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The Isoelectric Point of Lead Magnesium Niobate

Aylin M. Deliormanlı,[†,‡] Erdal Çelik,[§] and Mehmet Polat[‡]

[‡]Chemical Engineering Department, Izmir Institute of Technology, Urla, Izmir, Turkey

[§]Metallurgy and Materials Engineering Department, Dokuz Eylül University, Izmir, Turkey

Lead magnesium niobate (PMN) is an important relaxor ferro-electric material commonly used in multilayer capacitor and actuator manufacturing owing to its high dielectric constant and superior electrostrictive properties. However, the isoelectric point of this material in water is not known and there is justification for a detailed investigation. In this work, the isoelectric point (IEP) of aqueous PMN suspensions were determined as a function of solids concentration. Results showed that IEP of the PMN suspensions strongly depended on the solids loading. The IEP was between pH 9 and 10 at particle concentrations between 10 to 20 vol%. The IEP shifted gradually to a lower pH value as the particle concentration decreased. Solubility experiments showed that Pb^{2+} and Mg^{2+} ions dissolved from the PMN surface, especially in the acidic pH range. The study provides a new insight on the aqueous stability of perovskite materials which possess more than one soluble cation in their structure.

I. Introduction

LEAD magnesium niobate (PMN) is a relaxor ferroelectric material, which is characterized by a diffuse phase transition over a broad temperature range and a frequency-dependent maximum in its relative dielectric permittivity.[1] It has many potential applications such as multilayer ceramic capacitors, actuators, and electro-optic devices.[2] It also finds applications in motors, pumps, optical scanning systems, and vibration isolators.[3]

The manufacturing of multilayer electronic devices composed of perovskite materials such as PMN generally involves a colloidal process, which requires preparation of colloidal suspensions. However, the behavior of PMN particles in water medium has yet to be clarified. The few studies on this subject include the preparation of PMN-lead titanate (PMN-PT) suspensions in solvents other than water[4–6] whereas detailed work is present on barium titanate system in water.[7,8] Therefore, understanding of the PMN–H_2O system is essential in producing high-quality PMN ceramics.

The isoelectric point (IEP) is an important parameter in the PMN–H_2O system because it determines the stability of the colloidal particles in liquid medium. It is the pH value at which the apparent charge of the particles is zero.[9] Therefore, the electrostatic repulsion between the interacting particles is eliminated at the IEP. Under such a condition, particles become unstable and tend to coagulate. Ceramic oxides generally have well defined and characteristic IEP values.[10] On the other hand, it is possible for a powder to exhibit multiple IEP values due to specific adsorption, dissolution, and/or precipitation reactions.[11,12]

V. Hackley—contributing editor

[†]Author to whom correspondence should be addressed. e-mail: aylindeliormanli@iyte.edu.tr

Perovskite materials such as PMN have the general chemical formula, ABO_3 (A = K, Na, Ca, Ba, Pb, Mg, etc.) and (B = Ti, Nb, Zr, etc.). In perovkites, the cation at the A site is generally soluble in water whereas the B-site cation that is only slightly soluble overall the practical pH range. Therefore, the A-site cation undergoes incongruent dissolution leaving an interface that is relatively rich in the B-site cation. Because of this fact, determination of the IEP of the perovskite materials such as PMN cannot be made by titration of the stock suspensions at a single solids loading.[13]

Paik and Hackley investigated the effect of solids concentration on the IEP of barium titanate. They reported that the particle surface charge was influenced by solids concentration in aqueous suspensions of barium titanate. They observed a systematic acidic shift in the isoelectric pH with decreasing solids concentration.[7]

In this study, the dependence of the IEP of PMN suspensions on solution pH and solids loading was investigated. The solubility characteristics of the cations that constitute PMN were examined as a function of pH.

II. Experimental Procedure

PMN, $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder produced by the combustion spray pyrolysis method was provided by Praxair Specialty Ceramics (Woodinville, WA). Powder purity is 99.9% as reported by the manufacturer. Bulk density (Helium pycnometer Micromeritics 1330) and the Brunauer–Emmett–Teller surface area (Micromeritics ASAP 2400, Norcross, GA) of the powder are measured to be 7.967 g/cm^3 and 1.168 m^2/g, respectively. Particle size distribution of the powder was measured using a particle size analyzer (Model CAPA-700, Horiba, Ltd., Tokyo, Japan) and the d_{50} of the powder was around 2.0 μm. Other materials used in the work are Niobium (V) oxide (Alfa Aesar, 99.9% metal basis), lead (II) oxide (Alfa Aesar, Ward Hill, MA, 99.9%), and magnesium oxide (Analytical reagent, Mallinckrodt AR, Paris).

