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ENHANCED PROCESSING OF PEROVSKITE $Pb(Mg_{1/3}Nb_{2/3})O_3$ RELAXORS THROUGH UNDERSTANDING THE SURFACE CHEMISTRY OF THE COMPONENT POWDERS

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ABSTRACT

It is well known that the relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$ [PMN] is difficult to prepare in the perovskite form without the appearance of pyrochlore phase(s). The appearance of pyrochlore is related to the reactivity of the refractory oxide MgO in relation to the other phases in the $PbO\text{-}Nb_2O_5$ binary system. Ceramic processes that improve the reactivity of the oxide MgO, such as better mixing/milling-dispersibility enhance the formation of the perovskite phase. Characterization of the surface chemistry of the component powders, Nb_2O_5, $PbCO_3$ and $MgCO_3$, especially in terms of their Isoelectric Points revealed that electrostatically dispersed suspensions could be realized at pH levels > 11. In conjunction with high energy attrition mixing/milling, very homogeneous and reactive powder could be achieved. Upon calcination, the formation of pyrochlore was greatly suppressed.

INTRODUCTION

In recent years lead-based perovskites, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ [PMN] have shown great promise for application in both capacitors and electrostrictive actuators.(1,2) It is well known, however, that such relaxor materials are difficult to prepare in the perovskite form without the appearance of pyrochlore phase(s), (e.g. $Pb_3Nb_4O_{13}$). The appearance of pyrochlore phase(s) is related to the reactivity of the refractory oxides in relation to the other phases in the $PbO\text{-}Nb_2O_5$ binary system. For the case of PMN, the refractory oxide is MgO. Thus, ceramic processing that improves the reactivity of the oxide MgO, such as better milling/mixing-dispersibility, enhances the formation of the perovskite phase.

Perovskite formation associated with conventional ceramic processing of PMN, has been improved by the novel columbite precursor method developed by Swartz and Shrout.(3) The columbite precursor process allows for the elimination of pyrochlore phases by first pre-reacting the B-site cation oxides (MgO and Nb_2O_5) prior to reaction with PbO. The columbite precursor method has been quite successful in eliminating, or reducing, the problem of pyrochlore formation in perovskite relaxors. However, this process often requires a high calcination temperature (> 1000° C) and subsequent milling steps that complicate the fabrication process. It is the purpose of this paper to show that the problem of pyrochlore formation in PMN can be minimized through a basic understanding of the physical and chemical characteristics of the system, particularly the surface chemistry, of the component powders. With this information, which includes specific surface areas, particle size, isoelectric points, etc., optimum dispersion and enhanced milling efficiency may be realized leading to the fabrication of perovskite PMN without using the columbite precursor method.

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EXPERIMENTAL METHODS AND RESULTS

Powder Characterization

The raw materials used in this study were white lead $2PbCO_3 \cdot Pb(OH)_2$[a], technical grade Nb_2O_5[b] and Magnesium Carbonate $MgCO_3$[c]. The component powders were characterized by determining their as-received surface area, loss on ignition (LOI), and particle size. Equally important as particle size, the degree of agglomeration of the powders was estimated from the ratio of the median equivalent spherical volume from the particle sizing technique to the average volume calculated from specific surface area measurements. The ratio, designated as the average agglomeration number, AAN(4) represents an estimate of the number of primary particles in each agglomerate.

The surface area, LOI, median particle size, and AAN values for the component powders are reported in Table I. No particle size value and thus AAN value for the $MgCO_3$ powder was reported due to its intrinsically poor dispersion characteristics.

For comparison of particle sizes and the degree of agglomeration, SEM photomicrographs of the powders were also taken and shown in Figure 1. From these photos and from Table I the magnesium carbonate was found to be highly porous (spongy) and highly agglomerated where some agglomeration was observed for the niobium oxide and the white lead powder.

