Preparation of Perovskite $Pb(B_{0.5}Nb_{0.5})O_3$ (B = Rare-Earth Elements)

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Abstract. $Pb(B_{0.5}Nb_{0.5})O_3$ (B = Sc, Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) powders were prepared from mixed nitrate solutions by a chemical coprecipitation method. This method produced very small particles ($\sim$30 nm) with good compositional homogeneity. These powders were highly reactive upon calcination. The powders of the systems (B = Sc, Tm, Yb and Lu) yielded $\sim$100% perovskite phase after calcination between 800°C and 1000°C for 1 h. For the system with B = Er, 93% perovskite phase was formed at 900°C for 1 h. For the other systems of the elements (B = Y, Nd, Sm, Eu, Gd, Tb, Dy and Ho) with a larger ionic size, perovskite compounds were not formed up to 1100°C. The stability and the possible formation of the compounds with a perovskite structure for the $Pb(B_{0.5}Nb_{0.5})O_3$ series were discussed.

Keywords: perovskite, chemical preparation, powder, niobium compound, relaxor

1.   Introduction

The lead-containing niobate ferroelectrics have excellent properties, such as high dielectric constants over a wide temperature range, large electromechanical coupling factors for piezoelectric, electrooptical properties, and comparatively low firing temperatures. For example, several transparent ceramics have been developed for optical use [1–3]. These studies revealed the importance of the chemical homogeneity [1], purity [2] and sinterability [3] of the powder when fabricating high-quality transparent ceramics. For the fabrication of such advanced ceramics, there has been interesting work in the synthesis of advanced powders, which reduces the firing temperature without degrading the properties of the materials.

The objectives of the present work are to prepare the advanced $Pb(B_{0.5}Nb_{0.5})O_3$(B = Sc, Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) (abbreviated as PBN) powders by a coprecipitation method and to prepare the perovskite PBN compounds from the powders. The stability of the perovskite phase synthesized is discussed in terms of ionic radius, electronegativity difference, tolerance factor and bond valence sum.

2.   Experimental Procedure

The niobium precursor solution as a source of niobium was prepared from an aqueous niobium oxalate solution [4]. Clear aqueous solutions between 0.02 and 0.04 M PBN with stoichiometric compositions were prepared by mixing the niobium precursor solutions with the corresponding nitrate solutions. The mixed nitrate solutions were hydrolyzed with 15 M ammonia water. The coprecipitates were washed with water, rinsed with acetone and then dried at 80°C for 24 h. Upon calcination, 0.5 g of the as-dried powder was held for 1 h in the furnace which was allowed to equilibrate at the desired temperatures, and quenched to room temperature. In order to determine the effect of the PbO atmosphere on the formation of perovskite PHoN and thermal stability of perovskite PLuN, the specimens were heated in a crucible in the presence of atmospheric powder (a mixture of $PbZrO_3$ and PbO).

Table 1. Reaction products for calcined PBN powders.

	Ionic radii (nm)	Electronegativity difference	Temperature (°C)					
			600	700	800	900	1000	1100
Sc	0.0745	1.95	Pe (92)[†], Py	Pe (97), Py	Pe (100)	Pe (100)	Pe (100)	Pe (100)
Lu	0.0861	1.98	Py (v)[‡]	Pe (96), Py	Pe (100)	Pe (100)	Pe (100)	Pe (91), BN
Yb	0.0868	2.00	Py (s)	Pe (75), Py	Pe (100)	Pe (100)	Pe (100)	Pe (90), BN
Tm	0.0880	1.98	Py (s)	Pe (28), Py	Pe (97), Py	Pe (100)	Pe (100)	Pe (80), BN
Er	0.0890	1.98	Py (l)	Py (l)	Pe (28), Py	Pe (93), Py, BN	Pe (60), Py, BN	Py, BN
Y	0.0900	1.98	Py (l)	Py (l)	Py (l)	Py, BN	Py, BN	Py, BN
Ho	0.0901	1.98	Py (l)	Py (l)	Py (l)	Py, BN	Py, BN	Py, BN

Pe, perovskite; Py, pyrochlore; BN, rare-earth niobate

[†]Percentage of perovskite phase $= I_{Pe}/(I_{Pe} + I_{Py} + I_{BN}) \times 100$; I_{Pe}, (110) perovskite for rhombohedral or (220) for pseudo-monoclinic; I_{Py}, (222) pyrochlore; I_{BN}, (121) rare-earth niobate.

[‡]Percentage to intensity of 100% pyrochlore phase; (v), <10%; (s), 10–15%; (l), >15%.

3.   Results and Discussion

3.1.   *Formation of Perovskite Compounds*

All the as-dried powders were found to be amorphous when examined with an X-ray diffractometer and consisted of agglomerates of small particles ranging in diameter from 25 to 30 nm from scanning electron microscopic observations. The powders have an average specific surface area of 118 m²/g (single point BET).

