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Phase formation studies in ZnB''_2O_6 and $Pb(Zn_{1/3}B''_{2/3})O_3$ (B'' = Nb,Ta)

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Abstract

Phase developmental stages in ZnO + B''_2O_5 (B'' = Nb,Ta) on heat treatments were investigated by powder X-ray diffraction (XRD). Desired phases of the B-site precursor compositions formed directly from the reactants for B'' = Nb, whereas the formation was indirect when B'' = Ta. Similar studies were attempted for PbO + $\frac{1}{3}ZnB''_2O_6$, where only pyrochlore phases were developed, instead of desired perovskite. The overall results are discussed in comparison with other cases of $(B',B'')O_2$ and $Pb(B',B'')O_3$.

Keywords: A. Powders: solid-state reaction; B. X-ray methods; D. Perovskites

1. Introduction

Many complex-perovskite relaxors of $Pb(B',B'')O_3$ (showing frequency-dependent dielectric relaxation) have been prepared and characterized [1–3]. During the syntheses of such lead-based relaxor ceramics, care must be taken to avoid the formation of pyrochlore phase(s), presence of which is well-known to be detrimental to dielectric properties [3–5]. It has also been reported that perovskite formation yields could be substantially enhanced by two-stage reaction of columbite process [6,7] (or more precisely B-site precursor method [8,9]). The general reaction routes can be expressed as follows:

$$B'O + B''O \rightarrow (B', B'')O_2$$

and

$$PbO + (B', B'')O_2 \rightarrow Pb(B', B'')O_3.$$

where B' and B'' are respectively lower and higher valence cations of Mg^{2+}, Zn^{2+}, Fe^{3+}, $\cdots$ and Nb^{5+}, Ta5+, W^{6+}, $\cdots$. In the process, chemicals of $B'O$ and $B''O$ are preferentially reacted to form B-site precursor compositions of $(B',B'')O_2$, followed by further reactions of the product with PbO for the formation of the desired perovskite phase. Thereby, formation of harmful pyrochlore(s) could be effectively suppressed by bypassing the direct reaction between PbO and $B''O$, especially when B'' is Nb and/or Ta. Successful results have been reported for many compositions, including $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN [6,7,9–11]), $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT [11,12]), $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN [8,9,13]), $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT [13]), etc.

So far, phase formation stages have been reported for PMN [6,9,14–16], PMT [17], PFN [8,9,15,18–20], PFT [21], $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW [8,18,19,22,23]), $Pb(Mg_{1/2}W_{1/2})O_3$ (PMWc [24]), $Pb(Zn_{1/2}W_{1/2})O_3$ (PZW [24]), PMN–PFN [25], $Pb(Zr_{0.48}Ti_{0.52})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ [26], $Pb_{1.83}Mg_{0.29}Nb_{1.71}O_{6.39}$ [27], $Pb_2FeWO_{6.5}$ [28], etc. It is also known, however, that even the B-site precursor method was not effective in the formation of perovskite for $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Ta_{2/3})O_3$ (PZN and PZT, respectively), where only the pyrochlore phases resulted instead [10,12,29,30]. Nevertheless, comprehensive studies on phase formation can hardly be found. In the present study, therefore, the reaction routes of ZnB''_2O_6 and $Pb(Zn_{1/3}B''_{2/3})O_3$ (B'' = Nb,Ta) were investigated. Powder mixtures of the B-site precursor ZnB''_2O_6 compositions were heat-treated at different temperatures and were characterized by X-ray diffraction for phase identification. Similar studies were repeated for PbO + $\frac{1}{3}ZnB''_2O_6$ and the results are compared with other compositions of $(B',B'')O_2$ and $Pb(B',B'')O_3$.

2. Experimental

All starting materials were oxide chemicals of $\geq$99.5% purity. During the reaction, only required amounts of the

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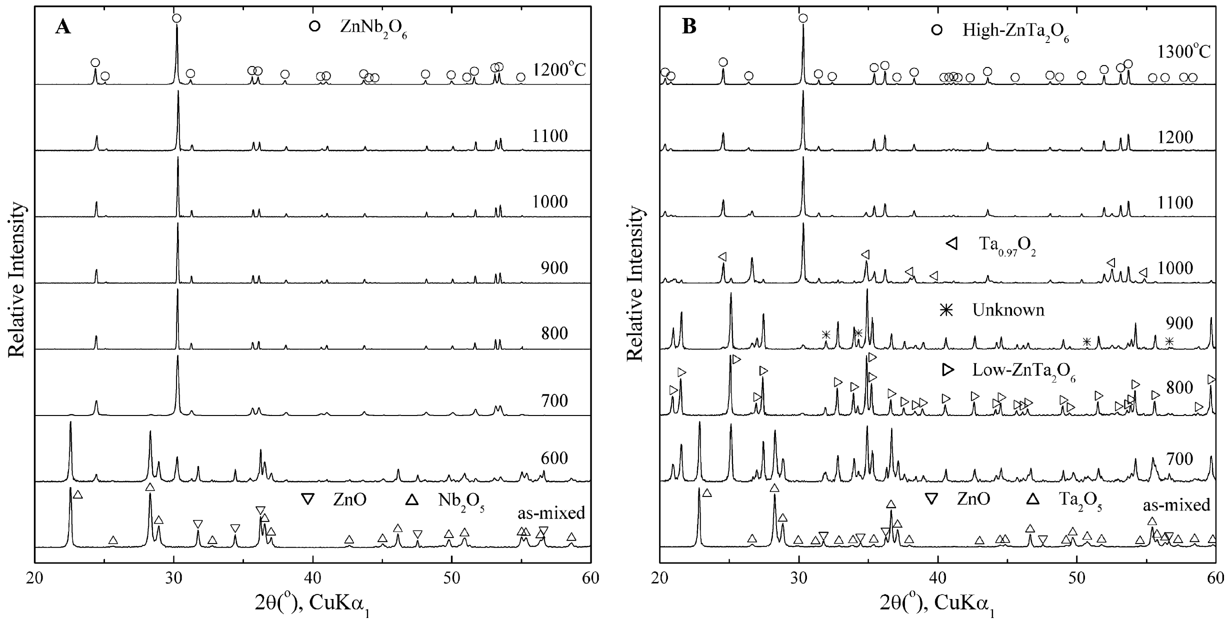