Table I. Powder Characteristics

Material	L.O.I.	Specific Surface Area (m^2/g)	Median Particle Size (µm)	AAN
White Lead ($PbCO_3$)	14.2%	0.82	3.5	34
Niobium Pentoxide (Nb_2O_5)	0.3%	2.04	1.4	10
Magnesium Carbonate ($MgCO_3$)	59.1%	24.5	---	---

Dispersion Behavior

In order to prepare homogeneous powder mixtures the dispersion characteristics/behavior of the component powders were studied. Basically there are two types of dispersion mechanisms used to prepare stable powder suspensions or slurries; (1) electrostatic repulsion and (2) steric or electrosteric interactions from adsorbed polymers. The two types of dispersion mechanisms are depicted in Figure 2. Obviously, to utilize the above dispersion mechanisms one must

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(a)Hammond Lead Products, White Lead HLP-A (99%), Hammond, IN.

(b)Fansteel Metals, Techgrade Nb_2O_5 (99.5%), Muskegee, OK.

(c)Fischer Scientific Co., Magnesium Carbonate, purified grade, Pittsburgh, PA

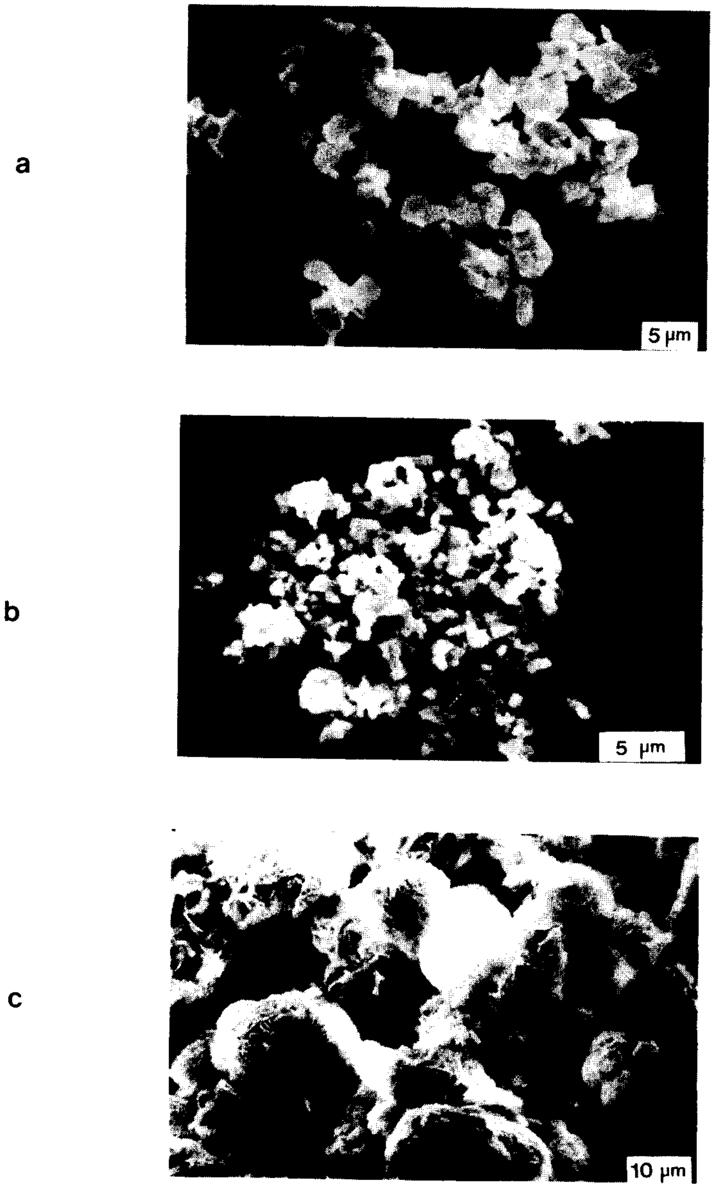

Figure 1. SEM photomicrographs of the component powders 'a'-$PbCO_3$, 'b'-Nb_2O_5, and 'c'-$MgCO_3$.

understand the nature of the surface chemistry of the powders.

Investigation of the surface chemistry involved the determination of the isoelectric points (IEP) of the component powders. A commercial electrophoresis apparatus(d) was used to determine the electrophoretic mobilities. The zeta-potentials, calculated using the Smoluchowski equation(5), were plotted as a function of solution pH to determine the IEP (i.e., the pH point value through interpolation at which the polarity of the zeta-potential changes). The IEPs were found to be at pH 3.5, 7, and > 12 for Nb_2O_5, white lead, and $MgCO_3$ respectively. Due to dissolution of $MgCO_3$, the IEP determination was estimated.