Aqueous PMN suspensions of varying pH values were prepared at different solids loadings ranging from 0.001 to 20 vol% using deionized water. Suspensions were magnetically stirred for 24 h prior the measurements at room temperature. pH adjustments were performed using 1M solutions of HNO_3 and NH_4OH. The pH of the suspensions were controlled during the stirring period and further adjustment were performed when necessary. Because the addition of simple electrolytes do not affect the IEP (although it affects the magnitude of the ζ potential), no care was taken to control the electrolyte concentration such as by using a background electrolyte.

Solubility of Pb^{2+}, Mg^{2+}, and Nb^{5+} ions in the PMN structure was examined using inductively coupled plasma-atomic emission spectrometer (ICP-AES Optima 2000 DV Perkin Elmer, Norwalk, CT). For this purpose, suspensions prepared at 5 vol% according to the procedure described in the previous section were centrifuged at 4000 rpm for 1 h to obtain a clear supernatant. Supernatants were further filtered from 0.02 μm

microfilters to eliminate any possible particles in solution. The amounts of Pb^{2+}, Mg^{2+}, and Nb^{5+} in particle-free supernatants were determined using ICP-AES at different pH values.

ζ potential measurements were performed using a ζ sizer (Malvern 3000 HS, Malvern Instruments, Ltd., Worcestershire, U.K.) with aqueous dip cell apparatus whose electrodes were properly cleaned before each measurement to avoid contamination. The device makes use of the laser Doppler microelectrophoresis technique for the ζ potential determination. The ζ potential of particles was calculated from their electrophoretic mobility by means of the Henry correction of the Smoluchowski equation[14]:

$$\mu = \frac{2\varepsilon\zeta}{3\eta}f(\kappa a)$$

where μ is the electrophoretic mobility, η is the aqueous solution viscosity, and $f(\kappa a)$ the Henry coefficient. In this work an $f(\kappa a)$ of 1.5 was used through the measurements. Because this technique allows measurements only in dilute suspensions, samples were diluted before measurement using sedimentaion and followed by redispersing of a small amount of sediment redispersed with the supernatant. The measurements were periodically checked against a calibration standard with a ζ potential of -50 (± 5) mV. Experiments were performed in triplicate, and the results given are the average of 10 measurements.

ζ potentials of concentrated suspensions were also determined directly by electrokinetic sonic amplitude measurements using an electroacoustic analyzer (ESA-9800, Matec Applied Sciences, Northborough, MA). The solids loadings in this case were 0.1, 5, and 10 vol%. The ESA apparatus makes use of the so-called electroacoustic effect created by the application of a high-frequency AC field in the order of 1 MHz to the suspension. If particles carry any electrostatic charge, they will oscillate around the position of rest. Such an oscillation generates a pressure wave in the liquid that can be detected and correlated to the ζ potential. Because the technique is capable of measuring the ζ potential of concentrated suspensions, the samples were used without any dilution. To ensure dispersion the suspensions were ultrasonicated for 2.5 min using an ultrasonic horn (550 Sonic Dismembrator, Fisher Scientific, Pardubice, Czech Republic) before the measurements. The ESA measurements were checked against a 10 vol% Ludox suspension having a ζ potential of -38 mV. Experiments were performed in triplicate, and the results given are the average of 10 measurements.

III. Results and Discussion

Cation dissolution from the PMN surfaces was examined as a function of solution pH. Figure 1 indicates the amount of cation concentrati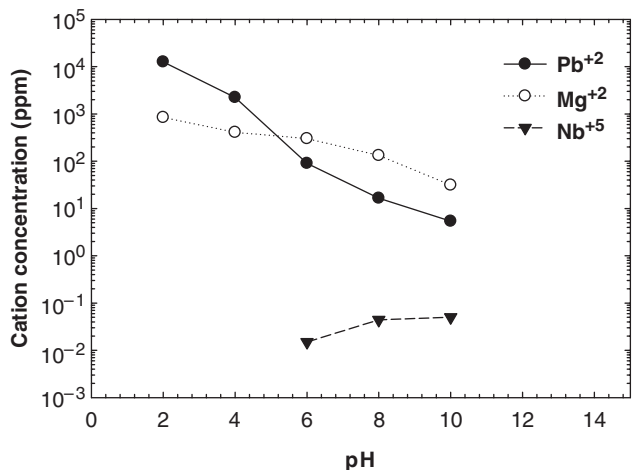on in solution after 24 h for a solids loading of 5 vol%. The graph shows that the lead and magnesium ion concentrations increase with decreasing pH. Especially the Pb^{2+} concentration increases dramatically in the acidic region and reaches 12 620 ppm at pH 2. Though the Mg^{2+} dissolution was also pH dependent, the dissolution rate was almost an order of magnitude smaller compared with that observed with the Pb^{+2} at low pH values. But it was observed that Mg^{2+} dissolution was significant at neutral pH values. On the other hand, Nb^{+5} showed a rather low dissolution under the same conditions. The Nb^{+5} concentrations in the acidic region were below the detection limit of the analyzing device. Therefore, PMN behaves both like an insoluble oxide and like a partially soluble inorganic salt. Insoluble oxide can be approximated to the Nb_2O_5 component whereas the salt is in the form of PbO and MgO in the PMN structure.

