Processing, sintering characteristics and dielectric properties of barium-substituted Pb$(Mg_{1/3}Nb_{2/3})O_3$–PbTiO$_3$ solid solution

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Solid solutions in the lead-based relaxor system Pb$(Mg_{1/3}Nb_{2/3})O_3$–PbTiO$_3$ were modified by minor substitutions of Ba in the Pb-site of the perovskite lattice. The modified compositions were calcined at 830 °C for 3 h to yield fine-grained, single-phase perovskite materials. A small amount of excess MgO(0.05 wt %), which mostly served as a sintering aid, was added to the calcined batches and the resulting mixtures were sintered at temperatures between 1150 and 1250 °C for periods ranging from 3 to 5 h. The substitutions of BaO for PbO in the perovskite solid solution lattice caused a progressive lowering of the Curie point with increasing BaO content. On average, the Curie point decreased by about 10 °C for each mole of BaO substituted for PbO. Among the various Ba-substituted solid solutions studied, the one with a nominal composition Pb$_{0.99}$Ba$_{0.01}$[$(Mg_{1/3}Nb_{2/3})_{0.9}$Ti$_{0.1}$]O$_3$, which has a Curie point located near 28 °C, exhibited excellent dielectric properties. On sintering at 1250 °C for 3 h, this composition yielded a density near 96% of the theoretical density. The peak dielectric constant of the composition at 1 KHz was slightly higher than 22 000, and the corresponding tanδ value was 1.5% with a specific resistivity of $2.5 \times 10^{12}\,\Omega\,cm^{-1}$.

1. Introduction

Perovskite solid solutions in the system Pb$(Mg_{1/3}Nb_{2/3})O_3$–PbTiO$_3$ are known to exhibit excellent dielectric properties and are currently of interest as materials for multilayer capacitors [1–6]. The use of these solid solutions for capacitor applications depends, to a large extent, on the composition and processing technique by which single-phase materials exhibiting superior dielectric properties are readily obtained. As often is the case, an unwanted pyrochlore phase is formed during the processing of the solid solutions, the presence of which even in minute quantities, has been associated with inferior dielectric properties [7–9]. Numerous attempts have been made so far to evolve a simple and reproducible fabrication technique by which a pyrochlore-free material with improved dielectric properties was obtained. Among these attempts, the use of high-purity precursor materials and repeated calcination at elevated temperatures [10], reactions between prefabricated MgNb$_2$O$_6$ and PbO [3, 11] and between prefabricated Pb$_3$Nb$_2$O$_8$ and MgO [12], additions of excess MgO [3, 4, 13–15] and/or excess PbO [3, 5, 13–15] to the stoichiometric solid solution compositions are found to yield near pyrochlore-free perovskite materials suitable for multilayer capacitor applications. Seemingly, the addition of excess PbO and/or MgO to the solid

solutions has some beneficial effect on the sintering characteristics and microstructure development of the resulting ceramics. Nevertheless, particular attention must be given to the nature and amount of these additives and to the optimization of the sintering process all of which must be carefully controlled with a view to enhance the dielectric properties of the resulting materials.

The present investigation primarily deals with the effect of minor substitutions of barium on the sintering characteristics and dielectric properties of perovskite solid solutions in the lead-based relaxor system Pb$(Mg_{1/3}Nb_{2/3})O_3$–PbTiO$_3$. Previous studies concerned with the dielectric properties of Ba-substituted Pb$(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions have either used BaTiO$_3$ as the substituent [16, 17] or dealt with more complex compositions in which both *a*- and *b*-sites of the perovskite lattice were simultaneously modified by multiple ions, i.e. the *a*-site with Ba^{2+} or Sr^{2+}, and the *b*-site with Zn^{2+} [18, 19]. However, in these studies, the exact role of the alkaline-earth ions as substituents for the perovskite solid solutions was not clearly understood. Nevertheless, it has been generally recognized that minor substitutions of Ba^{2+} and Sr^{2+} on the Pb^{2+}-site of the perovskite Pb$(Mg_{1/3}Nb_{2/3})O_3$ lattice led to a decrease in the Curie temperature with a corresponding increase

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in the dielectric constant. In the present study, a solid solution with the nominal composition $90Pb(Mg_{1/3}Nb_{2/3})O_3–10PbTiO_3$ was chosen as the base material. This composition is known to exhibit a maximum dielectric constant of 15 000 near its Curie point of 39 °C [1–3]. Minor substitutions of Ba^{2+} for Pb^{2+} to the perovskite solid solution lattice were made to obtain a series of modified compositions exhibiting a progressive shift of the Curie point towards lower temperatures. The compositions were subjected to a controlled sintering profile to obtain high densities and a uniform microstructure resulting in improved dielectric properties.