(d)Rank Brothers Mark II electrophoresis apparatus, Cambridge, U.K.

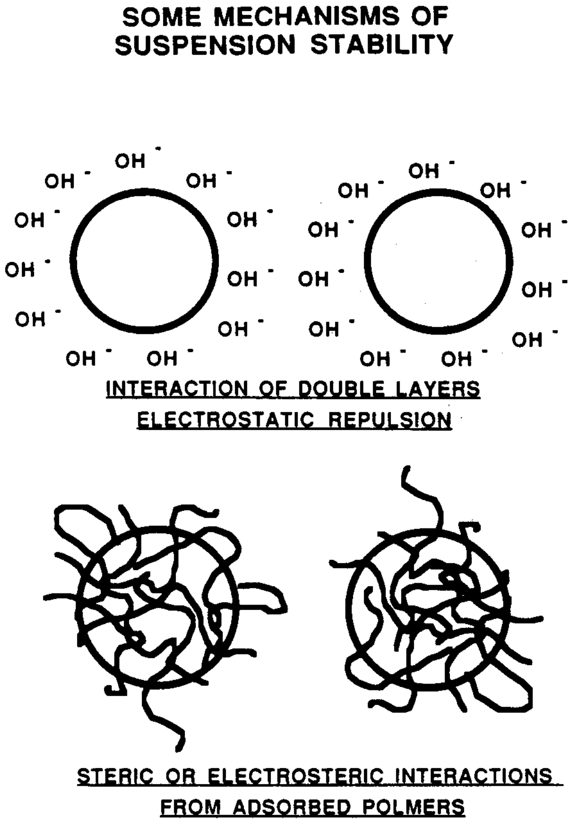

Figure 2. Schematic of "electrostatic repulsion" and "steric hinderance" dispersion mechanisms.

Milling Techniques

Dispersion by electrostatic repulsion is only metastable, in that a certain fraction of interparticle collisions, per unit time results in coagule formation, especially when new surfaces are created and particle number concentration increases during comminution. Therefore two types of high energy milling techniques were evaluated: vibratory(e) and attrition(f). For the comparison of milling behavior, equivalent slurries, comprised of 30 vol% Nb_2O_5, deionized H_2O and 0.5 wt% ammonium polymethacrylate dispersant(g), were prepared. The results are shown in Figure 3, where it is found that surface area increase was approximately 10 times more efficient for attrition milling. Therefore, attrition milling was used for the remainder of this study.

To demonstrate the possibility of using electrostatic repulsion dispersion, slurries comprised of 30 vol% Nb_2O_5 powder and deionized H_2O were attrition milled as a function of pH. The solution pH was adjusted using ammonum hydroxide (NH_4OH) with the viscosity(h) determined (@ 60 rpm/spindle #3) as an indicator of the degree of dispersion. Figure 4 shows a plot of viscosity as a function of slurry pH demonstrating electrostatic dispersion as the slurry pH is changed away from the IEP.

(e)Sweco, Inc., Model M-18-5, Florence, KY.

(f)Union Process, Inc., Model 01, Akron, OH.

(g)Rohm and Haas, Tamol-901, Philadelphia, PA.

(h)Brookfield Model LVF Viscometer, Stoughton, MA.

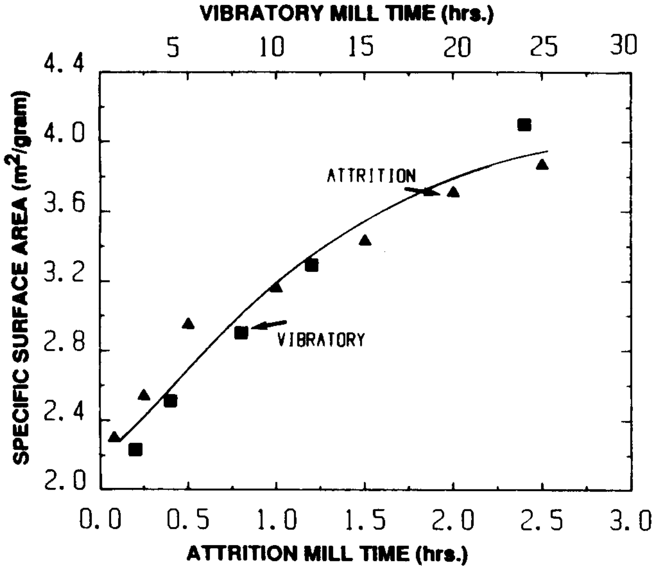

Figure 3. Specific surface area as a function of milling time for vibratory and attrition milled Nb_2O_5 powder.

