnesium-Niobat-Titanat (PMNT), $0{\cdot}95\{Pb(Mg_{1/3}Nb_{2/3})O_3\}-0{\cdot}05PbTiO_3$ *ist durch die Einführung von Kobalt-Ionen durchgeführt worden. Gesinterte Keramiken werden aus Edukten PMNT, CoO und PbO in einer einstufigen Reaktion hergestellt. Es wird festgestellt, daß die Technik das Sintern von PMNT in reduzierenden* CO_2*-Atmosphären verbessert. Außerdem hängt das dielektrische Verhalten der Co-dotierten Keramiken von der verwendeten Sinteratmosphäre ab. Während in Luft eine Umwandlung von 'relaxor' zu normalen ferroelektrischen Eigenschaften bei Zufügen von Kobalt vorkommt, werden 'relaxor'-Eigenschaften bei allen Co-Konzentrationen in* CO_2 *beibehalten. Dieser Unterschied kann auf die variierenden Oxidationszustände der Kobalt-Ionen zurückgeführt werden, da die in Luft gesinterten Proben eine Kombination von* Co^{2+}*- und* Co^{3+}*-Ionen enthalten sollen. In Keramiken, die in* CO_2 *gesintert worden sind, sollen die Kobalt-Ionen im Vergleich nur einen Oxidationszustand von +2 aufweisen. Die Relevanz dieser Erwägungen für die Bildung von Dipolen und für das Verständnis von 'relaxor' ferroelektrischen Keramiken wird hervorgehoben, wobei das beobachtete Verhalten mit dem von Mn-dotiertem PMNT verglichen wird.*

1 Introduction

Recent work has demonstrated that the 'relaxor' dielectric response of PMNT, $0{\cdot}95\{Pb(Mg_{1/3}Nb_{2/3})O_3\}-0{\cdot}05PbTiO_3$ can be converted to that of a normal, non-dispersive ferroelectric by doping with manganese.[1] In particular, it was found that the transition from 'relaxor' to normal properties was strongly dependent on sintering atmosphere: when sintered in air, a sharp reduction in the frequency-dependence of the relative permittivity was observed for Mn-doping levels as low as 1 mol-%. On sintering in less oxidising carbon dioxide

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atmospheres, however, doping levels of approximately 6 mol% manganese were required to effect a comparable reduction in frequency dispersion. A crystal-chemical rationalisation was proposed, whereby octahedrally coordinated Mn^{3+} ions were considered to give rise to large local electric dipoles. These were thought to perform a 'bridging' function between the polarisation clusters present in undoped PMNT, thus forming macroscopic ferroelectric domains. The difference in dielectric properties between air- and CO_2-sintered samples was attributed to different degrees of oxidation of manganese from the +2 to the +3 oxidation state.

One of the questions arising from this earlier work is whether other transition metal ions exhibit similar behaviour. Accordingly, this article is concerned with the dielectric properties of PMNT doped with cobalt, rather than manganese.

The chemical compositions of the Co-doped ceramics investigated here may be represented as, $0{\cdot}95\{Pb(Mg_{(1-x)/3}Nb_{2(1-x)/3}Co_x)O_{3-\delta}\}-0{\cdot}05\{PbTi_{1-x}Co_xO_{3-\delta}\}$, with $0 \leq x \leq 0{\cdot}3$. Here δ signifies the uncertainty in oxygen-content as a result of possible variations in the oxidation state of the cobalt ion. It has the value $x(2-\langle n_{Co}\rangle/2)$, where $\langle n_{Co}\rangle$ is the mean cobalt oxidation number. Non-zero values of δ reflect the function of the cobalt ions as acceptor dopants, as part of a strategy for reducing the concentration of free electrons which would otherwise be present in undoped PMNT when sintered in more reducing atmospheres.

In comparing the behaviour of cobalt and manganese as acceptor dopants, three main issues emerge:

1. the relative ease of oxidation of cobalt from the 2+ to the 3+ oxidation state compared to the corresponding behaviour of manganese;
2. the effectiveness of Co^{3+} compared to Mn^{3+} ions in forming 'bridging' dipoles;
3. the upper limits of substitution of cobalt and manganese in the parent PMNT phase.