2. Experimental procedure
2.1. Sample preparation and characterization

A series of $Pb(Mg_{1/3}Nb_{2/3})O_3–PbTiO_3$-based solid solutions were prepared by the solid state reaction technique using appropriate amounts of reagent grade PbO, $BaCO_3$, MgO, Nb_2O_5 and TiO_2. Because these type of solid solutions are difficult to obtain without the formation of an undesirable pyrochlore phase, the columbite precursor method, as used by several workers [3, 11], was employed to obtain phase pure materials. In this method, prefabricated $MgNb_2O_6$ and $PbTiO_3$ were mixed with appropriate proportions of PbO and $BaCO_3$ powders to yield a range of solid solution compositions with a general formula $Pb_{1-x}Ba_x[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$, where x ranged from 0.005 to 0.03. The mixtures thus obtained were pressed into pellets and then placed between $Pb(Mg_{1/3}Nb_{2/3})O_3$ setters inside a closed alumina crucible filled with prefabricated $Pb(Mg_{1/3}Nb_{2/3})O_3$ coarse powders. This procedure was found to be very effective for minimizing the PbO-loss as well as for preventing any undue contamination from the crucible and the surrounding materials during the firing process. The pellets were calcined at 830 °C for 3 h in air to ensure the formation of single-phase perovskite-based materials suitable for capacitor applications. At the end of the firing period, the specimens were cooled to room temperature, weighed to determine the PbO losses incurred during firing, and then subjected to various analyses to identify the phases present. The crystalline phases present in the specimens were characterized by X-ray powder diffraction (XRD) using Ni-filtered CuK_α radiation. The various XRD patterns obtained were compared with those listed in the JCPDS card file. The pyrochlore phase present in the fired specimens was detected from its characteristic (2 2 2) reflection.

2.2. Sintering characteristics and microstructure development

The initial effort was mainly directed towards assessing the parametric relationships between sintered density and microstructural characteristics as a function of sintering temperature. By this effort, the optimum sintering conditions for obtaining a high density and a uniform microstructure were evolved. As a standard

practice, a small amount of MnO_2 (0.02 wt %) was added to the modified solid solution compositions prior to sintering that helped lowering the dissipation factor (tan δ value) of the ceramics. The mixtures thus obtained were pressed into capacitor discs using a polyvinyl alcohol–water solution as a binder, stacked inside an alumina crucible with a tightly fitted lid and then sintered at temperatures between 1150 and 1250 °C for periods ranging from 3 to 5 h. At the end of the firing period, the sintered discs were cooled inside the furnace and their physical and dielectric properties evaluated.

2.3. Property measurements

The bulk densities of the sintered specimens were determined by the liquid displacement method using xylene as the immersion liquid. For microstructural analysis, selected specimens were prepared by the standard grinding and polishing techniques to obtain suitably polished surfaces and then lightly etched with a 10% HNO_3–0.5% HF–water solution. Both the polished and the fracture surfaces of the specimens were analysed by a scanning electron microscope (SEM) using secondary as well as back-reflection emissions. The phases present in the specimens were identified by an energy dispersive X-ray analyser (EDX) in conjunction with the XRD. The average grain sizes of the sintered specimens were determined from the SEM micrographs using representative areas exhibiting homogeneous grain size distributions.

