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Preparation Of Perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Using $\text{Pb}_3\text{Nb}_2\text{O}_8$ And MgO

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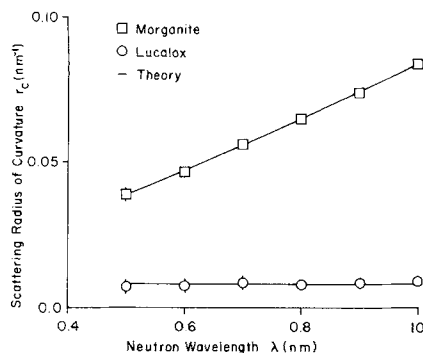


Fig. 4. Theoretical (lines) and experimental (squares and circles) scattering radius of curvature, r_c , vs neutron wavelength, λ , for both sintered alumina samples.

of morganite, there is considerable beam broadening, and both the void fraction of voids (10.5%) and the average void diameter (1.48 μm) have been determined. However, no multiple scattering

was evident from Lucalox even though it was 2.5 cm thick. With sintered materials, the SANS measures both open and closed porosity.

This technique offers a nondestructive approach for studying porosity throughout the bulk of the material. Although sintered materials have been discussed presently, other studies are in progress involving porosity in green-state ceramics, changes in porosity during sintering experiments,⁷ and effects of defects on porosity during the sintering process. Powder characterization studies of particles from 0.1 to 3 μm have included particle size, shape, and size distributions,⁵ as well as small-particle and agglomerate size determinations. Theoretical extensions of the multiple scattering approach and the addition of cold source capabilities at the NBS reactor will allow measurements and analyses of pores, particles, or inclusions to 20 μm . This determination should allow in situ monitoring of the sintering process from the green state to fully sintered ceramics.

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Preparation of Perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Using $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO

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The synthesis of perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ from an equimolar mixture of $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO was studied by solid-state reaction techniques. An addition of 1 wt% excess MgO to the stoichiometric composition enhances the formation of the cubic perovskite phase. The absence of free PbO in the initial starting materials minimizes the volatilization loss during firing, thereby reducing the possibility of any compositional change and resulting in a substantial improvement of the perovskite phase purity over the conventional mixed-oxide processing.

THE perovskite compound $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has recently received considerable attention in the area of electronic ceramics because of its excellent dielectric and ferroelectric properties.¹⁻⁴ Although the existence of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and its stability at elevated temperatures have been established beyond doubt, the synthesis of the compound from the precursor oxides remains difficult. This is due mainly to the inevitable formation of an unwanted pyrochlore phase during the initial stages of

the reaction between the precursor oxides. The kinetics for the conversion of the pyrochlore phase to perovskite are very slow and necessitate repeated firing for prolonged periods at elevated temperatures. Since the presence of the pyrochlore phase even in small quantities in the final product is detrimental to the dielectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, its formation during the reaction process must be eliminated. Furukawa *et al.*⁵ were first to recognize the beneficial effect of excess MgO on the formation of the pyrochlore-free perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and observed a significant improvement of the dielectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ceramics with the addition of ≈ 1 wt% excess MgO . Swartz *et al.*⁶ have proposed an alternative

method in which prefabricated MgNb_2O_6 and PbO were reacted at 800°C to form $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. These workers have confirmed that the pyrochlore phase was eliminated by the addition of an excess MgO . The present communication is intended to show that the compound $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ can be prepared by the solid-state reaction between $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO at 900°C. Since there is no free PbO involved in this synthesis, the volatilization loss that occurs during the synthesis of the compound from the precursor oxides can be completely eliminated.

EXPERIMENTAL PROCEDURE

Lead niobate ($\text{Pb}_3\text{Nb}_2\text{O}_8$) used in this study was prepared by the solid-state reaction of appropriate proportions of high-purity reagent-grade PbO and Nb_2O_5 . Since $\text{Pb}_3\text{Nb}_2\text{O}_8$ and PbO form a eutectic at 830°C in the system PbO - Nb_2O_5 ,⁷ the reaction temperature for the preparation of $\text{Pb}_3\text{Nb}_2\text{O}_8$ used was 820°C. $\text{Pb}_3\text{Nb}_2\text{O}_8$ thus prepared was mixed with an equimolar amount of MgO , pressed into a pellet, and then fired in two calcination steps at 800°C for a combined period of 6 h with intermittent cooling, crushing, and mixing which were followed by a final heat treatment at 900°C for 4 h. Compositions containing an excess of MgO (1 to 2 wt%) were subjected to identical firing conditions. At the end of the firing period, the products were analyzed by X-ray powder diffraction (XRD) using Ni-filtered $\text{CuK}\alpha$ radiation and scanning electron microscopy (SEM) equipped with EDX attachments.

