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Ordering in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$ Solid Solutions

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Compositional ordering was found to occur in the ferroelectric $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–antiferroelectric $x\,Pb(Mg_{1/2}W_{1/2})O_3$ solid solution system. X-Ray diffraction and neutron profile fitting structure refinement were used to refine one such composition with $x = 0.9$. The paraelectric structure of compositions with $x < 0.2$ is that of the disordered perovskite (space group *Pm*3*m*), whereas for $0.2 \leq x < 1.0$ the structure is that of ordered perovskite (space group *Fm*3*m*). The oxygen octahedra in the ordered state are regular but no longer equivalent.

Introduction

The $PbMg_{1/3}Nb_{2/3}O_3$–$PbMg_{1/2}W_{1/2}O_3$ solid solution system between the relaxor ferroelectric lead magnesium niobate (PMN) and the ordered antiferroelectric lead magnesium tungstate (PMW) exhibits a number of interesting features, from both the structural and dielectric points of view.

At room temperature PMN has the cubic perovskite structure (space group *Pm*3*m*), with no evidence of long-range ordering of magnesium and niobium in the octahedral sites, although there are some indications of short-range order. The weak field dielectric properties are strongly dispersive, with a broad frequency-dependent maximum in ϵ' between 0 and -15°C, and a corresponding broad maximum in ϵ'' at slightly lower temperatures. The properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ are summarized in the Landolt Bornstein tables (*1*). At room temperature PMW has an orthorhombically distorted perovskite structure, with a unit cell measuring $4a \times 4a \times 4a$, where a is the normal perovskite lattice constant. The quadrupled lattice parameters are caused by (i) a three-dimensional ordering of the dissimilar cations (Mg^{2+} and W^{6+}) in the octahedral sites of the ABO_3 structure, leading to unit cell doubling; and (ii) antipolar shifts in the cation positions, which cause additional doubling (*2*). At 39°C, PMW undergoes a phase transition from the quadruple cell to a double cell with the disappearance of the orthorhombic distortion (*3*). Since the room temperature phase does not exhibit dielectric hysteresis it has been classified as antiferroelectric.

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The dielectric properties of the PMN–PMW solid solution series have been studied by Nomura *et al.* (*4*). Relaxor ferroelectrics are characterized by a dielectric dispersion range ($T_{\max}$ at 1 MHz–$T_{\max}$ at 1 kHz) representing the shift of the weak field permittivity maximum $\epsilon'_{\max}$ to higher temperature with increasing measuring frequency. The dispersion range increases up to 60 mole% PMW, and then for higher PMW concentration decreases rapidly, until at 80 mole% PMW the transition behavior is abrupt.

This paper is concerned primarily with the ordering phenomenon and the structural properties of the PMN–PMW system as revealed by X-ray and neutron diffraction techniques.

Diffraction Studies

The samples used in this study were ceramic specimens in the solid solution series $(1 - x)\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$x\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$, with $0.0 < x < 1.0$. Eleven samples at 0.1 mole fraction increments were prepared from reagent grade PbO, MgO, Nb_2O_5, and WO_3 by the same ceramic techniques used in making specimens for dielectric measurements (*4*).

X-Ray powder diffraction patterns were taken at room temperature using CuK_α radiation and a slow 2θ scan (0.4°/min). Superstructure lines appeared for compositions with $0.2 \leq x < 1.0$. These extra lines were indexed as the 111, 311, 331, 511, 531, and 551 reflections of a face centered cubic lattice about 8 Å along the edge. The composition dependence of the doubled lattice parameter determined from least squares refinements is shown in Fig. 1.

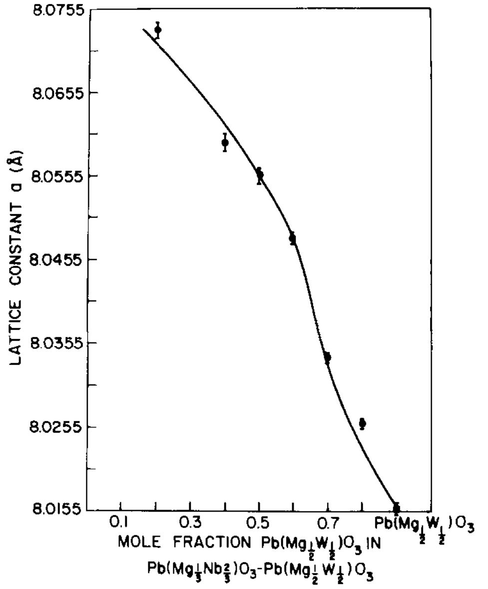

FIG. 1. Lattice parameters of the PMN–PMW system.