For dielectric property measurements, the surfaces of the sintered discs were ground and cleaned, and their geometric dimensions, i.e. diameter and thickness, were determined. An electroless Ni-coating, which served as an electrode, was applied to the parallel faces of the discs to ensure good electrical contact. The dielectric experiments were performed in an automated system consisting of a temperature control chamber in which the discs were placed between tightly-fitted contacts and the whole assembly was connected to a capacitance bridge. For all specimens, the capacitance with the corresponding tan δ values were measured at a frequency ranging from 1 to 100 kHz over the temperature range of −10–100 °C. At least three specimens from each composition were used for these measurements, the final values obtained being the average of three consistent readings. The resistivity values of the capacitors were obtained at room temperature using a picoammeter at an appropriate test voltage applied across the specimens.

3. Results and discussion
3.1. Powder preparation

In examining the key issues relevant to the enhancement of the dielectric properties of the modified solid solutions, the first and foremost task was to obtain a single-phase composition with its Curie point shifted to near room temperature. This was accomplished by substituting an appropriate amount of Ba^{2+} for Pb^{2+} in the perovskite lattice. Preliminary attempts to prepare the modified solid solutions with minor

substitutions of Ba^{2+} for Pb^{2+} indicated that the reaction between the various constituents must be performed within a narrow temperature range to yield a single-phase perovskite material without any detectable amount of the unwanted pyrochlore phase. The XRD patterns of the heat-treated specimens revealed that the individual mixtures must be calcined for, at least, 3 h at 830 °C to obtain a near single-phase material. Seemingly, at temperatures below 800 °C the reaction was partially complete and, as a result, the perovskite solid solution phase contained a significant amount of the undesirable pyrochlore phase. On the other hand, prolonged firing at temperatures above 850 °C resulted in the formation of a small but detectable amount of the pyrochlore phase probably due to an excessive PbO-loss from the specimens. Evidently, the PbO-loss incurred during the reaction process was very high ($>1\%$) when the reaction temperatures exceeded the melting point of PbO (888 °C). This observation is consistent with an earlier published study [20] in which the reaction chemistry in the system $PbO–MgO–Nb_2O_5–TiO_2$ and its relevance to the processing of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3–PbTiO_3$ solid solutions have been dealt extensively. In this study, it has been reported that a high loss of PbO during firing generally favours the formation of the pyrochlore phase; which once formed, coexists with the perovskite solid solution.

3.2. Powder characteristics

A characteristic feature of the Ba-substituted $Pb(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions as observed in the present study was the high content of the perovskite phase with a particle size in the submicrometre range. Various data obtained by the XRD and SEM analyses indicated that the reaction products consisted of pyrochlore-free perovskite solid solutions. It was evident that the substitution of Ba^{2+} in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ solid solution lattice allowed the formation of a fine-grained powder with a uniform distribution of particles as compared with a large grain-size distribution of the undoped solid solution. Seemingly, minor substitutions of BaO to the solid solution enhanced the reaction process and, as a result, the reaction temperature for the formation of the perovskite phase was significantly lowered. It is likely that a low reaction temperature coupled with an enhanced reaction rate resulted in the creation of a large number of nuclei of the perovskite crystals that remained homogeneously dispersed in a highly dense powder matrix. With increasing temperature, the reactivity of these crystals was enhanced in the numerous nucleation sites within the matrix and led to the formation of a fine-grained product. An SEM micrograph showing the grain morphology of a Ba-substituted solid solution is shown in Fig. 1. As can be seen in this micrograph, the material appears mostly in the form of a fine grained powder that seems to have agglomerated in many areas within the matrix. The particle-size distribution of the powder is narrow with an average grain size of less than 0.5 μm. The formation of a single-phase perovskite solid solution with submicrometre particle size seems to have far reaching consequences for the improvement of the densification process and subsequent enhancement of the dielectric properties. These points are elaborated in the following sections.