Enhanced Milling/Dispersion of PMN

Based on the observations above and corresponding IEPs, dispersion of white lead, Nb_2O_5, and $MgCO_3$ powders by electrostatic repulsion should be realized at a high slurry pH levels. A slurry, pre-adjusted with ammonia to give a slurry pH > 11 prior to the addition of the appropriate amounts of component powders for stoichiometric PMN was prepared. Difficulties in obtaining a suspension pH > 11 led to a final solids loading of ~ 20 volume percent which resulted in a viscosity (~ 300 CPS) compatible with the attrition mill. The slurry was milled for a period of 8 hrs with the pH and viscosity being measured as a function of mill time.

As found during the milling of the individual component powder Nb_2O_5, with the creation of new surfaces and partial dissolution of $MgCO_3$, the pH of the slurry was found to change downward as expected. To stabilize the slurry viscosity and pH, additional amounts of ammonia was added during the milling cycle. Stabilization of the slurry could also be enhanced by the addition of polyelectrolyte dispersant (Tamol-901), but if the pH was maintained > 11, none was required.

For further characterization, samples from the slurry were removed at various time intervals. Upon drying, the milled power was characterized by specific surface area. As shown in Figure 5, the S.A. of the milled component powders was found to increase, dramatically at first, with milling time.

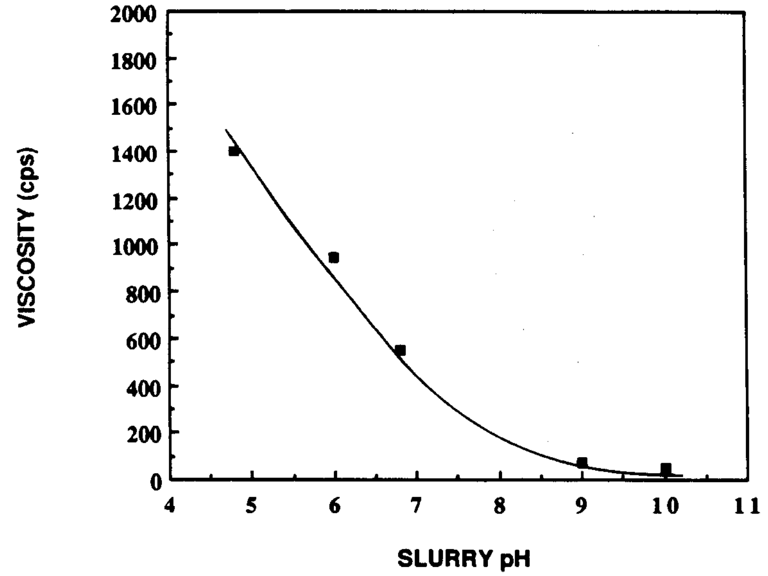

Figure 4. Viscosity as a function of pH for a 30 vol% slurry of Nb_2O_5 powder.

Calcination of PMN

To demonstrate the importance of enhanced milling resulting in improved homogeneity and reactivity of the component powders, especially $MgCO_3$, a calcination study was performed. Samples from the milling study at different time intervals were calcined in alumina crucibles at 850° C for 1 hr. The degree at which the reaction took place was determined by powder X-ray diffraction where the quantities of perovskite and pyrochlore ($Pb_3Nb_4O_{13}$) phases were determined. The relative amount of phases was determined from the X-ray diffraction intensities by:

$$\%\ \text{Perovskite} = \frac{I_{(110)\ \text{perovskite}}}{I_{\text{perovskite}} + I_{(222)\ \text{pyrochlore}}}$$

Figure 6 shows the relative amount of pyrochlore as a function of milling time. As shown, the amount of pyrochlore was found to drastically reduce with milling time. At a milling time of 8 hrs, greater than 95% phase pure perovskite was achieved. Note: only the pyrochlore $Pb_3Nb_4O_{13}$ phase was observed.