Table 1 summarizes the reaction products of the calcined powders with an ionic size in six-coordination [5], electronegativity difference [6] between the cation and oxygen, and percent perovskite. The perovskite compound is basically ionic. A large electronegativity difference causes a strong ionic bond and can stabilize the structure. The values of the electronegativity difference for the rare-earth elements are the same except for Sc, Yb and Eu (2.00). The perovskite compounds were, however, obtained only for the systems of B = Sc, Lu, Yb, Tm and Er. The others failed to produce a perovskite. It is immediately obvious that there is a general limitation on the sizes of the B site ions and radius ratios which can be tolerated in the perovskite structure. For the systems with larger B cations, the A—O and B—O bondings are too weak to construct the perovskite structure containing an octahedral of B cations surrounded by oxygens.

The minimum temperature at which the perovskite compounds become the main phase shifted from 600°C (Sc) to 900°C (Er). Presumably, the perovskite PScN and PLuN are directly formed from the as-dried powders with good chemical homogeneity. On the other hand, for the systems of Yb, Tm and Er, the perovskite formation reaction competes with the pyrochlore formation, indicating that the difference in the free energy between the two reactions is small. Thus, perovskite PScN and PLuN relative to the pyrochlore compounds are thermodynamically more stable than the perovskites PYbN, PTmN and PErN.

The percentage of perovskite in Table 1 shows that the temperature range where the perovskite phases may stably exist in a narrow range as the ionic size of these rare-earth elements increases. At higher temperatures, the perovskite PScN did not decompose at 1100°C in air, while the perovskite PErN significantly decomposed even at 1000°C. For studying the thermal decomposition at the higher temperature, the single-phase perovskite PLuN powder obtained by calcination at 1000°C was reheated at 1100°C. The intensity of the strongest XRD diffraction peak of each phase versus heating time is indicated in Fig. 1. In air, the
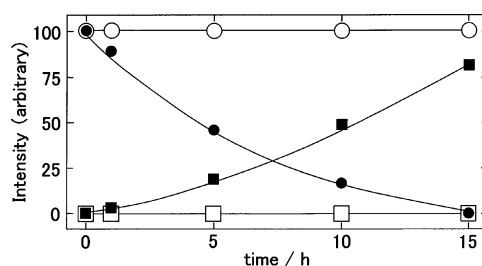

Fig. 1. X-ray diffraction intensity plotted versus time at 1100°C: in air ●, perovskite $Pb(Lu_{0.5}Nb_{0.5})O_3$; ■, $LuNbO_4$: in PbO atmosphere ○, perovskite $Pb(Lu_{0.5}Nb_{0.5})O_3$; □, $LuNbO_4$.

Table 2. Lattice parameters for perovskite PBN compounds.

	Lattice parameters				
PBN	a (nm)	b (nm)	α (°)	β (°)	Unit-volume (m^3)$\times 10^{-29}$
PScN	0.4088	–	89.80	–	6.832
PLuN	0.4156	0.4150	–	90.57	7.168
PYbN	0.4163	0.4149	–	90.60	7.190
PTmN	0.4172	0.4131	–	90.71	7.193
PErN	0.4186	0.4106	–	90.86	7.194

perovskite PLuN directly decomposed into LuNbO$_4$ like the metastable perovskite PErN [7] prepared under high pressure. When heated in the PbO atmosphere, it did not decompose. The atmosphere of PbO suppresses the following reaction.

$$\text{perovskite PLuN} \rightarrow (1/2)\text{LuNbO}_4 + \text{PbO} \uparrow$$
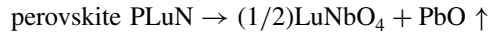
Thus, the thermal stability of the perovskite PLuN is controlled by the temperature and the partial pressure of PbO.

The lattice parameters of the perovskite compounds were determined using the powders calcined between 900°C and 1000°C (Table 2). Perovskite PScN with the smallest radius in the rare-earth ions has a rhombohedral unit cell. The Lu, Yb, Tm and Er analogues with a larger radius deviate from the ideal cubic structure and have a pseudo-monoclinic structure. The unit-volume linearly expands with increasing ionic radii from Sc to Yb and then, is saturated at the radius of Tm and Er.

Perovskite PYN could not be produced and has not yet reported by other researchers. Perovskite PHoN with a monoclinic structure was reported by Kupriyanov and Fesenko [8]. They prepared the compound by the double calcinations of stoichiometric mixtures of the starting materials in an atmosphere of PbO. However, we could not obtain the perovskite PHoN by calcining the chemically prepared PHoN powder in the PbO atmosphere. Other researchers [9, 10] also could not obtain the perovskite PHoN by mixed oxide methods. Perovskite PYN and PHoN are not formed at ambient pressure.