3.3. Sintering characteristics

In evaluating the sintering characteristics of the Ba-substituted solid solutions, it was generally recognized that densification of the various compositions was mostly controlled by solid state processes in which no significant material transport from the particle volume and/or from the grain boundaries occurred during sintering. As a result, a large amount of residual porosity, which mostly appeared in the form of intergranular pores, was retained in the sintered specimens. Thus, particular attention was given to both compositional control and optimization of the densification
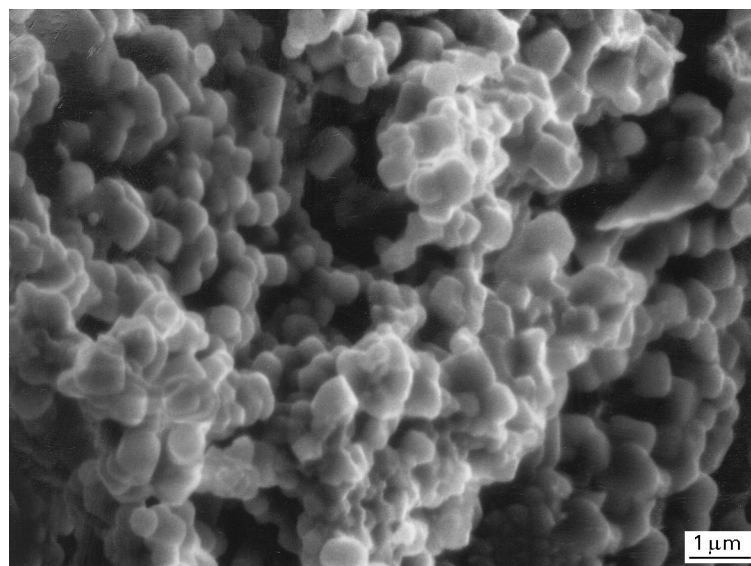

Figure 1 SEM photomicrograph of a Ba-substituted $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution calcined at 830 °C for 3 h showing the morphology of the grain structure.

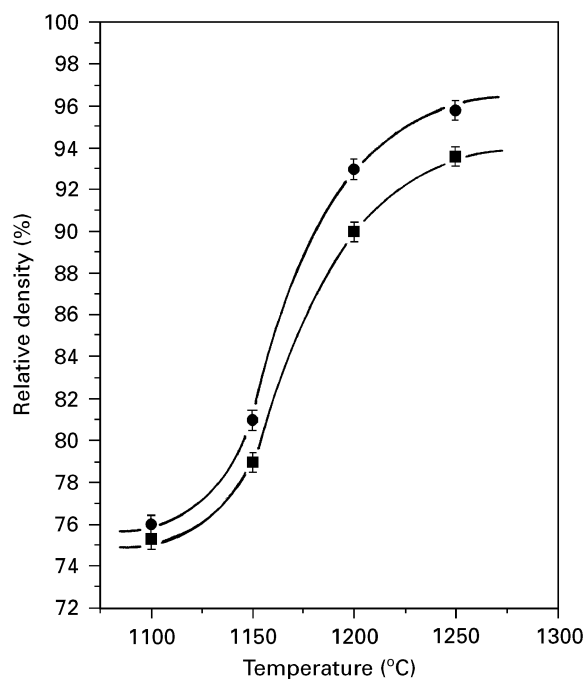*Figure 2* Densification characteristics of $Pb_{0.99}Ba_{0.01}[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution with excess MgO used as an additive. (●) MgO-doped solid solution, (■) undoped solid solution.

process with a view to obtain high densities and to allow a uniform grain growth to occur during sintering of the material. Evidently, a minor addition of excess MgO, which essentially served as a sintering aid, was found to be beneficial for the densification of the solid solutions. This observation is consistent with previously reported studies [1–5, 13]. In the present study, a preliminary attempt to evaluate the sintering characteristics of the solid solutions revealed that an addition of 0.05 wt % excess MgO was needed to obtain specimens with high densities and improved dielectric properties. The effect of excess MgO on the densification behaviour of a Ba-substituted $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ is shown in Fig. 2. As is evident from this figure, the sintered density increased with the addition of excess MgO and reached a value near 96% of the theoretical density at the sintering temperature of 1250 °C. The SEM micrographs of a sintered specimen showing the grain morphology are exhibited in Fig. 3a and b. It is evident from these micrographs that a dense microstructure with an average grain size ranging from 2 to 8 μm has formed at this sintering temperature.