Previously, Neubrand *et al.*[8] investigated the dissolution of Ba^{2+} ions from the barium titanate in water. They found that the amount of barium leached increased as the pH decreases. In fact, the increase in the dissolved metal ion concentration with decreasing pH was considered to be a general behavior for most perovskites in water.

Adair *et al.*[13] reported that the dissolution types were dictated by the ceramic materials and the solution pH. According to their study most multicomponent metal oxides such as barium titanate generally follow incongruent types of dissolution, but the dissolution mechanism strongly depends on the pH. In our study, similar to barium titanate system in the absence of any surface carbonates, the Pb–Mg–Nb–H_2O system undergoes incongruent dissolution with selective leaching of Pb^{2+} and Mg^{2+} in the pH range between pH 2 and 10. However, unlike the barium titanate, in the PMN system niobium oxide-rich matrix does not totally dissolve below pH 2. Because the solubility of Nb^{5+} was very low compared with other cations in PMN structure and increases with increasing pH as shown by the experiments. Previously Paik and Hackley[7] showed that for barium titanate system, the dissolution process can be divided into three stages. First stage is an incongruent dissolution in the first few minutes after initial contact with the acidic solution. It is followed by a mass transport-limited second step. A similar dissolution process is valid for the PMN–water system. In the first step, Pb^{2+} and Mg^{2+} must diffuse out through a growing reactive surface layer. In the final stage, dissolution slows down considerably and the following possibilities may arise: a steady-state equilibrium concentration is reached, a thick the depletion layer may form and leads to passivation; or the particles are completely converted to Nb-rich phase.[7]

Figures 2 and 3 show the variation in ζ potential as a function of solids concentration obtained by microelectrophoresis and electroacoustic methods, respectively. Although slight differences were observed, in general the IEP values obtained using both methods were in good agreement with each other. As it was
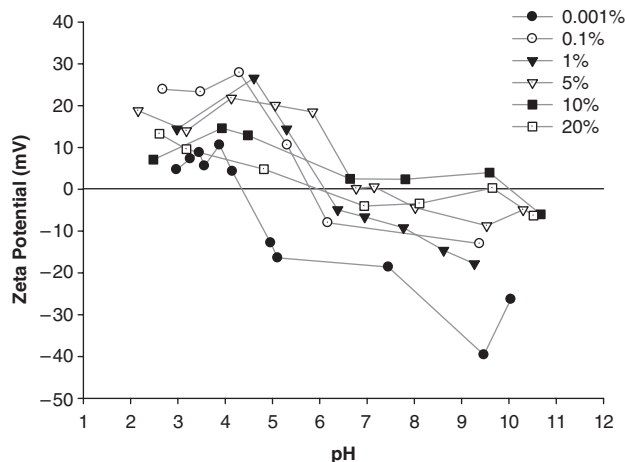

Fig. 1. Dissolved Pb^{2+}, Mg^{2+}, and Nb^{+5} ion concentration as a function of solution pH, solids loading 5 vol%.

Fig. 2. The isoelectric point of lead magnesium niobate suspensions at various solids loadings, microelectrophoresis method.
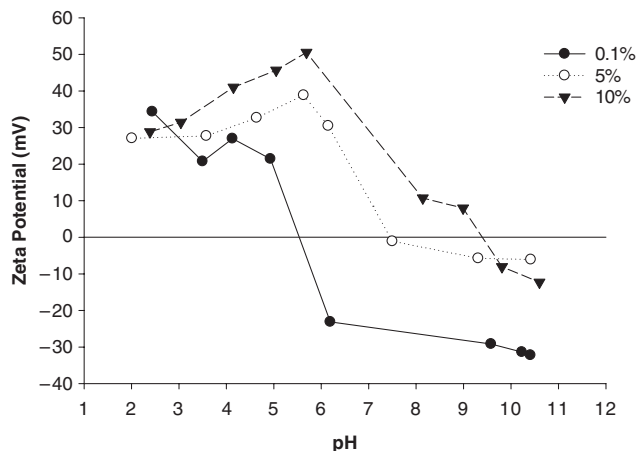
Fig. 3. The isoelectric point of lead magnesium niobate suspensions at various solids loadings, electroacoustic method.

