

# Synergistic effects of ultrasonication and mechanochemical treatment on the synthesis of fine-grained $\text{Pb}(\text{Zn}_x\text{Mg}_{1-x})_{1/3}\text{Nb}_{2/3}\text{O}_3$ perovskite

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An aqueous suspension comprising powders of  $\text{PbO}$ ,  $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2$ , and  $\text{Nb}_2\text{O}_5$  was prepared in the proportion, corresponding to the stoichiometry of  $x\text{PZN} - (1-x)\text{PMN}$  with  $x=0.5$ , where PZN and PMN stand for  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$  and  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ , respectively. The complex suspension was subjected to ultrasonication while agitation milling. Development of amorphous mixed hydroxide layer on the surface of the reactant particles was enhanced by virtue of simultaneous sonochemical and mechanochemical effects. These simultaneous effects result in the formation of an order of magnitude finer PZMN particles by subsequent calcination up to  $850^\circ\text{C}$  in air, presumably due to enhanced nucleation by ultrasonication in the amorphous gel layer. Mechanism of fine PZMN formation was further discussed in terms of dissolution – precipitation and stoichiometry of the precursor prior to heating.

Key words: *sonochemistry, mechanochemistry, PZMN, perovskite, synergistic effect*

## 1. INTRODUCTION

We tried to synthesize phase pure perovskite of  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PZN) or  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) via a soft-mechanochemical route [1]. While phase pure PZN perovskite was not available,  $x\text{PZN} - (1-x)\text{PMN}$  with  $x$  up to 0.7 was obtained by starting from a mechanically activated precursor of  $\text{Pb}(\text{Zn}_x\text{Mg}_{1-x})_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PZMN). It is not quite easy, however, to control simultaneously the grain size or other properties dominating fine structure, since the process rests upon the principle of kinetic stabilization.

Various attempts were already made to synthesize high value-added materials by using non-thermal and non-conventional strategy other than a mechanochemical process, by exerting e.g., plasma, magnetic field or ultrasonication [2,3]. Although there may be any kinds of hybrids to use more than two of those unusual energy sources, simultaneous application of ultrasound and mechanical stressing seems to be highly promising, since they may enhance with each other to expect synergistic effects [4].

We therefore attempt in this study to apply these two effects simultaneously to obtain fine-grained and phase pure  $0.5\text{PMN} - 0.5\text{PZN}$  solid solution, by using agitation mill in an ultrasonic bath, which we call a sono-mechanochemical reactor. Since sono-chemistry makes sense only when it is exerted in the presence of liquid phase, we first developed appropriate aqueous suspension as a reaction mixture to subject to a combined sonochemical and mechanochemical effects. Here, we not only examine the phase composition and particle morphology, but also reaction processes in

which dissolution precipitation is involved. Whether and to what extent synergistic effects are observed are other important questions worth answering in this study.

## 2. EXPERIMENTAL

A reaction mixture for  $\text{Pb}(\text{Zn}_{1/2}\text{Mg}_{1/2})_{1/3}\text{Nb}_{2/3}\text{O}_3$  ( $x = 0.5$ ) (0.5PZMN) was prepared from a stoichiometric powder mixture comprising  $\text{PbO}$ ,  $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Nb}_2\text{O}_5$  and dispersed in water to obtain  $100\text{cm}^3$  aqueous suspension of 2.5wt% of total solid serving as a reactant mixture, which we named "intact".

A mechanochemical reactor comprises an ultrasonic bath (45kHz) equipped with an agitation mill (with 550g 1mm yttria-stabilized zirconia beads, contained in a 200ml tall beaker and operated at 600rpm) as shown in Fig. 1. Pretreatment was carried out with three variations, i.e. by a mere agitation milling (MC) and its