3.4. Dielectric properties

As stated earlier, partial substitutions of Ba^{2+} for Pb^{2+} in the perovskite solid solution lattice caused a significant lowering of the Curie point T_C. Fig. 4 shows the effect of minor substitutions of BaO on the lowering of the T_C of a series of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solutions with different $PbTiO_3$ contents. In general, these compositions can be represented by the general formula Pb_{1-x}–Ba_x–$[(Mg_{1/3}Nb_{2/3})_{1-y}Ti_y]O_3$, where x ranges from 0.005 to 0.015 and y ranges from 0.06 to 0.12. As evident from this figure, the T_C decreased with increasing BaO content regardless of the amount of $PbTiO_3$ present in the solid solutions. On average, T_C decreased to about 10 °C for each mole of BaO substituted for PbO in the solid solution lattice. Of the various solid solutions examined, the one with a composition $90Pb(Mg_{1/3}Nb_{2/3})O_3$–$10PbTiO_3$, and, thus can be represented by the chemical formula $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ was of particular interest because of its superior dielectric properties when compared with the other solid solution compositions. The T_C of this particular composition, which was located near 39 °C, progressively shifted to lower temperatures with increasing substitutions of BaO in the perovskite lattice. The changes in the sintered density, T_C and the dielectric properties of this solid solution with various substitutions of BaO are given in Table I.

From the data given in Table I, it is evident that the Curie point, T_C, of the solid solution $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ shifted progressively from 39 °C to lower temperatures with increasing substitutions of BaO for PbO in the perovskite lattice. The highest value of the dielectric constant was attained with a substitution of 1 mol % BaO, which can be represented by the composition $(Pb_{0.99}Ba_{0.01})$-$[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$. However, with further increase in the BaO content, a progressive lowering of T_C with decreasing dielectric constant was observed. Thus, compositions with a BaO content of 2 mol % and higher showed a shift of T_C from 28 °C to below room temperature with a progressive lowering of the dielectric constant value.

The temperature characteristics of the dielectric constant of $Pb_{0.99}Ba_{0.01}[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ with the corresponding tan δ values are shown in Fig. 5a and b, respectively. As is evident from these figures, the dielectric properties exhibited by this composition are characteristic of a relaxor material in which the phase transition near T_C occurred within a broad temperature

TABLE I Curie temperature (T_C), density and dielectric properties of the Ba^{2+}-substituted $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solutions

| Solid solution composition[a]	T_C (°C)	Density (g cm^{-3})	Maximum dielectric constant	Tan δ (%)	Resistivity (Ω cm^{-1})
$Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$	39	7.80	15 000	3.2	2.5×10^{11}
$(Pb_{0.995}Ba_{0.005})[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$	34	7.82	17 400	2.6	2.5×10^{11}
$(Pb_{0.99}Ba_{0.01})[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$	28	7.84	22 200	1.8	2.4×10^{12}
$(Pb_{0.98}Ba_{0.02})[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$	18	7.82	19 500	1.5	2.6×10^{12}
$(Pb_{0.97}Ba_{0.03})[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$	8	7.80	15 400	1.5	2.6×10^{12}

