

An X-ray Photoelectron Study on Mechanochemical Reactions toward Ferroelectric Lead Zinc Niobate

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Charge-transfer at the initial stage of mechanochemical reaction on the system on PbO, $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ and Nb_2O_5 was examined in detail by chemical shifts of Pb4f, Zn3d and Nb3d binding energies, using X-ray photoelectron spectroscopy (XPS). X-ray diffraction peaks corresponding to $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ appeared. XPS peaks of Pb4f electrons were observed at about 142.3 and 147.0eV. After milling a stoichiometric mixture for 1h, new XPS peaks appeared, which are most likely due to the charge-transfer across new chemical bonds, Pb-O-Nb and Pb-O-Zn. Mechanochemically prepared precursors containing such bridging bonds turned out to be favorable for the formation of phase pure complex perovskite compound, $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$, on subsequent heating.

Key words: mechanochemical reaction, precursor, charge-transfer, PZN

1. INTRODUCTION

Lead zinc niobate, $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$, is an ABO₃ perovskite, which has high dielectric properties [1,2]. Two basic requirements for stability of perovskite structure are ionic radius and amount of ionic bonding [3]. PZN is extremely difficult to form, chiefly because Zn^{2+} cation prefers four-fold coordination as in wurtzite ZnO which is strongly covalently bonded and unfavorable for a perovskite structure [4].

PZN can be obtained by milling a mixture of starting materials, but the perovskite phase contained in the PZN precursors changes into pyrochlore during subsequent heating because of thermodynamic instability [5]. To further explore better precursors, mechanisms of the mechanochemical reaction toward PZN should be elucidated.

In this study, we focus on changes of chemical states with phase transition during mechanical stressing on the starting mixture.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of the sample

Starting materials are individual oxides, PbO (Massicot, Orthorhombic, 99.9%, Soekawa Chemical), Nb_2O_5 (Orthorhombic, 99.9%, Wako Pure Chemical) and basic carbonic zinc, $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ (99.9%, Kishida Chemical). Basic carbonic zinc is used as a starting material instead of zinc oxide to improve incipient reactivity of reactants via acid-base reaction. All these starting materials are guaranteed grade chemical reagents and used as purchased.

Two compositions of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ and 0.9 were prepared from off-stoichiometric mixture, to examine a role of $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ containing hydroxyl groups in starting mixtures during mechanical stressing and to explain processes of mechanochemical reaction without thermal treatment.

Mechanical activation was carried out by using a multi-ring type mill (MICROS MIC-0, Nara Machinery) [6,7] at 1850 rpm for 0.5, 1, 2 and 3h in air.

2.2 Characterization of the sample

Crystallographical phase analysis was made by X-ray diffractometry (XRD) (Rigaku, RINT-2000) using $\text{CuK}\alpha$.

Changes in the chemical states and charge-transfer by mechanical stressing were examined by X-ray photoelectron spectroscopy (XPS) (JEOL, JPS-90MX), using $\text{MgK}\alpha$ radiation with etching for 0, 3, 6 and 9 seconds. For observation of XPS, powders were scattered on a carbon tape attached on the sample boat without pressing or forming. Gold foil was used for charge up correction, *i.e.*, by setting the binding energy value of $\text{Au}4f_{7/2}$ to be 83.8eV.

3. RESULTS AND DISCUSSION

3.1 Phase change by mechanical stressing

Changes in the X-ray diffractogram by milling mixtures corresponding to $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ and 0.9 are shown in Figs.1 and 2, respectively. The peaks of starting materials disappear and new broad peaks are obtained after mechanical stressing. PbO phases are changed from massicot to litharge simply by slight mechanical stressing, *i.e.*, milling for 0.5 (b) or 1h (c) in Fig.1 and 2. In the mixture $x=0.1$, the XRD peaks of PbO (Litharge) remain in all the milled mixtures in Fig.1. In contrast, in the sample $x=0.9$, PbO (Litharge) phases disappear after milling for 2h and intensity of perovskite phases is increased as shown in Fig.2. Thus, $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ produce perovskite complex compound PZN by milling with PbO and Nb_2O_5 , and prefers to react with PbO during mechanical reaction to form PZN precursor.