These questions form the basis of the discussion in Section 4.

2 Experimental

The parent PMNT material was a 95:5 PMN-PT powder with low sintering temperature, as supplied by TAM Ceramics, Niagara Falls, USA and designated Y5V 183U. Doped samples of composition $0{\cdot}95\{Pb(Mg_{(1-x)/3}Nb_{2(1-x)/3}Co_x)O_{3-\delta}\}-0{\cdot}05\{PbTi_{1-x}Co_xO_{3-\delta}\}$ were prepared by combining powders of CoO (Aldrich 99+ pure) and PbO (BDH Analar Grade), with the PMNT powder. Compositions with values of x equal to 0, 0·0045, 0·0112, 0·0223, 0·0438, 0·0650, 0·1000, 0·2000 and 0·3000 were prepared, corresponding to doping levels of up to 30 mol-% cobalt. Samples were balled milled in isopropyl alcohol (IPA) with 3 mm zirconia (Y-TZP) media for 16 h, in order to achieve homogeneous mixing. Particle size analysis was carried out on the slurry with a Malvern Mastersizer, in order to ensure that no significant change in particle size had occurred during milling. The slurry was subsequently dried and passed through a sieve of mesh 20 μm. Pellets were pressed at 25 MPa by means of a 19 mm pseudo-double-ended uniaxial die. No organic binders were used. Samples were sintered at 1000°C for 3 h, as these conditions had been found to maximise the relative permittivity of the undoped PMNT. Two batches of pellets were produced, one sintered in air and the other in CO_2. A standard muffle furnace was employed for air firings, with CO_2-sintering carried out in a tube furnace with a steady flow of CO_2 gas. Flow-rate was set with mass-flow controllers. A calibration of the furnace temperature-controller was carried out, in order to compensate for the effects of the gas-flow. This was achieved by means of a thermocouple placed in the vicinity of the samples. Microstructures of sintered pellets were examined by SEM.

Disk-shaped samples for dielectric measurement of thickness 1·5 mm were sawn from sintered pellets. Samples were polished using 1200 grit silicon carbide paper and cleaned with water and acetone, before being dried at 180°C for 2 h. Gold electrodes were evaporated on to both faces of the sample and subsequently covered with silver dag. Samples were allowed to dry in air before being placed in an oven at 180°C for 2 h. Measurements of complex impedance were carried out for the frequency range 100 Hz–1 MHz at temperatures between −55 and 150°C.

Powder X-ray diffraction analysis was carried out on crushed sintered pellets, using a Siemens D500 X-ray diffractometer. KCl was added to the powders as an internal standard.

3 Results

3.1 Powder X-ray diffraction

Diffraction patterns for all 18 sintered samples (nine sintered in air and nine in CO_2) indicated that, to a good approximation, a cubic unit cell with lattice parameter a_o could be adopted in all cases. XRD analysis indicated that all the samples were phase pure, except the 30 mol% sample, which contained < 2% free CoO. Plots of a_o vs x are given in Fig. 1. It is seen that a_o remains approximately constant for both the air and CO_2 sintered samples. This is to be contrasted with the

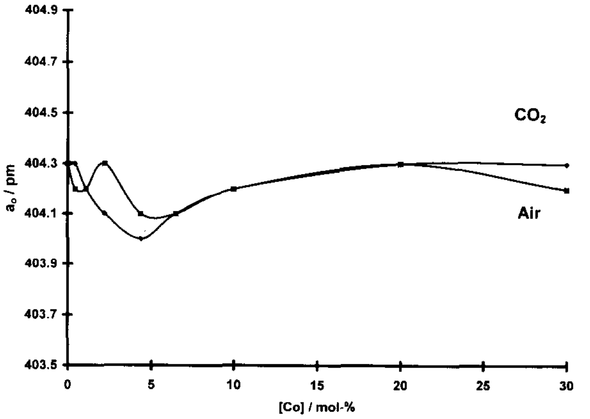

Fig. 1. Variation of cubic lattice parameter, a_o, at 25°C with cobalt concentration for samples sintered in air and in carbon dioxide.

