Effect of compositional modifications on microstructure development and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solutions

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Abstract

The effect of minor additions of excess MgO and PbO on the sintering characteristics, microstructure development and dielectric properties of perovskite-based $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solutions was investigated. Both MgO and PbO are compatible with the $Pb(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions and thus, these phases co-exist with one another during sintering at elevated temperatures. On sintering a solid solution composition $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ with minor additions of MgO, the excess MgO remained as a discrete phase in the ceramics at temperatures up to 1230 °C and inhibited grain growth. Above this temperature, MgO combined with the solid solution to form a liquid phase, which caused an enhancement of the densification process. On sintering the solid solution with excess PbO, a low-temperature melting PbO-rich liquid phase was formed, which promoted the densification process with inhomogeneous grain growth. Simultaneous additions of 1.0 wt.% MgO and 2.0 wt.% PbO to the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution and sintering the resulting material at 1000 °C for 3 h led to the formation of a dense and homogeneous microstructure consisting of evenly distributed grains with an average grain size of 10 μm. The peak dielectric constant of this composition (at ≈38 °C), measured at a frequency of 1 kHz, was 18,000 with a dissipation factor of <2%. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Pb(Mg, Nb)O₃; PMN-PT; Relaxors

1. Introduction

In the processing of perovskite solid solutions in the lead-based relaxor system $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, formation of an unwanted pyrochlore phase has long been recognized as a major problem for widespread use of these materials as multiplayer capacitors.[1–4] The presence of the pyrochlore phase in the sintered ceramics, even in small quantities, has been associated with inferior dielectric properties of the materials.[5,6] Numerous attempts have been made so far to develop a processing technique in which the formation of the undesirable pyrochlore phase is suppressed. Among these, the Columbite processing technique,[7] in which prefabricated $MgNb_2O_6$ is reacted with an appropriate proportion of PbO, has been widely used in the synthesis of phase-pure perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$-based

materials. During the last several years, numerous studies[8–10] have been reported in the literature in which the Columbite processing technique was modified by using different sets of reactants as precursor materials. A different solid state processing technique[11] in which prefabricated $Pb_3Nb_2O_8$ is reacted with an appropriate proportion of MgO to yield a phase-pure product has also been used in the synthesis of pyrochlore-free perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$.

In addition to the above mentioned difficulties in the processing of phase-pure $Pb(Mg_{1/3}Nb_{2/3})O_3$-based perovskite solid solutions, another area of concern, which has an important bearing on the dielectric properties of these materials, is the densification behaviour and associated microstructure development of the ceramics using various additives that form a liquid phase at low temperatures. Normally, the perovskite solid solutions are sintered at temperatures between 1200 and 1300 °C to obtain a densified product exhibiting superior dielectric properties. In most cases, minor additions of excess

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MgO and/or PbO are used as additives to enhance the densification process, which in turn, results in an enhancement of the dielectric properties of the sintered materials.[1,2,5,12–14] It has been observed that when minor amounts of excess MgO are added to a stoichiometric solid solution composition, the fraction of the undesirable pyrochlore phase is reduced and thus, the proportion of the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase in the final product is substantially increased. However, this finding has been contradicted in a recent study[15] in which it has been reported that an addition of excess MgO neither enhances the reaction process nor does it help in obtaining a phase-pure perovskite solid solution. In another study,[16] it has been reported that large additions of excess MgO ($\approx$4 mol%) give rise to the formation of $Mg_4Nb_2O_9$, the presence of which in the sintered ceramics leads to a a degradation of the dielectric properties of the materials.

Numerous studies have been carried out so far to densify $Pb(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions with minor additions of excess PbO.[1,2,5,14,17–20] In these studies, it has been generally observed that the addition of excess PbO to the solid solutions results in the formation of a low-temperature melting PbO-rich liquid phase below the melting point of PbO (886 °C). The liquid thus formed spreads in the grain boundaries of the ceramics and causes an enhancement of the sintering process with rapid grain growth. However, with the formation of this liquid phase, PbO starts to volatilise off from the specimens and leads to a compositional change, which adversely affects the dielectric properties of the ceramics. Thus, widespread use of PbO as a sintering aid has not been considered as a viable means for the enhancement of the dielectric properties of the solid solutions.