Blasse (*5*) has suggested that in perovskite solid solutions between ordered and disordered end members there is a strong tendency for the ordered end member to "force" similar ordering on the disordered component for a major part of the phase diagram. In $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$–$\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$ solid solution system 1:1 ordering can exist with site occupancy of the form: $\mathrm{Pb_2^{2+}}\, B'B''\mathrm{O_6^{2-}}$ with $B' = \mathrm{Mg^{2+}_{2+x/3}\,Nb^{5+}_{1-x/3}}$ and $B'' = \mathrm{W^{6+}_x\,Nb^{5+}_{1-x}}$.

A trial structure based on space group *Fm*3m with a ~8 Å and eight formula units per unit cell was tested for the ordered prototypic structure just described with *B* site cations in two distinct crystallographic sites *B*′ and *B*″. The atomic positions in space group *Fm*3*m* are 8 Pb in (8c): 1/4, 1/4, 1/4; 4 *B*′ in (4a): 0, 0, 0; 4 *B*″ in (4b): 1/2, 1/2, 1/2; and 24 0 in (24c): *x*, 0, 0.

Least-squares refinement of data was carried out for the 0.9 PMW:0.1 PMN composition by X-ray and neutron diffraction. Integrated X-ray intensities for 22 reflections were obtained from counter data using an automated Rigaku Giegerflex powder diffractometer and CuK_α radiation. The intensity data were collected four times. Before each run the loose powder was repacked in the sample holder to avoid preferred orientation effects. The intensity data were corrected for background and

Lorentz-polarization factor but no absorption correction was applied. It became evident from the initial refinement procedure that the positional and thermal parameters of the oxygen atom were highly correlated. The X-ray data were incapable of giving reasonable information about the oxygen atom shifts. Therefore, it was helpful to refine the structure from neutron diffraction data.

Neutron data were collected at the Brookhaven high flux beam reactor at room temperature from the same powder used in the X-ray studies. Pyrolytic graphite in the (002) and (004) reflection position was used as monochromator and analyzer, respectively. The neutron wavelength was 2.463 Å, higher order components being removed with a pyrolytic graphite filter. Scanning was performed at 0.05° intervals over each of the peak positions within an angular range 2θ of 25–125°. The structure analysis was carried out by means of the profile refinement technique (*6*) and (*7*) with the following scattering lengths: 0.94, 0.71, 0.58, 0.52, 0.48 × 10^{-12} cm for Pb, Nb, O, Mg, and W, respectively. The variables used in the refinement were: an over all scale factor, three half-width parameters defining the Gaussian line profiles, the

TABLE I

OBSERVED AND CALCULATED NEUTRON INTENSITIES, *d* SPACINGS, AND REFINED PARAMETERS OBTAINED BY NEUTRON DIFFRACTION

hkl	d_c	I_c	d_o	I_o
111	4.630	334	4.622	266
200	4.008	681	4.006	813
220	2.834	8133	2.831	8014
311	2.418	39	2.416	48
222	2.315	21713	2.314	21723
400	2.004	28750	2.004	29081
331	1.840	355	1.839	357
420	1.792	763	1.792	730
422	1.636	6033	1.636	6182
511	1.543	441	1.543	468
333	1.543	281	1.543	298
440	1.471	37315	1.471	37461

Atom	*x*	*y*	*z*	*B* (isotropic)	$B_{11}{}^{a}$	$B_{22} = B_{33}{}^{a}$
Pb	0.25	0.25	0.25	2.6(1)		
Mg/Nb1	0.00	0.00	0.00	0.4(1)		
W/Nb2	0.50	0.50	0.50	0.4(1)		
0	0.2595(3)	0.00	0.0		0.9(2)	1.7(1)

[a] In the expression exp $[-1/4\,(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2\,B_{12}hka^*b^* + 2\,B_{13}hla^*c^* + 2\,B_{23}klb^*c^*)]$.

$R_1\% = 0.99$, $R_1 = 100\,\Sigma[I_{(\mathrm{obs.})} - \frac{1}{c}\,I_{(\mathrm{calc.})}]/\Sigma I_{(\mathrm{obs.})}$.

