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Comment on "Dielectric Properties of Lead-Magnesium Niobate Ceramics"

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IN A RECENT publication on the dielectric properties of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics, Swartz *et al.*[1] described the processing of pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ and presented data on the sintering behavior, grain-growth characteristics, and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with additions of excess MgO. This is not the first time that the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ capacitor ceramics have been reported in the literature. Furukawa *et al.*[2] dealt with this subject earlier and were first to recognize the beneficial effect of excess MgO on the formation of pyrochlore-free perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. They also reported a significant improvement of the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics with additions of excess MgO. Although this work has been referred by Swartz and Shrout[3] in an earlier publication on the fabrication of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$, they have made no mention of the same in the present article. It is apparent that the earlier reported data by Furukawa *et al.*[1] are highly relevant to the present article and, therefore, cannot be overlooked.

The present communication was prompted by two important aspects of the findings discussed by Swartz *et al.*[1] in their paper, namely, the formation of a lead niobate-based pyrochlore phase during the processing of $Pb(Mg_{1/3}Nb_{2/3})O_3$ and the role of excess MgO in the sintering characteristics and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$. It is felt that their conclusion regarding the lead niobate compound as the pyrochlore phase is more tentative than warranted by the experimental evidence and that their discussions regarding the sintering and dielectric properties related phenomena are open to alternate interpretation.

Swartz *et al.*[1] observed that at the initial stages of the reaction between the precursor oxide powders, a lead niobate-based pyrochlore phase was formed. These authors have referred to an earlier publication by Swartz and Shrout[3] in which the pyrochlore phase was identified as $Pb_3Nb_4O_{13}$. It was further stated that the pyrochlore $Pb_3Nb_4O_{13}$ which was initially formed by the reaction between PbO and Nb_2O_5 at 700° to 800°C subsequently reacted with PbO and MgO at 850° to 900°C to give the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$. However, the authors have not shown any experimental evidence to corroborate their findings and, for that matter, the reaction sequences proposed by them cannot be justified by means of valid chemical equations. Hence, there is no logical basis for the conclusion that the pyrochlore phase formed during the synthesis of $Pb(Mg_{1/3}Nb_{2/3})O_3$ was a lead niobate.

On the basis of a comprehensive study the present author made on the subsolidus phase equilibria in the system PbO-MgO-Nb_2O_5 using solid-state reaction techniques and X-ray powder diffraction, it has become evident that none of the hitherto known lead niobates was formed when a stoichiometric composition corresponding to the compound $Pb(Mg_{1/3}Nb_{2/3})O_3$ was equilibrated at temperatures between 700° and 900°C. The pyrochlore phase actually appears to be based on a rhombohedrally distorted crystal structure and forms by the direct reaction of the starting oxide powders. Relevant data in support of the formation and crystal structure of the rhombohedral pyrochlore phase will be presented in a separate article. However, it should be noted that many inorganic compounds which belong to the perovskite family are known to exhibit similar structural distortion that may be regarded as more or less slight modifications of the ideal structure.[4-6] In the case of $Pb(Mg_{1/3}Nb_{2/3})O_3$, reaction between the constituent oxides inevitably results in the formation of some rhombohedral pyrochlore phase which does not transform to the cubic perovskite phase under normal conditions regardless of the firing temperatures used. The alternative method proposed by Swartz *et al.*[1,3] in which prefabricated $MgNb_2O_6$ and PbO were reacted to form $Pb(Mg_{1/3}Nb_{2/3})O_3$ also has the drawback of not being completely free from the unwanted pyrochlore phase. Likewise, reaction between preformed $Pb_3Nb_2O_8$ and MgO readily yields the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ but not without a small amount of the pyrochlore phase. It is considered highly relevant to mention here the work of Furukawa *et al.*[2] who first pointed out that the pyrochlore phase disappears completely with a small addition of excess MgO. Apparently, that was exactly what Swartz *et al.*[3] did in their study to eliminate the pyrochlore phase. Thus, it is imperative that none of the aforementioned processes ensures a pyrochlore-free end product without the addition of an excess MgO.

Regarding the sintering characteristics and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$, Swartz *et al.*[1] have observed that an increase in maximum dielectric constant was related to an increase in both sintering temperature and excess MgO. According to these workers the increase in dielectric constant with excess MgO corresponded to an increase in grain size. However, the evidence obtained by the present author indicates that the grain growth phenomenon cannot be considered as the most important factor for the sintering process and, therefore, its correlation with the dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ cannot be fully justified. It seems more likely that the effective dielectric constant and the dissipation factor are in major part controlled by the amount of residual porosity present in the sintered sample. To elucidate the point more clearly, it is essential that liquid formation during sintering, which these authors have failed to identify, must first be considered. It has become evident by DTA that a liquid phase, presumably a eutectic between $Pb(Mg_{1/3}Nb_{2/3})O_3$ and MgO, is formed at ≈1300°C which has a marked effect on the sintering process and microstructure development of the sample. It was recognized that the densification and grain growth below this temperature are mostly controlled by solid state processes in which no appreciable material transport from the particle volume and the grain boundary between particles could be observed. As a result, no significant grain growth other than normal grain growth was found to occur with increasing sintering temperatures. Direct evidence in support of this conclusion was obtained by SEM. Figure 1(*A*) shows the micrograph of a sample containing 0.5 wt% MgO sintered at 1250°C for 3 h which exhibits a single-phase microstructure of varying grain size. In contrast, the micrograph of a sample containing 3 wt% MgO that was subjected to identical sintering conditions is shown in Fig. 1(*B*) which exhibits clearly the excess MgO in the form of discrete particles inhibiting grain growth. Sintering at temperatures above 1300°C resulted in the formation of a liquid phase which essentially enhanced the densification process and promoted grain growth. However, prolonged sintering at or above this temperature gave rise to an extensive PbO loss from the sample and the resultant variation in composition led to an inhomogeneous microstructure. The dielectric properties were found to be very sensitive to this compositional change and, in most cases, considerably high values for tan δ loss were obtained.