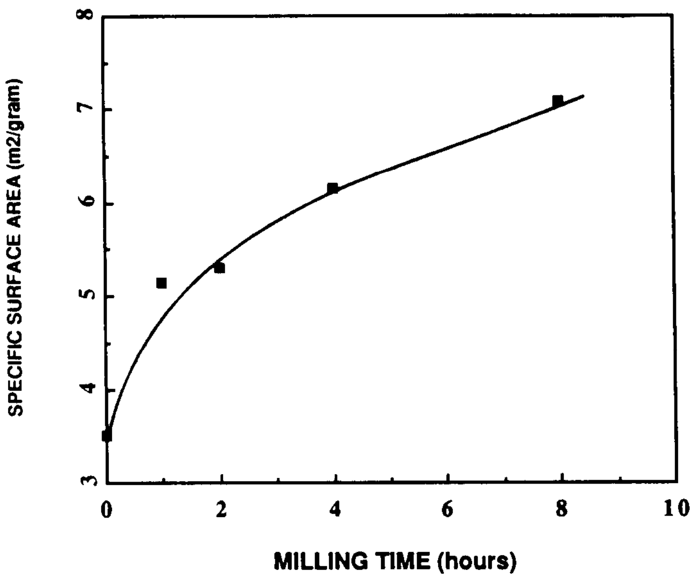

Figure 5. Specific surface area of P + M + N component powders as a function of milling time.

SUMMARY OF RESULTS

The reaction kinetics of the formation of perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ is believed to be related to the reactivity of the refractory oxide MgO to the binary $PbO-Nb_2O_5$ system. However, even when very reactive (high specific surface area) MgO powders are used in conventional processing of PMN ceramics, pyrochlore phase(s) predominate. The poor reactivity of perovskite formation is primarily related to poor dispersibility of MgO and thus results in inhomogeneous powder mixtures. The poor dispersibility of MgO powders, which are inherently highly agglomerated, was evident by its very high IEP (pH > 12) and dissolution at various pH levels leading to poorly dispersed and unstable suspensions.

Characterization of the surface chemistry of all the component powders, Nb_2O_5, white lead, and $MgCO_3$ especially in terms of their IEPs, revealed that electrostatically dispersed suspensions could be realized at pH levels > 11. In conjunction with high energy attrition mixing/milling, very homogeneous and reactive powder was achieved. Upon calcination, it was found that the formation of pyrochlore phase was greatly suppressed.

Though the pyrochlore phase was never completely eliminated, as one can through using the columbite precursor method, this work clearly demonstrated the importance of understanding the surface chemistry to allow for enhanced mixing/milling in the P + M + N system.

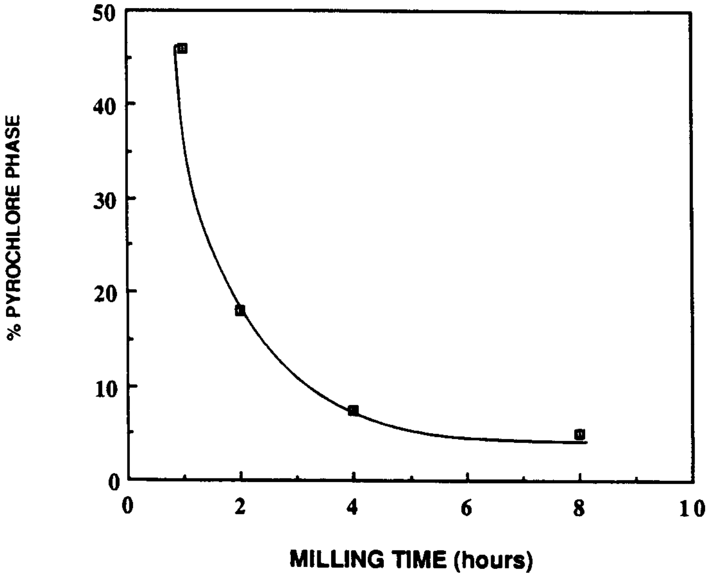

Figure 6. Relative amount of pyrochlore phase in calcined P + M + N as a function of milling time.

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