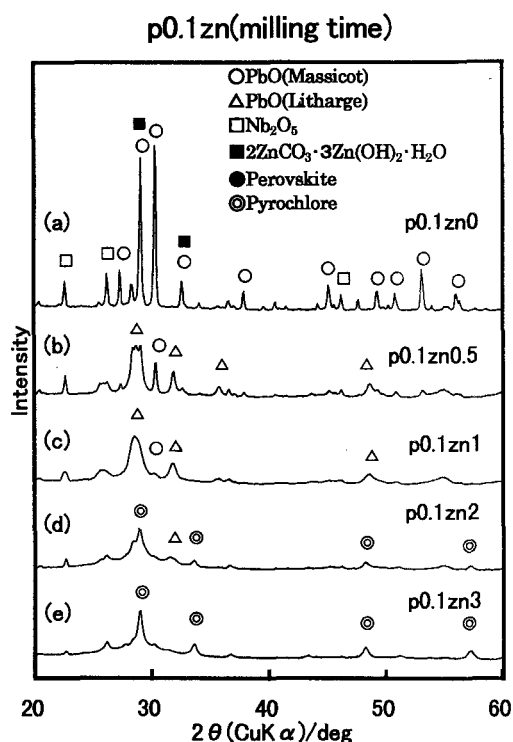


Fig1. XRD profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ after milling for 0(a), 0.5(b), 1(c), 2(d) and 3(e) hours

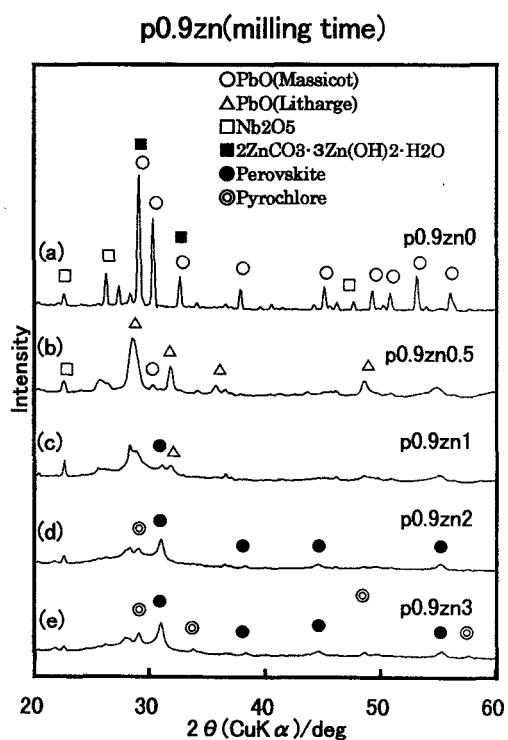


Fig2. XRD profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.9$ after milling for 0(a), 0.5(b), 1(c), 2(d) and 3(e) hours

The XRD peaks of stoichiometric PZN phases are observed in the mixtures $x=0.9$ after milling

for 1h (c) without heating. The intensity of perovskite phase peaks increases with milling time, as shown in Fig.2. On the other hand, no PZN phase is properly acquired in all the mixtures in Fig.1 ($x=0.1$), and pyrochlore phases (P_3N_4 cubic or P_2N_2 rhombohedral, probably) [8,9] are obtained in the mixtures milled for 2 (d) and 3h (e).

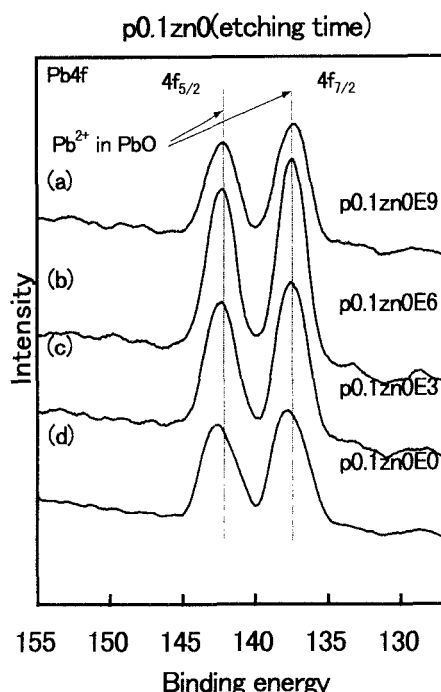


Fig.3 XPS profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ after etching for 0(d), 3(c), 6(b) and 9(a) seconds without milling

3.2 Surface of as-milled mixture

Pb4f XPS profiles are observed for the non-milled (Fig.3) and milled mixtures with $x=0.1$ for 3h (Fig.4) with etching for 0, 3, 6 and 9 seconds. No distinct changes of Pb4f XPS peaks at about 137.7 and 142.6eV before and after etching are detected in non-milled mixtures in Fig.3.