As stated earlier, an important aspect of the sintering process not considered by Swartz *et al.*[1] is the residual grain-

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boundary porosity which is inevitably present in the sintered compacts and which adversely affects the dielectric properties of the ceramics. Evidently, an excess MgO which occurs predominantly as a second phase in the sample acts to prevent further boundary migration during sintering and allows rapid elimination of the pores along the grain boundaries. Thus, a significant increase in both the firing shrinkage and final density can be accomplished with a small addition of excess MgO. Since the densification below 1300°C is controlled primarily by solid-state processes, complete elimination of the pore and rapid sintering of the compositions into dense ceramics are extremely difficult to achieve. Furthermore, during sintering a slower elimination of the large pores leads to variation in pore concentration and results in pore coarsening with increasing sintering time. Interestingly, the microstructure of a sintered sample exhibited by Swartz *et al.* clearly demonstrates this effect but, apparently, they have failed to recognize it. The microstructure in question is that of a composition containing 5% MgO sintered at 1200°C (Fig. 1(*B*) in Ref. 1) which shows clearly numerous pores located predominantly at the grain boundaries and grain junctions and a few isolated areas where the grain-coarsening effect is clearly visible. This effect is typical of the microstructures obtained by sintering at temperatures below 1300°C in which an appreciable amount of porosity occurs. Evidently, the dielectric properties are largely dependent on the nature and amount of porosity present at a particular sintering temperature and improve with increasing sintering temperature and decreasing pore content. Sintering at temperatures above 1300°C results in the formation of a liquid phase that enhances the densification rate and accelerates pore elimination. A significant grain growth is observed at these temperatures as is also evident from the grain-size data reported by the authors. However, a severe PbO loss from the sample which leads to changes in composition affects the densification process and results in the deterioration of the dielectric properties, particularly, the dissipation factor. It is noteworthy that Swartz *et al.*[1] measured the values of the dissipation factor at different sintering temperatures but did not report these in the article. It is not known why they chose to exclude these data, particularly, when they are highly relevant to understanding both the sintering process and the dielectric properties of the ceramics.

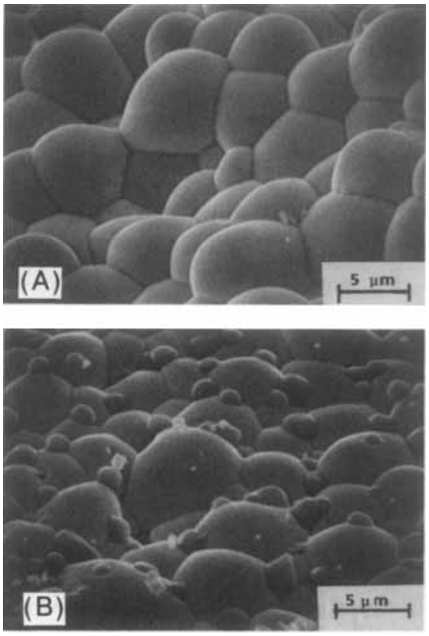

Fig. 1. Scanning electron micrographs of (*A*) $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.5 wt% MgO and (*B*) $Pb(Mg_{1/3}Nb_{2/3})O_3$-3 wt% MgO, both sintered at 1250°C for 3 h.

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Reply

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THE comment by Guha[1] on the dielectric properties of $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) ceramics[2] indicates some discrepancy between our results and those of Guha and also includes some objections to our work. Our reply is intended to clarify some of the confusion that was created by the comment and to explain why we feel that Guha's objections are unwarranted.

In responding to his comments, we wish to note first that perhaps inadvertently Guha is exploring a rather different range of MgO concentrations than in our earlier work. Our earlier studies[2,3] cited by Guha[1] refer to excess MgO concentration in the range 2 to 5 mol%, whereas Guha explores 0.5 wt% (12 mol%) and 3 wt% (72 mol%) excess MgO. With these differences it is perhaps not surprising that his results are rather different.

We would point out that our earlier studies were focused on developing a practical method for fabricating $PbMg_{1/3}Nb_{2/3}O_3$ and its solid solutions with $PbTiO_3$ in the useful perovskite structure without excessive unwanted pyrochlore phases or other low K phases. Our reports were not intended to be definitive studies of phase equilibria in these materials. Under reasonable calcining conditions, we demonstrated that the reaction between PbO and a preformed $MgNb_2O_6$ forms the perovskite with only a small (<2%) of undesired pyrochlore phase, whereas under similar calcining conditions a simple mixed oxide batch gave of the order of 30% pyrochlore. We also reported that a *small* excess of MgO used in conjunction with our method further reduced or even eliminated unwanted pyrochlore.

We never claimed to be the first to recognize the beneficial effects of MgO addition and indeed we know the Chinese have been using excess MgO in their PMN-based dielectric formulations for 20 years.[4] It is also quite clear that our technique is not the only way to make phase-pure perovskite PMN. We do, however, believe that it is superior to the mixed oxide method which requires repeated calcining at high temperature, with grinding and the con-

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