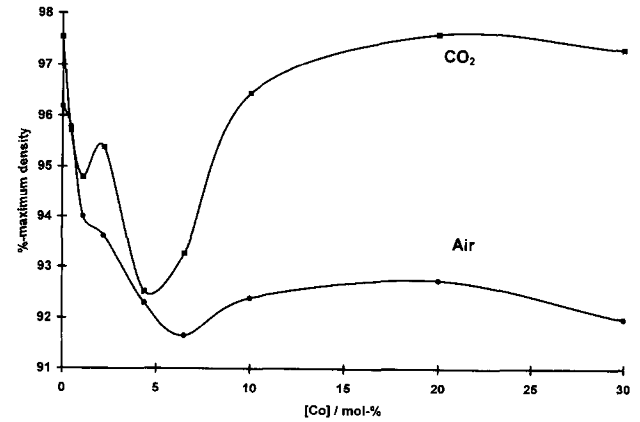

Fig. 2. Variation of density of sintered pellets, expressed as a percentage of calculated maximum density, with cobalt concentration.

observations for manganese-doping of PMNT, where a_o was found to increase with dopant concentration in CO_2-sintered samples.[1]

3.2 Sintered density

Densities of sintered pellets, expressed as a fraction of the maximum density, are plotted against cobalt concentration in Fig. 2 Here, maximum densities have been calculated from the observed lattice parameters (Fig. 1), assuming a δ-value equal to x. This is tantamount to making the approximation that all cobalt ions are in the $+2$ oxidation state. In the case of firing in CO_2, doping with cobalt is detrimental to densification at [Co]-levels of up to 6·5 mol-% However, a restoration in sintered density is observed at all higher doping levels. Air-sintered samples have consistently lower densities than their CO_2-sintered counterparts, with no marked restoration of density at [Co]-levels greater than 6·5 mol%. The mean grain-size of air-fired samples was found to decrease slightly with increasing cobalt concentration from 5·10 μm for $x = 0{\cdot}0045$ to 4·50 μm for $x = 0{\cdot}065$. A larger decrease in mean grain-size was observed for CO_2-sintered samples, falling from 5·60 to 4·44 μm between x-values of 0·0045 and 0·065.

3.3 Dielectric measurements

The variation of relative permittivity, ε_r, with temperature is given in Figs 3 for four representative samples. In Fig. 3(a)–(c), the progressive reduction in frequency dispersion can be observed for air-sintered samples with x-values of 0·0045 0·0223 and 0·0650, respectively. There is a concomitant reduction in maximum values of relative permittivity. The dielectric response in Fig. 3(c) is to be compared with that of Fig. 3(d), which corresponds to a sample of identical composition sintered in CO_2. In the latter, there are still significant relaxor properties, together with a higher maximum relative permittivity.

Trends in dielectric properties across the whole substitution range are summarised in Figs 4–6 by means of three parameters, the temperature of maximum permittivity at 1 kHz, $T(\varepsilon_{r,\max})$, relative permittivity at 1 kHz, $\varepsilon_{r,\max}$, and ΔT, the frequency-dispersion parameter, defined as $T(\varepsilon_{r\max})_{1\,\mathrm{MHz}} - T(\varepsilon_{r\,\max})_{100\,\mathrm{Hz}}$ Whereas $T(\varepsilon_{r,\max})$ falls steadily with increasing Co-concentration in CO_2-sintered samples, it always lies in the range between 15 and 30°C for air-sintered samples. Figure 5 shows the general reduction in $\varepsilon_{r,\max}$ with increasing cobalt concentration, with values in air-sintered samples consistently lower. It is seen in Fig. 6 that ΔT remains approximately constant in CO_2-sintered samples, indicating the maintenance of relaxor properties at all cobalt substitution-levels. In air-sintered samples, by comparison, the parameter falls from 18·85 to 2·82°C in the range between 0 and 4·38 mol% [Co], remaining essentially at this value up to cobalt concentrations of 20 mol%, before falling to 0·33°C at the highest substitution-level.