Although the beneficial effects of minor additions of excess MgO and PbO on the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-based perovskite solid solutions have been extensively investigated, little is known so far on the effect of simultaneous additions of MgO and PbO on the sintering characteristics, microstructure development and dielectric properties of these materials. In an attempt to develop low-temperature sintered $Pb(Mg_{1/3}Nb_{2/3})O_3$-based materials with minor additions of excess MgO and/or PbO,[21] it has been found that excess MgO partly dissolves in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ perovskite structure, while the major portion of MgO remains as a second phase in the grain boundaries of the solid solutions. In another study,[22] it has been observed that sintering $Pb(Mg_{1/3}Nb_{2/3})O_3$-based materials with excess MgO and PbO results in an increase in the fluidity of the liquid phase at 950 °C and leads to an enhancement of the densification process. However, it should be noted that sintering of ceramics to a high density in presence of a liquid phase is not always the objective for obtaining superior dielectric properties of

capacitor materials. On the other hand, formation of equilibrium phase assemblages with minor additions of one or more secondary phases and optimising the sintering conditions are far more important for the development of a homogeneous microstructure exhibiting desired grain morphology and grain boundary characteristics with superior dielectric properties. In the present study, a perovskite solid solution having a composition $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ was sintered with simultaneous additions of MgO and PbO at temperatures between 950 and 1100 °C. The densification behaviour and microstructure development of the sintered specimens were studied and the data thus obtained correlated with the dielectric properties of the materials.

2. Experimental

In the present investigation, a perovskite solid solution with a composition $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ was prepared by the hitherto known Columbite processing technique[7] and used as a starting material. In this technique, appropriate proportions of prefabricated $MgNb_2O_6$ and $PbTiO_3$ were reacted with PbO at 825 °C to yield a single-phase perovskite material. Prior to sintering, excess MgO in the amounts of 1, 1.5 and 2 wt.% and excess PbO in the amounts of 1, 2 and 2.5 wt.% were added to the prefabricated prevoskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution. This procedure was found to be necessary to avoid interactions between the precursor $MgNb_2O_6$ and free MgO to yield $Mg_4Nb_2O_9$.[16] It should be noted that because of the large difference in molecular weights between MgO and PbO, the amounts of excess MgO and PbO used as additives are expressed in weight percentage. A minor amount of MnO (0.03 wt.%) was added to all capacitor compositions in order to reduce dielectric loss. The mixtures were milled under alcohol in a polyethylene-lined ball mill with plastic-coated ZrO_2 balls and the resulting slurries were dried in air inside a heated chamber. The powder mixtures thus obtained were pressed in the form of discs and stacked on presintered $Pb(Mg_{1/3}Nb_{2/3})O_3$ setters inside an alumina crucible partly filled with calcined $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder. The crucible containing the specimens was covered with a tightly fitted lid and the assembly was placed inside a second alumina crucible having a slightly larger diameter. By this arrangement, the vapour pressure of PbO surrounding the specimens was increased and, as a result, the PbO loss during sintering was substantially reduced. The specimens were sintered at temperatures of 950, 1000, 1050 and 1100 °C for periods ranging from 1 to 5 h. At the end of the sintering process, the specimens were cooled inside the furnace and then analysed by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) for phase identification.

The XRD patterns were obtained by an automated X-ray diffractometer (Scintag Inc.,CA) using Ni-filtered CuK_α radiation at diffraction angles ranging from 10 to 70°. The patterns thus obtained were compared with the standard X-ray diffraction patterns of various known compounds as listed in the Powder Diffraction File.[23] The sintered specimens were analysed by a scanning electron microscope (SEM) (JCM-35CF, Jeol, Tokyo, Japan) equipped with an energy dispersive X-ray analyser (EDX) (Tracor Northern, Wisconsin, USA) using representative areas exhibiting homogeneous microstructures. The densities of the sintered specimens, as calculated from the weight and geometric dimensions of the pellets, were reported as percentage of theoretical density of the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution. The dielectric properties i.e. capacitance and corresponding tan δ values of the specimens were measured by an automated Hewlett-Packard impedance analyser in a temperature-controlled chamber at temperatures between −10 and 100 °C at frequencies of 1, 10 and 100 kHz. The data thus obtained were presented as temperature dependence of the dielectric constant, measured at these frequencies.