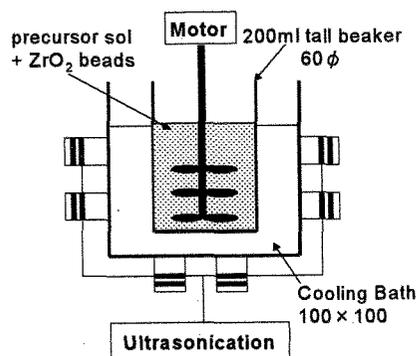


Fig.1 sono-mechanochemical reactor

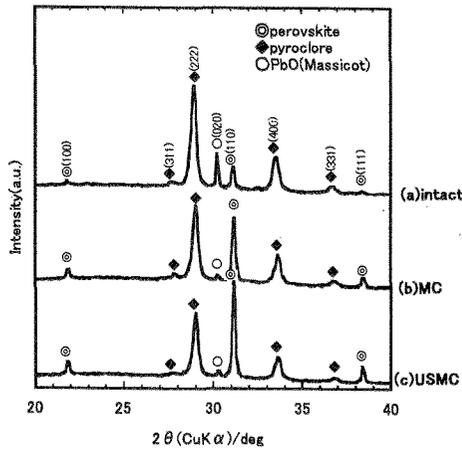


Fig.2 XRD profiles of PZMN precursor after heating up to 700°C

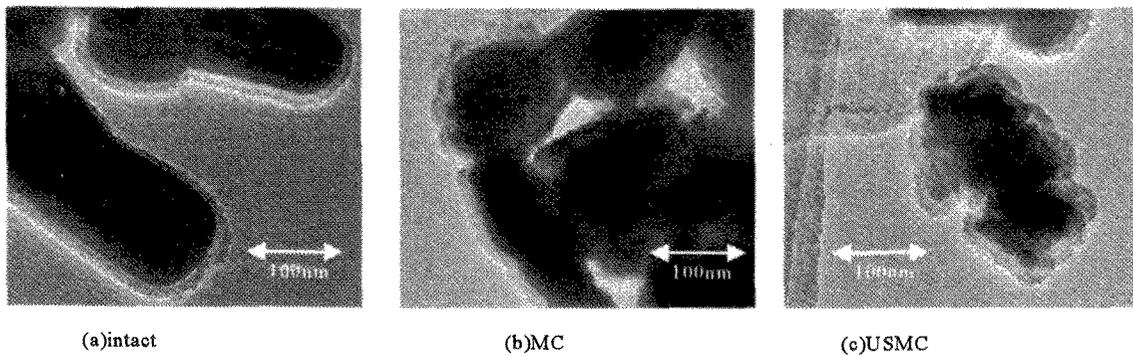


Fig.3 TEM image of PZMN precursor

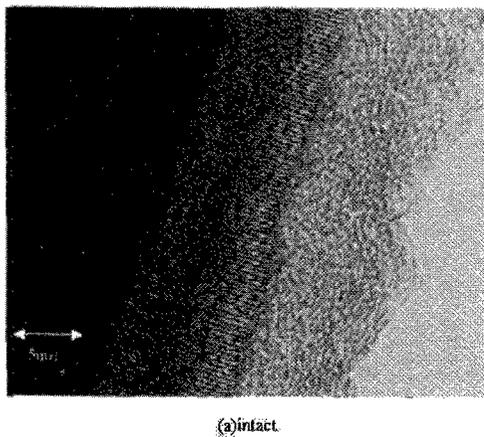


Fig.4 Magnificated TEM image of PZMN precursor

combination with ultrasonication (USMC). Total time of treatment was kept constant at 30min.

The pretreated reaction mixture was dried at 50 °C for 24 hours, and subsequently calcined in air at a constant rate of heating, 10K/min, up to either 700 °C or 850 °C and held for 1h. Calcination was carried out by the coexistence of a 1:1 by mol powder mixture to prevent vaporization of PbO. Characterization was carried out

by conventional X-ray diffractometry and various electron microscopies with simultaneous elemental analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1 Sono-mechanochemical effects on percent perovskite

X-ray diffractograms from the reaction products after calcining at 700 °C are displayed in Fig. 2 started from the precursor, intact (curve a), MC (curve b) and USMC (curve c). They are all mixtures of perovskite and pyrochlore. We obtained the values of percent perovskite from the conventional equation,  $X_{\text{pero}} = 100 \times I_{\text{pero}}(110) / [I_{\text{pero}}(110) + I_{\text{pyro}}(222)]$ .

Percent perovskite values are given in Table 1 for the samples calcined at 700 °C as well as at 850 °C. Table 1 reveals significant difference in  $X_{\text{pero}}$  depending on the precursor, with a superiority of USMC, although they

are not yet phase pure. The relative difference in  $X_{\text{pero}}$  disappears, however, at 850 °C.