4 Discussion

The above results provide a strong indication that the dielectric response of Co-doped PMNT is sensitive to sintering atmosphere. Since this has also been observed for manganese-doping,[1] it is instructive to compare the effects of doping with the two types of ion.

The cubic unit cell parameter at 25°C, a_o, was found to increase steadily with Mn-concentration in Mn-doped PMNT sintered in CO_2 (Fig. 7), whereas this parameter remains essentially constant at all Co-doping levels, for both CO_2- and air-sintering (Fig. 1). This can be interpreted in terms of the different ionic radii of the Co^{2+} and Mn^{2+} ions: $r^{VI}(Co^{2+})_{LS} = 65$ pm and $r^{VI}(Mn^{2+})_{LS} = 67$ pm.[2] Since these ions are substituting for

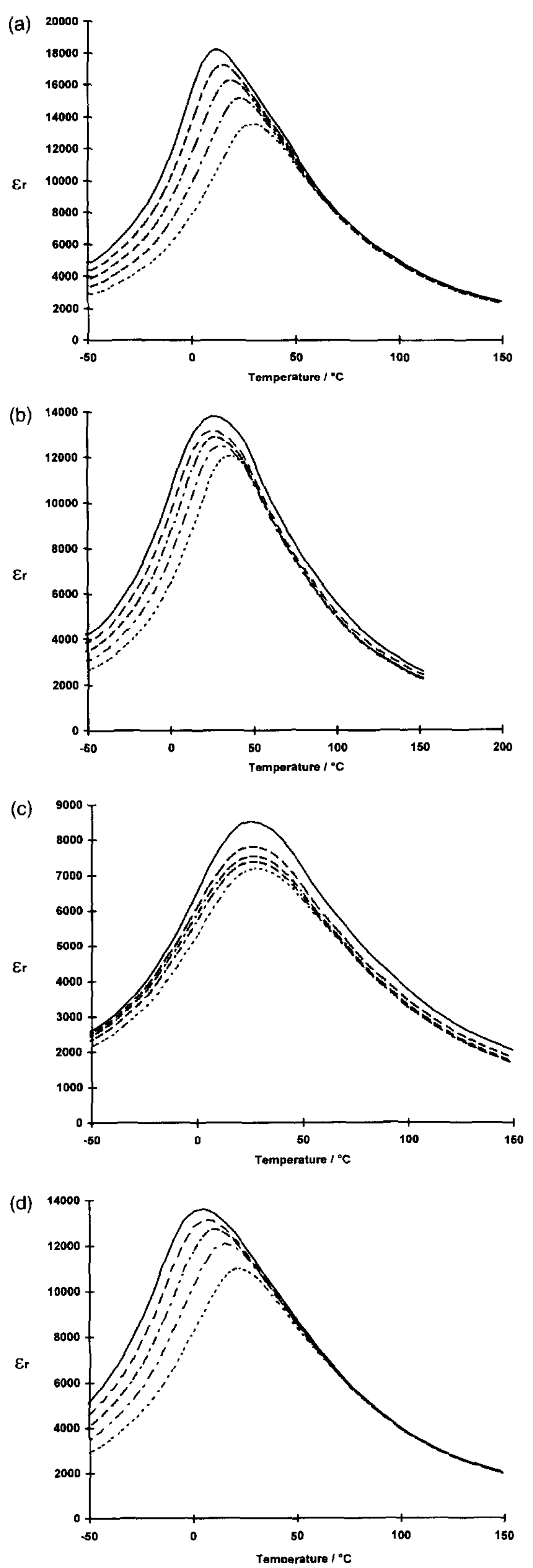

Fig. 3. (a) Variation of relative permittivity with temperature for the $x = 0{\cdot}0045$ composition sintered in air. The continuous curve corresponds to a signal field of frequency 100 Hz, with dashed lines representing frequencies 1 kHz, 10 kHz, 100 kHz and 1 MHz. The length of the dashes