3. Results and discussion

3.1. Characterization of perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solutions

In the present investigation, the solid solution $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ was sintered with minor additions of excess MgO at temperatures between 1000 and 1250 °C, whereas, those containing excess PbO were sintered at temperatures between 950 and 1100 °C. At these temperatures, a heat-treatment period of 3 h was found to be adequate for obtaining maximum density, regardless of the amount of excess MgO and/or PbO present in the specimens. XRD analysis of the various compositions containing excess MgO and PbO indicated that the initial phases present in the specimens did not undergo any compositional change when sintered at progressively higher temperatures. This is consistent with an earlier reported study[24] on the subsolidus compatibility relations between various phases occurring in the ternary system PbO–MgO–Nb$_2$O$_5$. However, with simultaneous additions of excess MgO and PbO and sintering the resulting materials at temperatures above 950 °C, a significant change in the densification behaviour, microstructure development and grain growth characteristics of the specimens was observed. For instance, on sintering the solid solution with excess MgO up to a temperature of 1200 °C, no appreciable change in density and an increase in the grain-size of the specimens was observed. In contrast, on sintering the solid solution with excess PbO at temperatures above

900 °C, a significant increase in density with a corresponding increase in the grain-size of the specimens was observed. Furthermore, compositions containing excess PbO incurred a weight-loss at temperatures above 1000 °C due mainly to the volatilisation of PbO from the specimens and, as a result, a small amount of pyrochlore phase was formed. However, in presence of excess MgO, a substantial decrease in the fraction of the pyrochlore phase was observed, which is consistent with the earlier reported studies.[1,12–14] In the following sections, the effect of minor additions of excess MgO and PbO on the sintering characteristics and microstructure development of the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution was first briefly discussed and then, the effect of simultaneous additions of MgO and PbO on the sintering characteristics, microstructure development and dielectric properties of the materials was elaborated.

3.2. The role of excess MgO on the sintering characteristics and microstructure development of perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution

Microstructural examination of the solid solution $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ that was sintered with various additions of excess MgO revealed that the excess MgO, which was almost always found to be present as a discrete phase in the grain boundaries of the sintered materials, enhanced the densification process by eliminating pores from the specimens. Seemingly, no liquid phase was formed in the specimens when sintered at temperatures up to 1200 °C and consequently, a high density was difficult to achieve. A SEM micrograph of the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing 2 wt.% excess MgO, sintered at 1200 °C for 3 h is shown in Fig. 1. As can be seen in this micrograph, the excess MgO, appearing in the form of small spherical particles, is randomly distributed in the solid solution matrix. However, on sintering this composition at
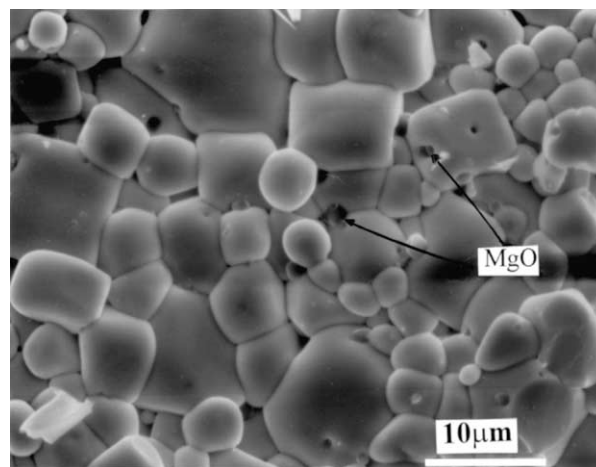

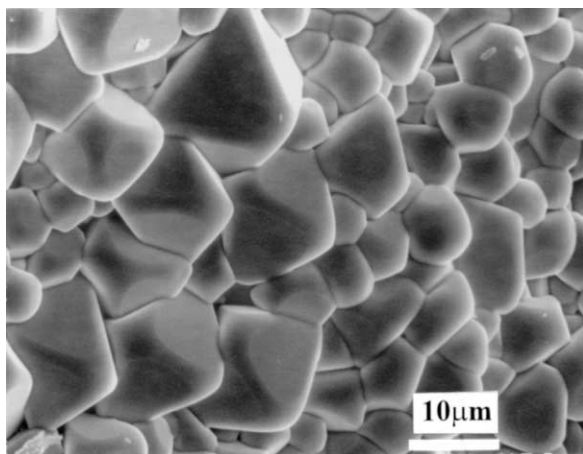Fig. 1. SEM micrograph of $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing 2 wt.% excess MgO, sintered at 1200 °C for 3 h.