Fig. 4. Isoelectric point of individual metal-oxides which constitute the lead magnesium niobate. Solids loading: 10^{-2} vol%.

described in the previous section, the electrophoresis method requires the use of extremely dilute suspensions. However, the ζ potential of concentrated suspensions can be directly measured using the electroacoustic method. In the current study samples for the electrophoresis technique were prepared from concentrated suspension by dilution. It is also important to note that the IEP values should depend only on the solid–liquid interfacial chemistry and not on the technique used to measure them.

IEP values that were determined using both the techniques were also tabulated in Table I. The agreement between micro-electrophoresis and electrokinetic sonic amplitude techniques at the overlap solids concentration of 0.1% serves to validate the methodology.

The shift in the IEP of the PMN suspensions to lower pH values at low solids concentrations can be explained based on the solubility considerations. When the PMN is suspended in water a surface layer rich in residual Nb^{+5} ions will be developed around the particle due to the deficiency of the dissolving Pb^{2+} and Mg^{2+} ions. Specifically, the surface layer forms because of mass-transport limited incongruent dissolution. Without the mass-transport limitation, the entire particle would be converted to the Nb oxide at sufficiently low pH and low solids concentration. The thickness of that layer is determined by both the pH to which it is subjected and the surface-to-volume ratio of the solid phase. A lower pH increases the dissolution rate and also accommodates a higher solubility limit for the dissolving A-type cations. Essentially, an Nb oxide-rich corona develops around a core of unmodified perovskite material. The thickness and level of depletion of the A-type cations in this corona determines the "acidity" of the particles. That is, the greater the depletion and the thicker the depletion layer, the lower the IEP, until the IEP approaches that of the more acidic Nb oxide. The solids concentration effect is due to the fact that at higher solids, more particle surface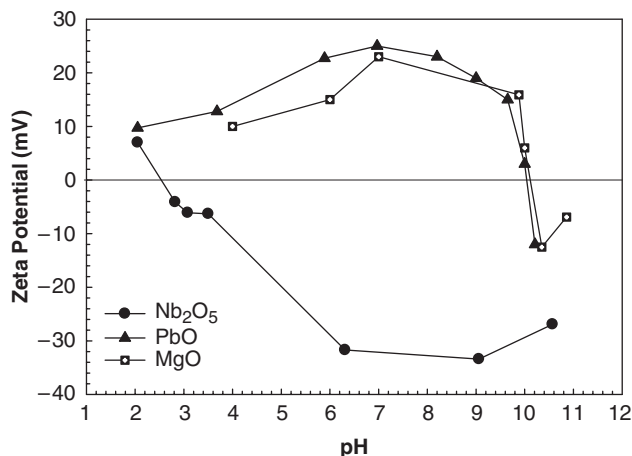 is available for dissolution to occur. This means that the pH-determined solubility limit of the dissolving cations will be reached more quickly and with less depletion of cations from any given particle. Thus the apparent IEP will not shift as much from the native material. At lower solids, the depletion zone of all particles in the suspension must increase in order to reach the same solubility limit for a given pH since the surface-to-volume ratio within the suspension is reduced. This results in a greater (acidic) shift in the IEP.[7]

The IEP of oxides that constitute the PMN were measured and the results are shown in Fig. 4. In the current study the IEP of native niobium oxide is determined at pH 2.6. Previously, Kosmulski[15] has reported the IEP of niobium oxide at pH 4.5. Therefore, the shift in the IEP of PMN suspensions to lower pH values may also be explained by the formation of a Nb_2O_5-rich structure at low solids concentrations.

IV. Conclusions

Chemical stability of PMN powders in water was investigated in this paper. Solubility experiments showed that Pb^{2+} and Mg^{2+} ions preferentially dissolve from the PMN surface as a function of pH. Dissolution of Pb^{2+} and Mg^{2+} increases with decreasing pH while Nb^{5+} dissolution is negligible under the same conditions. It is concluded that such incongruent dissolution in the Pb–Mg–Nb–H_2O system takes place in a wide pH range between pH 2 and 10.

IEP of PMN suspensions (10 vol%) in water was measured to be around pH 9.5 and pH 10 using electroacoustic and electrophoresis techniques, respectively. It was found that IEP shifts to lower pH values with decreasing solids concentration. The positive surface charge of the PMN was attributed to protonation of the amphoteric oxide groups and also to dissolution and readsorption of the dissolved cations from the solution phase to the PMN surface.

Table I. IEP of PMN Suspensions at Different Solids Concentrations

Solids concentration (vol%)	IEP	
	Microelectrophoresis	Electrokinetic sonic amplitude (ESA)
0.001	4.4	—
0.1	5.8	5.6
1	6.1	—
5	7.1	7.5
10	10	9.6
20	9.7	—

IEP, isoelectric point; ESA, electroacoustic analyser.

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