decreases with increasing frequency. (b)Variation of relative permittivity with temperature for the $x = 0{\cdot}0223$ composition sintered in air. Frequency is indicated as in Fig. 3(a). (c) Variation of relative permittivity with temperature for the $x = 0{\cdot}065$ composition sintered in air. Frequency is indicated as in Fig. 3(a). (d) Variation of relative permittivity with temperature for the $x = 0{\cdot}065$ composition sintered in CO_2. Frequency is indicated as in Fig. 3(a).

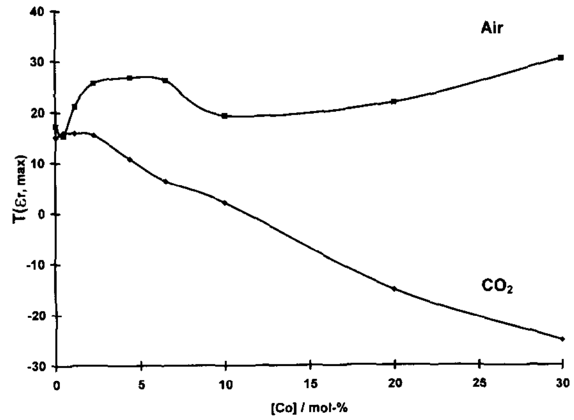

Fig. 4. Variation of temperature of maximum permittivity at 1 kHz, $T(\varepsilon_{r\max})$, with cobalt concentration for samples sintered in air and in carbon dioxide.

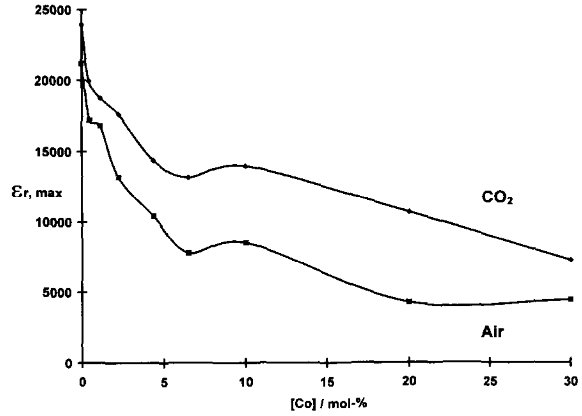

Fig. 5. Variation of maximum relative permittivity at 1 kHz, $\varepsilon_{r\max}$, with cobalt concentration for samples sintered in air and in carbon dioxide.

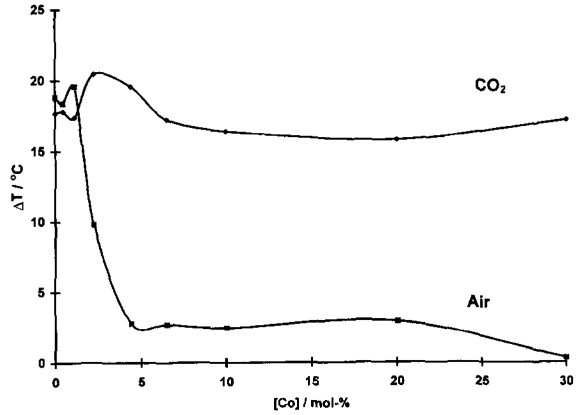

Fig. 6. Variation of frequency dispersion parameter, ΔT, with cobalt concentration for samples sintered in air and in carbon dioxide.