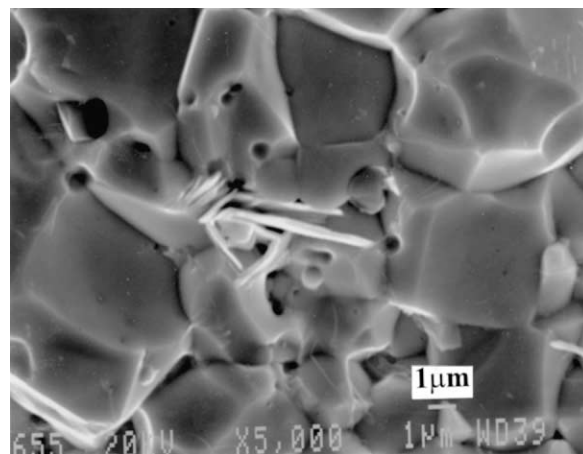Fig. 2. SEM micrograph of $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing 2 wt.% excess MgO, sintered at 1250 °C for 3 h.

Fig. 3. SEM micrograph of $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing 2 wt.% excess PbO, sintered at 1000 °C for 3 h.

temperatures above 1200 °C, a significant change in the overall morphology and grain-growth characteristics was observed. A SEM micrograph of this composition, sintered at 1250 °C for 3 h is shown in Fig. 2. The microstructure essentially consists of a single-phase material without the presence of any detectable amount of MgO in the specimen. The characteristic morphology exhibiting a dense microstructure with several large grains and a near homogeneous grain-size distribution seems to have developed in presence of a liquid phase during sintering at this temperature. To further explore the possibility of liquid formation with additions of excess MgO, a solid solution $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ containing 2 wt.% MgO was subjected to thermogravimetric (TG) and differential thermal analysis (DTA) up to a temperature of 1250 °C at a heating and cooling rate of 10 °C/min. The DTA trace indicated a sharp endothermic peak at about 1230 °C. However, a significant weight-loss was found to occur at this temperature due mainly to the volatilisation of PbO from the specimen. As a consequence, the exact temperature of liquid formation in this specimen could not be accurately determined. Notwithstanding the experimental uncertainties, the appearance of an endothermic peak at 1230 °C and the characteristic microstructural features as observed by SEM/EDX examination supported the conclusion that a liquid phase had formed in this specimen at this temperature.

3.3. The role of excess PbO on the sintering characteristics and microstructure development of perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution

In this investigation, minor additions of excess PbO were made to the prefabricated $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution and the resulting compositions were sintered at temperatures between 950 and 1050 °C

for 3 h. SEM/EDX analysis revealed the presence of a PbO-rich liquid phase in the specimens when sintered at these temperatures. This is consistent with the findings of Ye et al.,[25] who have reported the formation of a eutectic liquid in the binary system $Pb(Mg_{1/3}Nb_{2/3})O_3$–PbO with a melting temperature of 830 °C. The liquid, once formed, rapidly moved in the grain boundaries of the ceramics and led to a significant change in the density and grain growth characteristics of the specimens. In general, the amount of the liquid, formed during sintering, progressively increased with increasing PbO content of the specimens as well as with increasing temperature. At temperatures above 950 °C, the amount of the liquid was found to increase with a corresponding weight-loss due mainly to the volatilisation of PbO from the specimens. As a result, a slightly lower density values were obtained. A SEM micrograph of a $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution composition containing 2 wt.% excess PbO, sintered at 1000 °C for 3 h is shown in Fig. 3. The micrograph essentially consists of an inhomogeneous microstructure with a wide variation of grain size. The excess PbO, appearing mostly as white needles in the grain boundaries and grain junctions of the specimen, seems to have crystallized from the liquid during cooling. Although excess PbO has been known to be an effective sintering aid for the $Pb(Mg_{1/3}Nb_{2/3})O_3$-based perovskite solid solutions, the presence of a PbO-rich liquid phase in the grain boundaries caused a degradation of the dielectric properties of the materials.[14,18] In an earlier publication,[18] the present author has reported the sintering characteristics, microstructure development and dielectric properties of the perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution with various additions of excess PbO. It was observed that an addition of PbO in excess of 2 wt.% led to a lowering of the dielectric constant of the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution.