$R_2\% = 4.36$, $R_2 = 100\,\Sigma[y_{(\mathrm{obs.})} - \frac{1}{c}\,y_{(\mathrm{calc.})}]/\Sigma y_{(\mathrm{obs.})}$

$R_3\% = 8.52$, $R_3 = 100\,\sqrt{\Sigma w[y_{(\mathrm{obs.})} - \frac{1}{c}\,y_{(\mathrm{calc.})}]^2/\Sigma w[y_{(\mathrm{obs.})}]^2}$.

$R_{\mathrm{exp}}\% = 5.92$, the expected R-factor $= 100\,\sqrt{(N - P + C)/w[y_{(\mathrm{obs.})}]^2}$.

$I_{(\mathrm{obs.})}$, $I_{(\mathrm{calc.})}$ = observed and calculated integrated intensity of each reflection.

$y_{(\mathrm{obs.})}$, $y_{(\mathrm{calc.})}$ = observed and calculated profile data.

w = weight alloted to each data point.

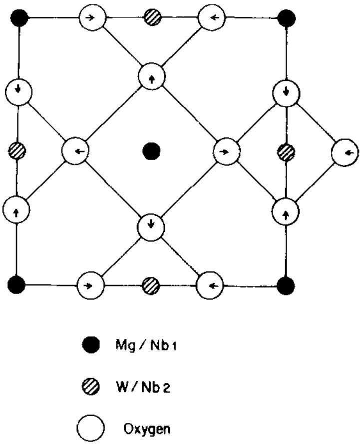

FIG. 2. Section of the ordered structure at height. $z = 0$.

counter zero error, the oxygen x coordinate, isotropic or anisotropic temperature factors, and unit cell parameters. The calculated and observed neutron intensities, R-factors, temperature factors, and the atomic coordinates (in lattice constant units) are listed in Table I. The fit between observed and calculated intensities is quite good. A section of the structure at zero height is shown in Fig. 2. Arrows represent the oxygen shifts from their ideal position (1/4, 0, 0, etc.) in the perovskite structure.

Discussion

A combination of X-ray and Neutron profile-fitting-structure refinement (PFSR) techniques was used to examine the compositional ordering in the $(1 - x)$ $Pb(Mg_{1/3}Nb_{2/3})O_{3-x}Pb(Mg_{1/2}W_{1/2})O_3$ solid solution system and to make a more detailed structure refinement of one PMW rich composition in this phase field. For compositions with $x < 0.2$ PMW the structure is that of the disordered perovskite type with lattice constant a ~ 4 Å and space group $Pm3m$. However, for higher PMW concentrations ($0.2 \leq x < 1.0$), a compositional ordering takesplace leading to a doubling of the perovskite unit cell constant, a ~ 8 Å, and the space group becomes $Fm3m$. Furthermore, no evidence of pseudosymmetric distortion was observed in any of the compositions with $0.2 \leq x < 1.0$ at room temperature. In addition to the cation ordering evidenced in the superstructure lines, the above neutron diffraction analysis shows clearly that the oxygen atoms undergo antiparallel displacements towards the smaller B'' cations (Fig. 2). The octahedra about the B' and B'' cations are regular but no longer equivalent. The metal–oxygen bond lengths determined by neutron diffraction together with the sum of the averaged atom ionic radii "IR" of Shannon and Prewitt (*8*), are listed in Table II. The agreement is quite reasonable. The room temperature neutron diffraction data for (x = 0.9 PMW) indicate a "softening" of the amplitude of thermal vibration of the oxygen octahedra ($B_{22} = B_{33} \gg B_{11}$). The reason for the softening comes about from the fact that this composition undergoes a phase transition near C̊ as suggested by the dielectric data (*4*). Conversely, the small B-factors for the cations do not indicate any displacement disorder, except for the large value for Pb, which we would expect to be displaced if the low temperature phase stemmed from tilting of the rigid oxygen octahedra. In future work we intend to use the profile fitting method to examine the low temperature phase transition and to explore the antiferroelectric phase boundary in this solid solution system.

TABLE II

METAL–OXYGEN BOND LENGTHS

Bond	Sum of "IR"	Neutron
Mg/Nb–O	2.12	2.080(2)
W/Nb–O	1.98	1.928(2)
Pb–O	2.89	2.835

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