Table 1 Percent perovskite

Temperature(°C)	intact	MC	USMC
700	18.2	46.6	61.0
850	7.5	89.5	88.6

#### 3.2 Microstructure of the products

Transmission electron micrographs of the precursor are given in Fig. 3. In every case, reactant particles are enveloped by a thin layer. This is by no means an artifact due to over-focusing, since the peripheral morphology of the outermost surface is different from that between the black core particles and gray surface layer. Rather, they are attributed to the precipitated product from the solution phase as a result of dissolution – precipitation reaction that takes place even under the macroscopic thermodynamic equilibrium. While the core particles exhibit fringe pattern, the surface layer is non-crystalline, as revealed by a transmission electron

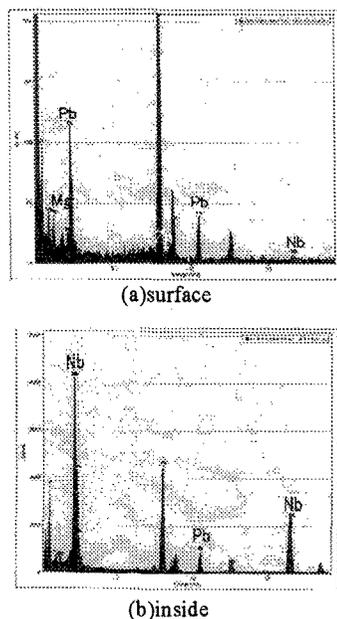


Fig.5 EDX profiles of PZMN precursor prepared by USMC: (a)surface amorphous layer, (b)inside of the particle

micrograph with higher magnification shown in Fig. 4.

Reexamination of Fig. 3 demonstrates that the average thickness of the surface amorphous layer is largest of all for the precursor prepared by USMC, followed by those of MC and intact. The morphology of the outermost surface is most rugged for USMC as well. This indicates that dissolution precipitation reaction at the solid / liquid interface is enhanced by simultaneous ultrasonication during agitation milling.

It is noteworthy that in the surface amorphous layer, the concentrations of Zn and Mg are higher, as shown in Fig. 5(a). This was revealed by energy dispersive X-ray analyzer (EDX) equipped with TEM. In contrast, Nb is richer in the interior of the particle (Fig. 5b). This may straightforwardly be interpreted by the difference in the solubility. This is consistent with the lattice spacing, corresponding to that of  $\text{Nb}_2\text{O}_5$  (orthorhombic phase) (001).

After calcining at  $850^\circ\text{C}$  for 1h, the microstructure, notably the grain size, makes significant difference, although percent perovskite is similar with each other (Fig.6). On the samples with USMC pretreatment, we observe a large number of particles as small as 100nm, together with much larger particles of ca  $1\mu\text{m}$ (Fig.6b). We infer the difference to be attributed to enhanced nucleation within a highly reactive surface amorphous layer due to ultrasonication with enhanced dissolution – precipitation by agitation milling. Although concrete evidences are yet to be found, it seems quite reasonable to assume that bombardment of the microcavity results in the preferential nucleation and increase in the

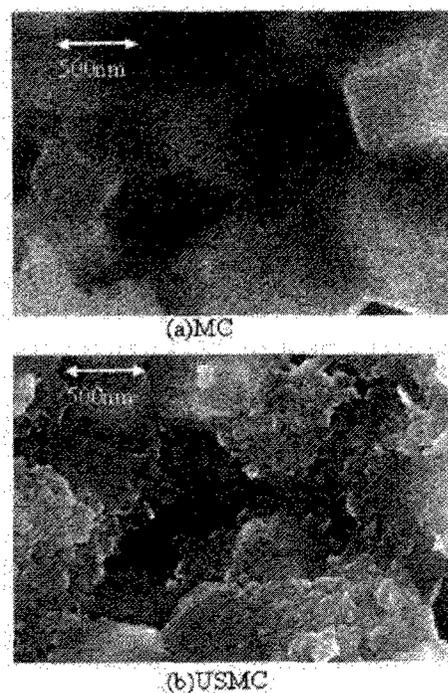


Fig.6 SEM image of PZMN precursor after heating up to  $850^\circ\text{C}$

dangling bond density simultaneously in the surface amorphous layer. Larger number of nucleation sites always induces larger number of particles and correspondingly smaller average particle size.