Table 1

Starting compositions, sintering conditions, relative densities and dielectric constants of perovskite solid solution $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ with various additions of excess MgO and PbO

Starting compositions (solid solution + additives)	Sintering conditions	Relative density (%)	Dielectric constant (ε_{max} at 38 °C)
$Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ + 1 wt.% MgO + 1 wt.% PbO	950 °C/3 h	95.40	15, 000
	1000 °C/3 h	96.30	15, 300
	1050 °C/3 h	96.50	15, 400
	1100 °C/3 h	96.40	15, 400
$Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ + 1 wt.% MgO + 2 wt.% PbO	950 °C/3 h	95.80	17, 200
	1000 °C/3 h	97.30	18, 000
	1050 °C/3 h	97.20	17, 800
	1100 °C/3 h	97.00	17, 500
$Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ + 1.5 wt.% MgO + 2.5 wt.% PbO	950 °C/3 h	95.95	16, 500
	1000 °C/3 h	96.40	17, 000
	1050 °C/3 h	96.30	16, 900
	1100 °C/3 h	96.10	16, 600

3.4. The effect of simultaneous additions of MgO and PbO on the sintering characteristics and microstructure development of perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution

Simultaneous additions of variable proportions of MgO and PbO were made to the prefabricated $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution and the resulting mixtures were sintered at temperatures between 950 and 1100 °C for a period of 3 h. The compositions investigated, sintering conditions, relative densities and maximum dielectric constant values obtained at different temperatures are summarized in Table 1. It can be seen from this table that the relative density increased with increasing sintering temperature as well as with increasing PbO content of the additive mixtures. A density over 97% of the theoretical density was achieved on sintering the solid solution with additions of 1 wt.%
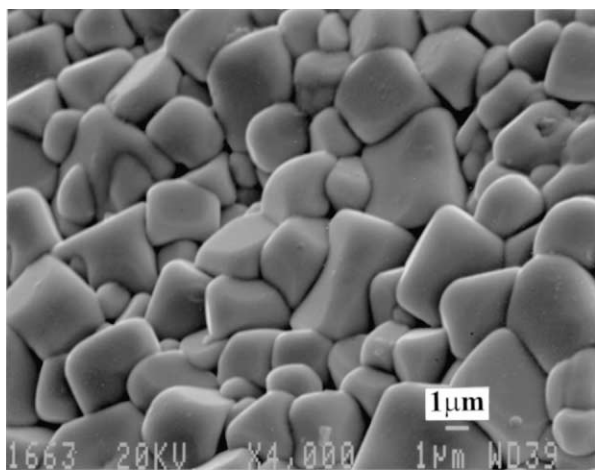

Fig. 4. SEM micrograph of $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing 1 wt.% MgO and 2 wt.% PbO, sintered at 1000 °C for 3 h.

MgO and 2 wt.% PbO at 1000 °C for 3 h. A SEM micrograph of this specimen is exhibited in Fig. 4, which consists of a near single-phase material with evenly distributed grains having grain size ranging from 3 to 10 μm. Also visible in this microstructure, a small amount of a second phase appearing as dark particles is present. This phase that coexists with the solid solution was identified as MgO by SEM/EDS analysis. Further increase in the sintering temperature (> 1000 °C) and/or an increase in the proportion of excess PbO (> 2 wt.% PbO) in the additive MgO/PbO mixture were found to cause a slight decrease in the density values, presumably, because of the PbO loss with a corresponding lowering of the dielectric constant values of the specimens.

From the microstructural characteristics of the sintered specimens, it has become clear that simultaneous additions of excess MgO and PbO to the $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution led to a dense and homogeneous microstructure. Evidently, the densification process was greatly enhanced by the presence of a liquid phase in the grain boundaries of the material. On the other hand, the excess MgO, which remained predominantly as a discrete phase in the grain boundaries of the ceramics, inhibited grain growth. Thus, the rapid grain growth that mostly occurred with additions of excess PbO was partially offset by the presence of excess MgO in the grain boundaries of the solid solution and led to the development of a homogeneous microstructure. It is apparent that the MgO and PbO contents of the additive mixture and the optimisation of the sintering temperature are the two important factors that must be controlled in the processing of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$-based solid solutions with a view to achieving a high density and a homogeneous microstructure exhibiting superior dielectric properties.