As shown in Fig.4, an apparent chemical shift of the bimodal profile peaking at about 139.7 and 144.6eV was observed on the sample without etching (d). Binding energies of Pb4f in the milled mixture for 3h are higher than non-milled one by 2eV. This shift occurs during mechanochemical reaction and seems to correspond to a single electron state of Pb4f. However, after etching, several new peaks appear and the centroid of the complex peaks shifts toward lower binding energy.

When the reactant mixtures are milled, surfaces of the mixtures are activated and apt to react with other species, e.g., oxygen, carbon or water molecule. This explains, if partly, why the

chemical states of the milled mixtures change, as shown in Fig.4, as a result of surface relaxation caused by adsorbed species.

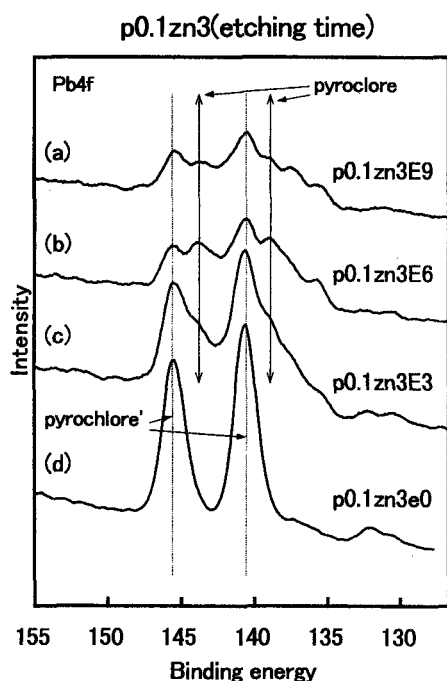


Fig.4 XPS profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ milled for 3h after etching for 0(d), 3(c), 6(b) and 9(a) seconds

3.3 Charge-transfer during milling

Pb4f XPS profiles of the mixtures etched for 6 seconds with milling for 0, 0.5, 1, 2 and 3h are shown in Figs.5 ($x=0.1$) and 6 ($x=0.9$). We already elucidated that PbO (massicot) is changed into PbO (litharge) by milling for 0.5, 1 and 2h in XRD profiles. Pb4f bimodal peaks Fig.5 (a) and Fig.6 (a) are divided into new Pb4f XPS peaks A and another bimodal peak by milling for 0.5h in Figs.5 (b) and 6 (b). Intensity of Peaks A corresponding to PbO (litharge) decreases with milling time but a small amount still remains in all the mixtures after milling for several times.

During mechanochemical reaction with PbO in PZN, two cases are expected to the reaction between PbO and $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and the reaction between PbO and Nb_2O_5 . The peaks of Pb4f S and S' are gradually shifted toward high energy during milling as shown in Fig.5 and 6. For $x=0.9$, peaks S are moved at about 142.0 and 146.8eV by milling for 2h in Fig.5 (d), and new shifted peaks are observed at the same binding energies in peaks S' by milling for 1h in Fig.6 (c). Hence, the Pb4f peaks shift toward higher binding energy by milling together with $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$. These shifts are due to bridging

bond of Pb-O-Zn, and, hence, depend on the amount of $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$. XPS profiles of Zn3d and Nb3d in the milled mixtures are also examined and Zn3d is shifted earlier than Nb3d during milling. According to O1s profiles of the milled mixtures, O1s of $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ has a higher binding energy than O1s of PbO or Nb_2O_5 and is shifted toward lower binding energy by milling, simultaneously with Zn3d peaks.