### 3.3 Effect of aging at high temperature

From the experimental results presented hitherto, we

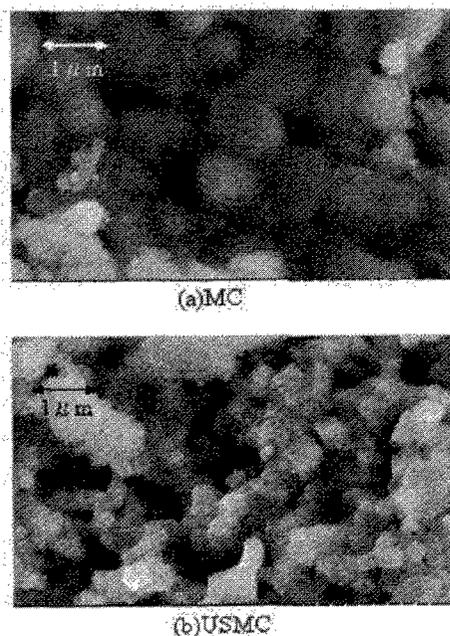


Fig.7 SEM image of PZMN precursor by aging for 3h after heating up to  $850^\circ\text{C}$

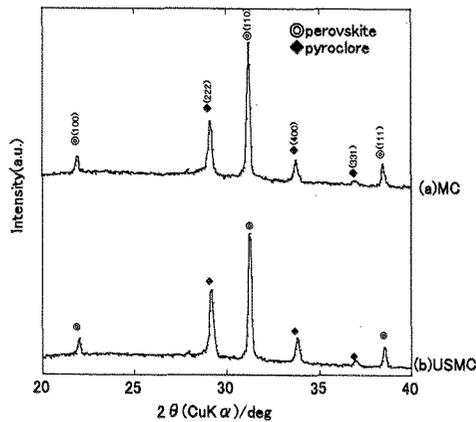


Fig.8 XRD profiles of PZMN precursor by aging for 3h at 50°C after heating up to 850°C

expected higher proportion of smaller particles from thicker amorphous layer at the surface. We therefore tried to enhance the dissolution - precipitation reaction at the solid / liquid interface by aging at elevated temperature for longer time, i.e. at 50 °C for 3h. Although the smaller particles were obtained after calcinations at 850 °C in USMC, the average particle size of the smaller particles became larger, i.e. from ca

Table 2 Percent perovskite of aged and pulse US samples

Samples	Aging		Pulsed USMC time (s)		
	MC	USMC	0.1	1	9.9
Pero%	70.9	64.6	69.0	67.5	66.3

0.1 μm up to ca. 0.5 μm (Fig. 7).

Unfortunately, however, the percent perovskite

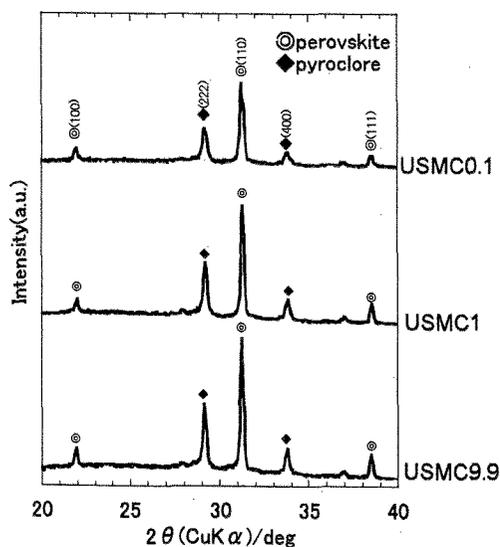


Fig.9 XRD profiles of PZMN precursor after heating up to 850°C

decreased significantly, as shown in Fig.8 and Table 2. This is presumably attributed to the intolerable deviation from the stoichiometry after enhanced dissolution - precipitation as mentioned above.

### 3.4 Effects of high frequency ultrasonication

One of the most important findings in the area of sonochemistry is the advantage of pulsed ultrasonication [5]. This could avoid excessive growth of the cavitation bubble ineffective to provide a high-temperature - high-pressure microenvironment, being typical for ultrasonication, by prolonged, continuous mode. We therefore tried to decrease the pulse width from conventional 60s down to 0.1s. As shown in Fig.9 and Table 2, however, percent perovskite decreased by shorter interval of ultrasonication. This again must be attributed to the off-stoichiometry due to enhanced dissolution - precipitation by higher effective ultrasonication. It is, therefore, important to enhance nucleation while keeping the stoichiometry of the surface amorphous layer. Further trial is now ongoing.

### 4. Concluding remarks

We demonstrated that simultaneous agitation milling and ultrasonication enables higher perovskite percent and smaller grain size of the solid solution  $0.5PbZr_{1/3}Nb_{2/3}O_3 - 0.5PbMg_{1/3}Nb_{2/3}O_3$ . This is likely to be attributed to the formation and activation of surface amorphous layer due to dissolution - precipitation reaction at the solid - liquid interface. However, excessive solid - liquid reaction leads to off - stoichiometry and decreases percent perovskite. Activation of surface amorphous layer while keeping the stoichiometry is therefore of utmost importance.

### References

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