$0{\cdot}95(Mg_{1/3}Nb_{2/3}), 0{\cdot}05Ti$, it is relevant to note that the mean ionic radius of the B-site ions prior to substitution is $0{\cdot}95/3r^{VI}(Mg) + 0{\cdot}95 \times 2/3r^{VI}(Nb) + 0{\cdot}05r^{VI}(Ti)$. Taking values 72, 64·5 and 60·5 pm for the Mg^{2+}, Nb^{5+} and Ti^{4+} ions, respectively, this is calculated to be 66·675 pm. Thus, in contrast to their manganese counterparts,

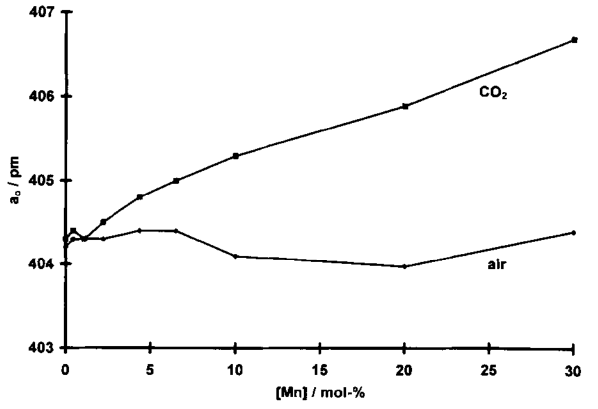

Fig. 7. Variation of cubic lattice parameter, a_o, at 25°C with manganese concentration for Mn-doped PMNT samples sintered in air and in carbon dioxide.

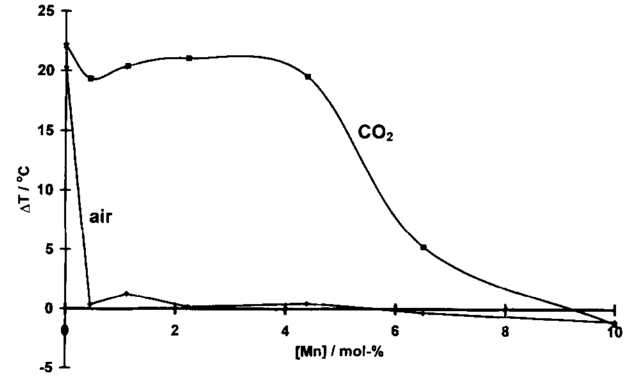

Fig. 8. Variation of frequency dispersion parameter, ΔT, with manganese concentration for Mn-doped PMNT samples sintered in air and in carbon dioxide.

Co^{2+} ions are smaller than the ions being replaced and no expansion of the unit cell is expected. Furthermore, as discussed previously,[1] undersized B-ions do not, in general, give rise to reductions in a_o. With respect to air-sintering, both Mn- and Co-doped samples show essentially no change in a_o with increasing substitution levels. In the case of Mn-doped PMNT, this observation led to the postulate that sintering in air leads to the creation of Mn^{3+} ions of smaller ionic radius of Mn^{3+} ions($r^{VI}(Mn^{2+})_{LS} = 58$ pm).[3] These would show large displacements from the centres of their O_6 octahedra, without any change in a_o. Moreover, these displacements were thought to be associated with the creation of large electric dipoles, which would be capable of 'bridging' polarisation clusters to form macroscopic ferroelectric dipoles.[1]

The similar variation of a_o with [Co] observed in both air and CO_2 does not *require* the existence of Co^{3+} ions in air-sintered samples. However, the progression from relaxor to normal ferroelectric properties (Fig. 3) in air suggests that oxidation from Co^{2+} to Co^{3+} is also occurring here. Considerations of ionic radii alone would suggest that the Co^{3+} ion should form even larger dipole moments than Mn^{3+}, since it has a smaller ionic radius ($r^{VI}(Co^{3+})_{LS} = 55$ pm).[3]

A comparison of Fig. 6 with the corresponding variation for manganese-doping of PMNT (Fig. 8)[1] points to differences in behaviour of the two transition metal ions. Considering first air-sintered samples, Mn-doping causes a rapid fall in ΔT from 20·28 to 0·39°C on the introduction of 0·45 mol% manganese. For Co-doping, however, the fall-off in ΔT is less rapid, falling from 18·85 to 2·82°C at the higher substitution level of 4·38 mol% cobalt. In connection with CO_2-sintered samples, it is seen that, whereas ΔT falls to the value obtained for air-sintering at a doping level of 9 mol% in Mn-substituted PMNT, cobalt-doping has no effect whatsoever on ΔT-values for samples sintered in carbon dioxide. Since it is the presence of 3+ ions which are thought to give rise to reduced frequency dispersion, the inference is that cobalt is less easily oxidised from the 2+ to the 3+ state than manganese. It appears also that no cobalt oxidation takes place at all in the CO_2 atmosphere, in comparison to the behaviour of manganese.