[a] Specimens sintered at 1250 °C for 3 h.
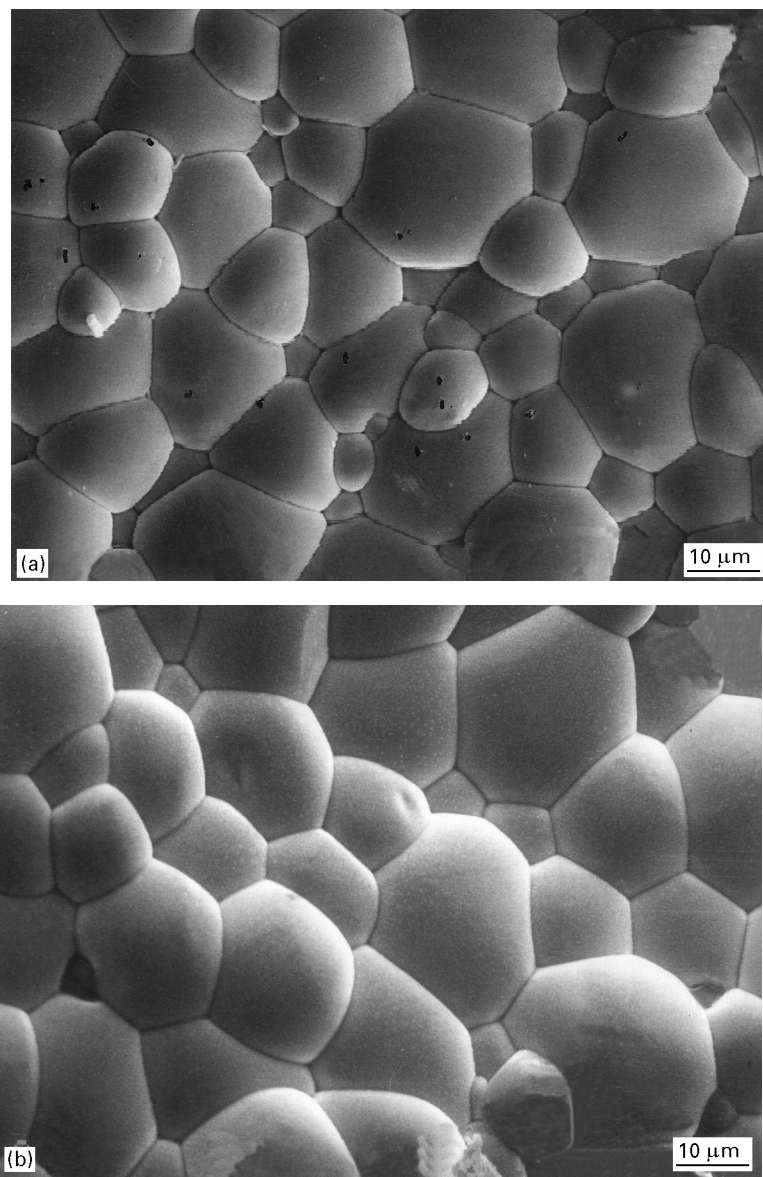
Figure 3 SEM photomicrographs of $Pb_{0.99}Ba_{0.01}[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution sintered at 1250 °C for 3 h: (a) semi-polished surface, and (b) fracture surface.
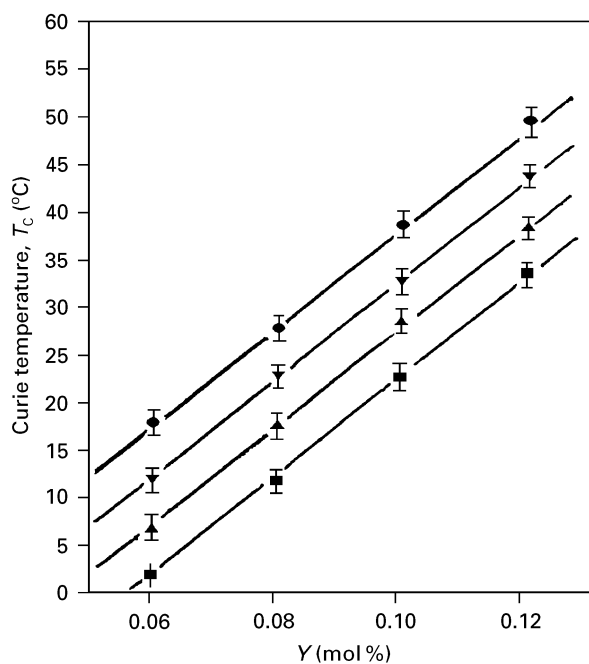
range. Also, both the dielectric constant and $\tan\delta$ loss maxima shifted towards higher temperatures with increasing frequency, which are typical of a relaxor material. The peak dielectric constant value obtained for this composition near its T_C (28 °C) and at 1 kHz was slightly higher than 22 000 (Fig. 5a). The $\tan\delta$ values were moderately high (>4%), particularly, at temperatures below the Curie point (Fig. 5b), which was typical for this type of relaxor material. However, beyond the Curie point, the $\tan\delta$ decreased rapidly with increasing temperature and reached a value of less than 1% at about 30 °C. The specific resistivity measured at room temperature was slightly higher than $2 \times 10^{12}\,\Omega\,cm^{-1}$.