3.5. The effect of simultaneous additions of MgO and PbO on the dielectric properties of the perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution

The perovskite $Pb[(Mg_{1/3}Nb_{2/3})_{0.9}Ti_{0.1}]O_3$ solid solution containing minor additions of excess MgO and PbO, when sintered at temperatures between 950 and 1100 °C, exhibited peak dielectric constants (≈38 °C) higher than 15,000 at a frequency of 1 kHz. It can be seen from the data given in Table 1 that a maximum dielectric constant 18,000 was achieved when the solid solution was sintered with additions of 1 wt.% MgO and 2 wt.% PbO at 1000 °C for 3 h. The temperature characteristics of the dielectric constant of this composition, measured at different frequencies (1, 10 and 100 kHz) are shown in Fig. 5. The characteristic frequency dependence of the dielectric constant of this composition exhibiting a shift of the permittivity maxima (ε_{max}) is typical of the lead-based relaxor materials. The dissipation factor (tan δ) obtained for this composition
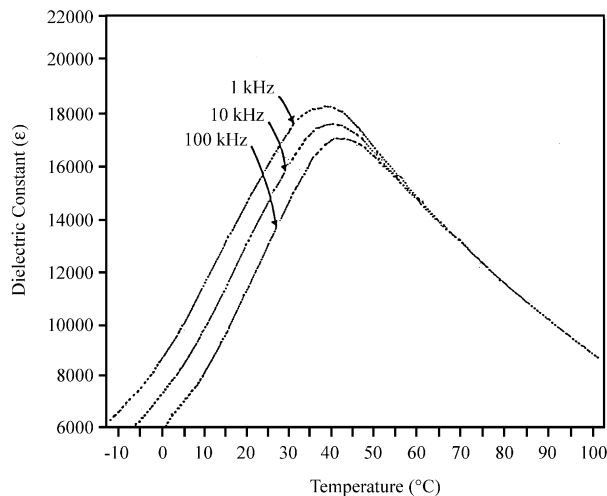
Fig. 5. Temperature characteristics of the dielectric constant of Pb[(Mg$_{1/3}$Nb$_{2/3}$)$_{0.9}$ Ti$_{0.1}$]O$_3$ solid solution with simultaneous additions of excess MgO and PbO, sintered at 1000 °C for 3 h.

below the Curie temperature (T_c) (not shown herein) was very high ($>5\%$), which rapidly decreased to a value near 2% above the T_c without showing any dispersion with the change in frequency. The dielectric constant of the solid solution was progressive lowered with increasing PbO content of the MgO/PbO mixtures as well as with increasing sintering temperature (Table 1). It is reasonable to believe that a high PbO content in the additive mixtures and an increase in the sintering temperature (>1000 °C) resulted in an increase in the amount of the PbO-rich liquid in the grain boundaries of the specimens. An increase in the liquid content resulted in an increase in the grain boundary thickness, thereby, causing a degradation of the dielectric properties of the material.

4. Conclusions

Simultaneous additions of excess MgO and PbO to a perovskite solid solution Pb[(Mg$_{1/3}$Nb$_{2/3}$)$_{0.9}$Ti$_{0.1}$]O$_3$ and sintering the resulting compositions at temperatures between 950 and 1100 °C led to the formation of dense materials exhibiting superior dielectric properties. The excess MgO, used as an additive, remained as a discrete phase in the grain boundaries of the material and inhibited grain growth. Whereas, additions of excess PbO to the solid solution allowed the formation of a PbO-rich liquid phase which remained predominantly in the grain boundaries of the ceramics and enhanced the densification process with rapid grain growth. On sintering the solid solution with a mixture containing 1 wt.% MgO and 2 wt.% PbO at 1000 °C for 3 h, a dense and homogeneous microstructure was obtained. The resulting material exhibited a peak dielectric constant of

18,000 at a temperature near 38 °C with a dissipation factor $<2\%$ at a frequency of 1 kHz.

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