3.2. Stability of Perovskite Compounds

Two kinds of analyses of the stability of the perovskite compounds A($B_{0.5}Nb_{0.5}$)O_3 (A = Pb, Ba, Sr and Ca) are made by considering the bond natures. Figure 2 shows a plot of the average electronegativity differences $(X_{A-O} + X_{B-O})/2$ versus the tolerance factor $(t = (r_A + r_O) / \sqrt{2}(r_B + r_O))$. Here, X_{A-O}

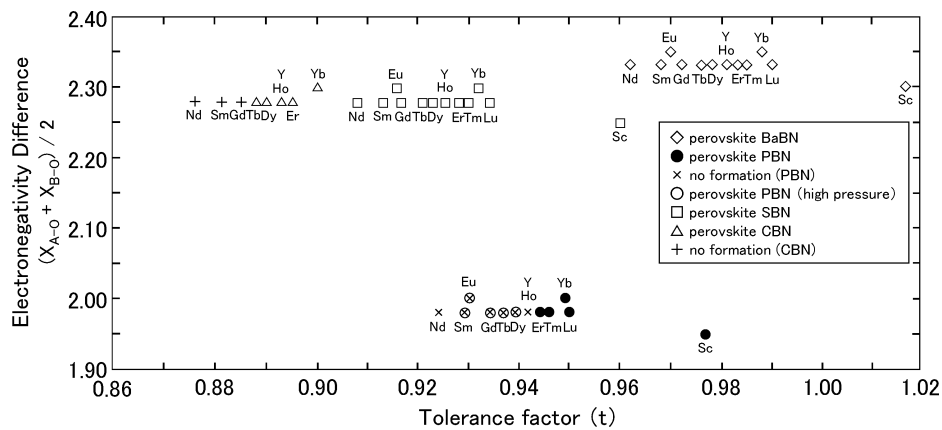*Fig. 2.* Plot of electronegativity difference versus tolerance factor for A($B_{0.5}Nb_{0.5}$)O_3 compounds.

Table 3. V_O in perovskite $A(B_{0.5}Nb_{0.5})O_3$ compounds.

	BaBN [12]	PBN	SBN	CBN [16]
Sc	1.97	1.77	1.95 [13]	—
Lu	1.99	1.81	1.99 [14]	—
Yb	2.00	1.83	2.03 [15]	2.11
Tm	1.98	1.85	2.03 [14]	—
Er	1.97	1.88	2.01 [14]	2.14
Y	2.02	×	2.07 [15]	2.12
Ho	1.98	×	2.02 [14]	2.16

—, no report; ×, no formation

and X_{B-O} indicate the electronegativity difference of oxygen ion and cation A, and cation B, respectively. The tolerance factor represents the degree of the structural distortion that the ionic radius causes [11]. The symbols r_A, r_B and r_O are ionic radii of cation A, cation B and oxygen ion. Perovskite $Ba(B_{0.5}Nb_{0.5})O_3$(BaBN) [12], $Sr(B_{0.5}Nb_{0.5})O_3$ (SBN) [13–15] and $Ca(B_{0.5}Nb_{0.5})O_3$ (CBN) [16] compounds are easily prepared. They have a high electronegativity difference (strong ionic bonding) and are stabilized over a wide tolerance factor range (0.888–1.017). Perovskite PBN with a low electronegativity difference is in a narrow tolerance factor range (0.944–0.977). At lower t values than PErN (0.944), several metastable perovskite compounds with larger cations (B = Dy, Tb, Gd, Eu, Sm) than Er have been prepared only under high pressure [7, 17].

Recently, the Pb—O bond nature in the perovskite structure was discussed by Cohen [18]. He calculated the electronic states of $PbTiO_3$ and concluded that the Pb 6s orbital and O 2p orbitals are strongly hybridized. Wakiya et al. [19] proposed a new quantitative method for estimating the stability of the perovskite compounds using the bond valence sum instead of the electronegativity difference and tolerance factor. The advantage of this method is that it is independent of whether the bonds are ionic or covalent in character. In the bond valence theory, the valence v_{ij} of the bond strength between a cation i and an anion j is defined so that the sum of all the valences from a given cation i with valence V_i obeys:

$$V_i = \Sigma_j v_{ij} \qquad (1)$$

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b] \qquad (2)$$

$$V_O = (V_A + V_B)/3 \qquad (3)$$

where R_{ij} is the bond valence parameter derived for a large number of bonds by Brese and O'Keeffe [20], d_{ij} is the length of a bond between anion i and cation j and b is the universal constant equal to 0.037 nm. V_O, V_A and V_B denote the bond valence sum of oxygen, the A site cation and B site cation, respectively. d_{ij} was calculated from the lattice parameters in Table 2 and the literature [12–16]. V_O is summarized in Table 3. The V_O for PBN relative to the other ABN is small. This is in agreement with the lower stability of the PBN compounds. However, V_O does not decrease, but tends to slightly increase with an increase in the ionic size of the rare-earth elements. Thus, it does not act as a complete indicator of the stability in this series.

4.   Conclusions

$Pb(B_{0.5}Nb_{0.5})O_3$ (B = Sc, Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) powders were prepared from mixed nitrate solutions by a chemical coprecipitation method. The powders of only the systems (B = Sc, Er, Tm, Yb and Lu) yielded perovskite compounds with a rhombohedral or pseudo-monoclinic structure after calcination.

The stability and the possibile formation of the perovskite compounds were discussed by ionic radius, tolerance factor, electronegativity difference and bond valence sum.

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