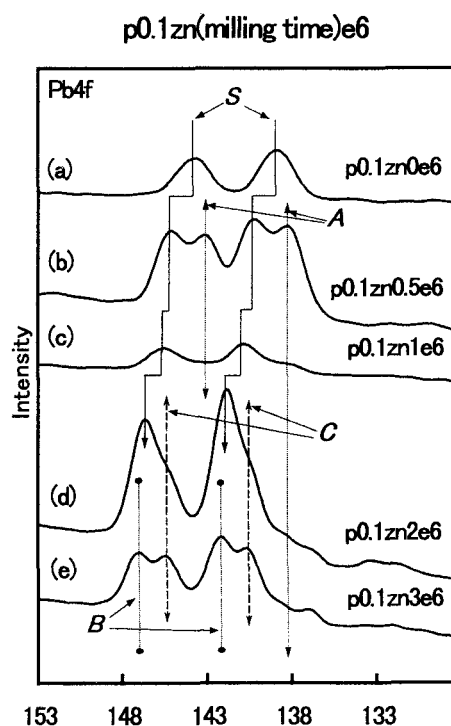


Fig.5 XPS profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.1$ etched for 6 seconds after milling for 0(a), 0.5(b), 1(c), 2(d) and 3(e) hours

After milling for 2 or 3h, peaks S and S' are further shifted to higher binding energy and another bimodal peaks B, C and D appear. Pb4f in Pb-O-Zn has higher binding energies than in Pb-O-Nb because strong interaction exists between oxygen and hydrogen of hydroxyl groups in $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Therefore, peaks B and D are most likely associated with in formation of a new bridging bond Pb-O-Zn.

Peaks S gradually shifted up to the location of peaks B by milling. Conversely, peaks D in Fig.6 do not shift by milling for 2 or 3h, while perovskite phases are obtained as main peaks in XRD Fig.2 (c) and (d). Consequently, peaks D at about 142.3 and 147.0eV are assigned to Pb4f corresponding to Pb-O-Zn bridging bonds in perovskite PZN. The binding energies of peaks B are slightly smaller than D, because of the lack of zinc to form perovskite as a B site ion.

Actually, no perovskite phases are detected in $x=0.1$ after milling and pyrochlore phases are obtained as shown in Fig.1.

XPS profiles of Nb3d shifted toward high binding energy in the mixtures after milling for 2h and Pb4f peaks C emerge after milling for 2h in Fig.5 (d) and 6 (d). Hence, peaks C correspond to Pb4f of bridging bond Pb-O-Nb in PZN system. These bridging bonds promote the formation of pure PZN phase by calcination of the milled mixture serving as a precursor.

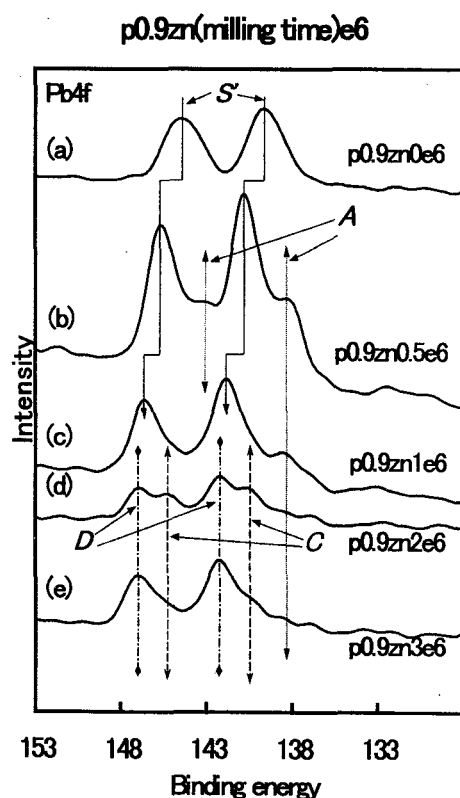


Fig.6 XPS profiles of $\text{PbZn}_{x/3}\text{Nb}_{2/3}\text{O}_3$ with $x=0.9$ etched for 6 seconds after milling for 0(a), 0.5(b), 1(c), 2(d) and 3(e) hours

4. CONCLUSION

Perovskite PZN is produced by milling for 1h without heating. The chemical states of the milled mixture change not only at the outermost surface but also interior of the particles with a gradual shift. PbO easily reacts with $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ under mechanical stressing to form PZN. Chemical state of Pb4f during milling due to Pb-O-Zn and Pb-O-Nb is traced in detail. Mechanochemical precursors containing bridging bonds, such as Pb-O-Nb and Pb-O-Zn, promote the formation of PZN on subsequent heating.

5. ACKNOWLEDGEMENT

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