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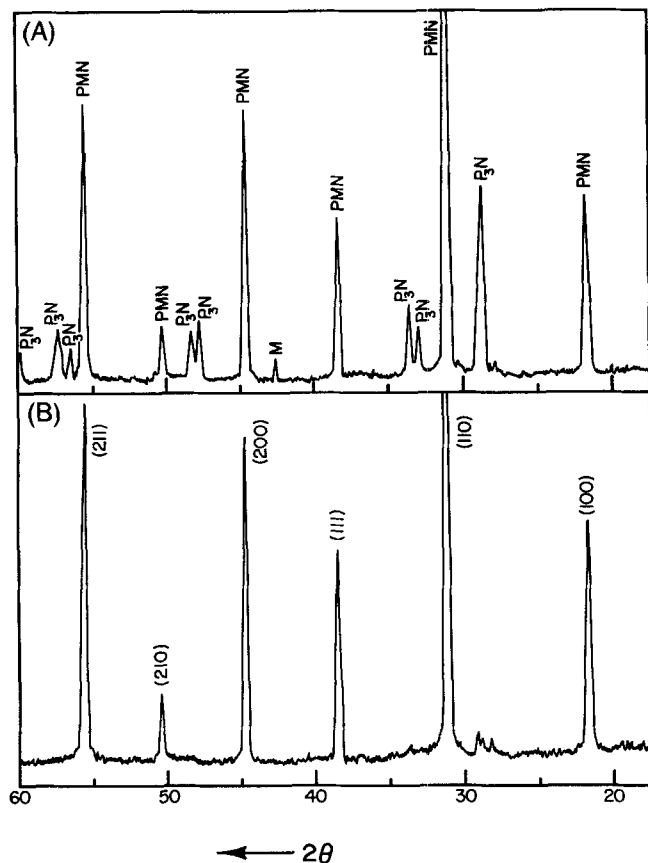
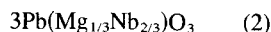
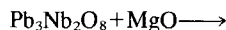
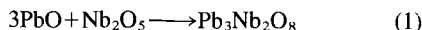


Fig. 1. X-ray powder diffraction pattern of an equimolar mixture of $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO (A) calcined at 800°C for 6 h and (B) fired with 1 wt% excess MgO at 900°C for 4 h. (PMN=cubic $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{P}_3\text{N}=\text{Pb}_3\text{Nb}_2\text{O}_8$, and $\text{M}=\text{MgO}$.)

RESULTS AND DISCUSSION

X-ray diffraction analyses performed on the fired mixtures indicated that, in the temperature range used, $\text{Pb}_3\text{Nb}_2\text{O}_8$ reacts with MgO to form the cubic perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ phase.⁸ Figure 1(A) shows the XRD pattern of an equimolar mixture after repeated calcination at 800°C indicating the presence of mainly the cubic $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ with some unreacted $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO . As can be seen, the presence of the pyrochlore phase could not be detected accurately because of overlapping of the major reflections of this phase and $\text{Pb}_3\text{Nb}_2\text{O}_8$. As the temperature was increased to 900°C , the amount of the cubic perovskite phase increased with corresponding decrease in both $\text{Pb}_3\text{Nb}_2\text{O}_8$ and MgO . However, a complete conversion to the cubic $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was made with an addition of 1 wt% excess MgO to the stoichiometric mixture. Figure 1(B) shows the XRD pattern of a mixture containing excess MgO that had been subjected to identical heat-treatment conditions indicating the formation of the cubic $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ with very little pyro-

chlore present. It is evident, therefore, that an addition of excess MgO enhances the reaction rate and allows the formation of the cubic perovskite phase. Thus, the overall reaction sequence observed by the XRD analysis can be represented by the following equations:



It can be seen from Eq. (2) that no free PbO is involved in the preparation of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and hence a firing temperature in excess of the melting point of PbO (889°C) can be used in the synthesis of the compound. Likewise, the loss due to volatilization of PbO is completely eliminated in this process and, consequently, the composition of the compound can be effectively controlled during the firing process.

The scanning electron micrograph of a fracture surface of the compact obtained on

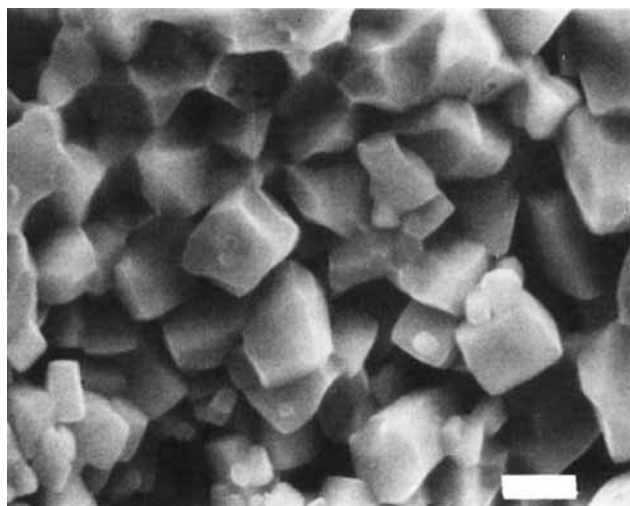


Fig. 2. Scanning electron micrograph of the fracture surface of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ sample fired at 900°C for 4 h (bar = $1 \mu\text{m}$).

firing at 900°C is shown in Fig. 2. As can be seen the morphology of the powder compact essentially reveals cubic grains with grain size varying within the range 0.5 to $2.0 \mu\text{m}$. The EDX analysis of the grains indicated the presence of lead, magnesium, and niobium in the sample.

The reaction sequence described herein provides yet another method of preparing $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and appears to be a substantial improvement over the conventional mixed-oxide process. The ease with which the pyrochlore-free perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ phase is formed largely depends on the amount of excess MgO added to the starting stoichiometric mixture and also on the firing temperature used for the synthesis of the compound.

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