These observations are consistent with the known oxidation behaviour of cobalt.[3] On heating in air, CoO can be converted to Co_3O_4 at temperatures between 600 and 700°C, although CoO is stable again at temperatures above 900°C. Unlike the case of manganese, where manganese (III) oxide (Mn_2O_3) can form at ca. 825°C,[4] the existence of Co_2O_3 has not been confirmed. Thus the highest oxide of cobalt, Co_3O_4, consists of cobalt in both the +2 and +3 oxidation states. A general conclusion to be drawn, therefore, is that oxidation of manganese to the +3 state takes place in air much more readily than is the case for cobalt. Likewise, in CO_2, the higher oxide Mn_3O_4 can form, although no oxidation to Co_3O_4 has been reported for cobalt(II)oxide.

Just as Mn(III)O_6 octahedral units are thought to give rise to large dipole moments in Mn-doped PMNT, comparable effects are anticipated for Co(III)O_6 units in the case of cobalt-doping. This follows from the existence of under-sized Co^{3+} ions within oxygen octahedra of dimensions determined by the parent PMNT material.

As discussed previously,[1] it remains an open question as to whether oxidation of the transition metal ion takes place prior to the perovskite-forming reaction or after this. Since substitution levels of up to 30 mol% cobalt can be accommodated without difficulty in the perovskite phase, it is likely that oxidation takes place *in situ* in the perovskite phase. The alternative, involving oxidation to Co^{3+} before reaction to form a perovskite, would create much smaller ions, of radius 55 pm compared to 65 pm for Co^{2+}. These would tend not to favour the formation of a perovskite phase. Current work on Mn-doped PMNT with $MnCO_3$ as a starting reagent suggests that there is an upper limit to the substitution of manganese of approximately 10 mol%, beyond which a single perovskite phase is not formed. The ability to stabilise Co-doped PMNT as a perovskite to 30 mol% levels may be related to the lower concentrations of Co^{3+} ions likely to be present in Co-doped PMNT samples compared to their manganese counterparts.

In general, the sensitivity of the cobalt-doped PMNT system to sintering atmosphere extends the ability to control the dielectric response chemically. As seen in Fig. 2, acceptable densities are obtained in CO_2 atmospheres by means of cobalt doping. Moreover, the relaxor response has been maintained. This is to be compared with manganese-doped PMNT, where, although acceptable densities are obtained in CO_2 atmospheres, a conversion to normal dielectric properties takes place.

Clearly there is more work to be done on the cobalt-doping of PMNT, both in terms of investigating ceramic processing variables and in understanding the the changes in the structures of the materials as the dielectric response changes. The scope of this ongoing work has been described previously.[1]

5 Conclusion

It has been shown that doping PMNT with cobalt is an effective technique for increasing its sinterability in less oxidising atmospheres, such as CO_2. This is of relevance to the continued development of dielectric ceramics which can be co-sintered with base metal electrodes. The introduction of cobalt into PMNT, followed by sintering in air, has profound effects on its dielectric properties. These have been interpreted in terms of the co-existence of Co^{3+} and Co^{2+} ions, with the former considered to be responsible for a transition between relaxor and normal ferroelectric properties. It is proposed that, through the formation of large dipoles, these ions are able to effect a change from a polarisation cluster type of structure to one consisting essentially of macroscopic ferroelectric domains. Since cobalt is more difficult to oxidise to the +3 state than manganese, the transition to normal ferroelectric properties requires a higher cobalt concentration than is the case for manganese-doping. Moreover, no transition to normal ferroelectric properties is observed for cobalt-doped samples sintered in CO_2.

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