Figure 4 Shift of the Curie temperature, T_C of a series of solid solution with the general composition $Pb_{1-x}Ba_x[(Mg_{1/3}Nb_{2/3})_{1-y}Ti_y]O_3$, where x ranges from 0.005 to 0.015 and y ranges from 0.06 to 0.12: (●) base composition, (▼) $x = 0.005$, (▲) $x = 0.01$, (■) $x = 0.015$.

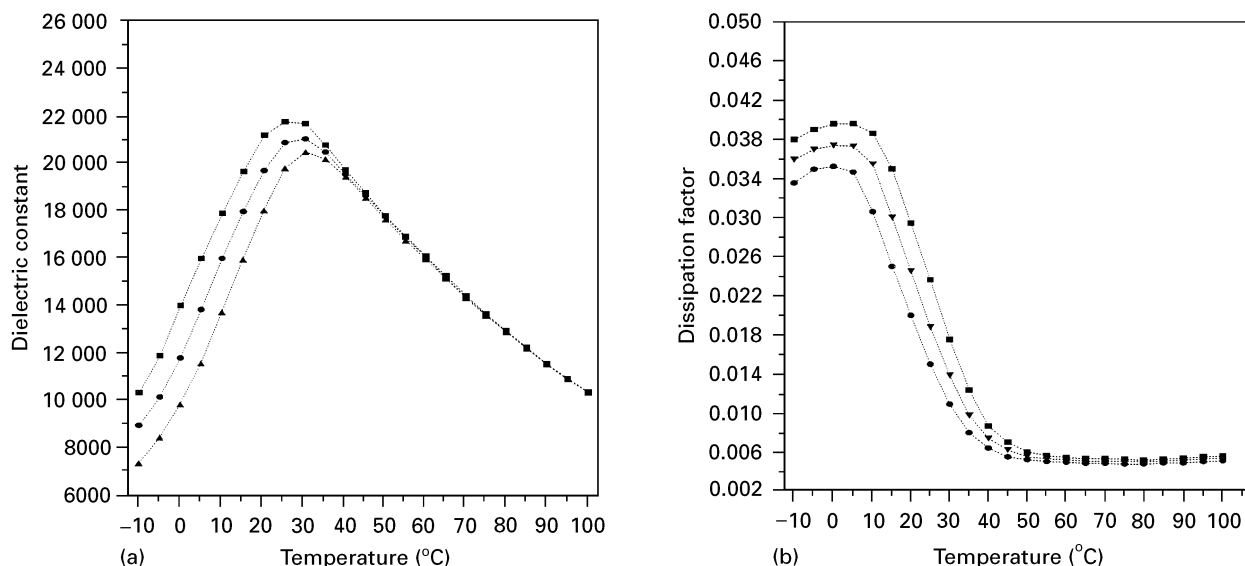*Figure 5* Temperature dependence of the dielectric properties of $Pb_{0.99}Ba_{0.01}[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solutions sintered at 1250 °C for 3 h: (a) dielectric constant, and (b) dissipation factor. For (a): (■) 1 kHz, (●) 10 kHz, (▲) 100 kHz. For (b): (●) 1 kHz, (▲) 10 kHz, (■) 100 kHz.

4. Conclusions

Minor substitutions of Ba^{2+} for Pb^{2+} in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solutions allowed the formation of fine-grained pyrochlore-free perovskite materials. The modified solid solutions were sintered at 1250 °C for 3 h to yield a density near 96% of the theoretical density. The dielectric constant of the solid solutions increased with increasing BaO content and reached a maximum value with 1 mol% BaO. A further increase in the BaO content in the solid solution resulted in a significant lowering of T_C along with a decrease of the dielectric constant value. A modified solid solution of a nominal composition $Pb_{0.99}Ba_{0.01}[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ with a Curie point near 28 °C exhibited superior dielectric properties. The maximum dielectric constant value of this solid solution at 1 kHz was slightly higher than 22 000. The corresponding $\tan\delta$ value was less than 2% with a specific resistivity of $2.4 \times 10^{12}\,\Omega\,cm^{-1}$.

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