Fig. 1. Room-temperature X-ray diffraction patterns of (A) $ZnO + Nb_2O_5$ and (B) $ZnO + Ta_2O_5$, heat-treated at several temperatures.

constituent chemicals were used, i.e., without excess addition of any component [6,7]. Powder mixtures for the reactions of $ZnO + B''_2O_5$ ($B'' = Nb,Ta$) were wet-milled for 12 h under alcohol (ZrO_2 media in polyethylene containers) in order to achieve intimate mixing. After drying for 24 h, powder batches were heated (rate = 300 °C/h) to selected temperatures and kept for 2 h (soaking time), followed by natural cooling. Investigated temperature ranges were from 500 and 600 °C (below the initiation of any detectable phase development between the reactants) for the Nb- and Ta-containing compositions, respectively, to those of interest with increments of 50 °C. Reaction products were examined by powder XRD in order to identify the developed phases.

Similar attempts were carried out for $PbO + {}^1/_3ZnB''_2O_6$. For the investigation, B-site precursor powders of $ZnNb_2O_6$ and $ZnTa_2O_6$ were separately prepared at 1150 and 1200 °C, respectively, for 2 h each with intermediate milling-to-drying steps in order to promote phase formation. Starting temperatures were 500 and 550 °C for the two sets of compositions. Developed phases of the prepared powders were also examined by XRD.

3. Results and discussion

XRD patterns of $ZnNb_2O_6$ and $ZnTa_2O_6$ B-site precursor compositions, prepared from constituent chemicals, are presented in Fig. 1(A) and (B), respectively, as a function of the heat-treatment temperatures. Relative fractions of the developed phases were determined semiquantitatively by comparison among the integrated intensity values of the major X-ray peaks and the results are plotted in Fig. 2. In the reaction of $ZnO + Nb_2O_5$, $ZnNb_2O_6$ (columbite structure, ICDD no. 37–1371) was developed directly in the temperature range of 500–750 °C at the expense of the reactant chemicals. The patterns at higher temperatures were basically identical to that of 700 °C and did not change significantly.

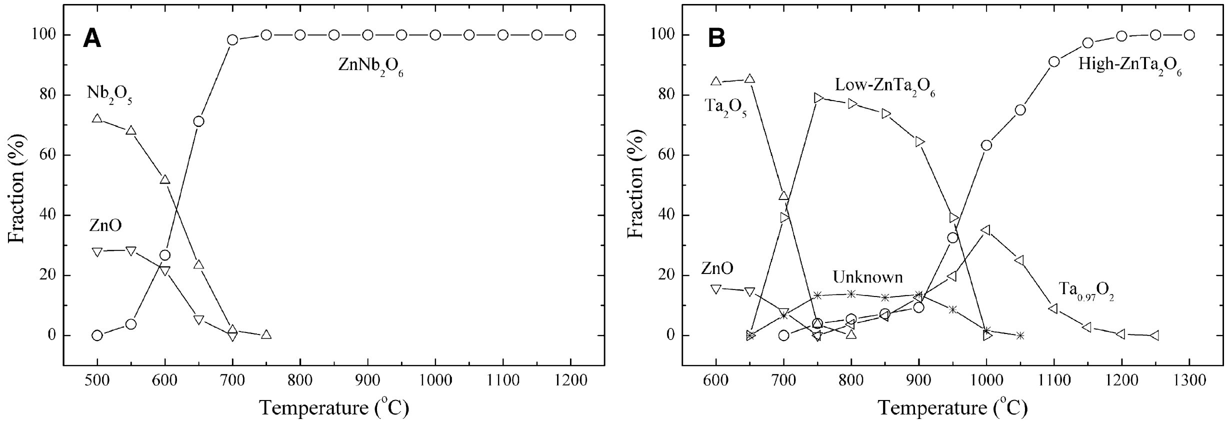

Fig. 2. Fractions of the phases developed in (A) $ZnO + Nb_2O_5$ and (B) $ZnO + Ta_2O_5$.

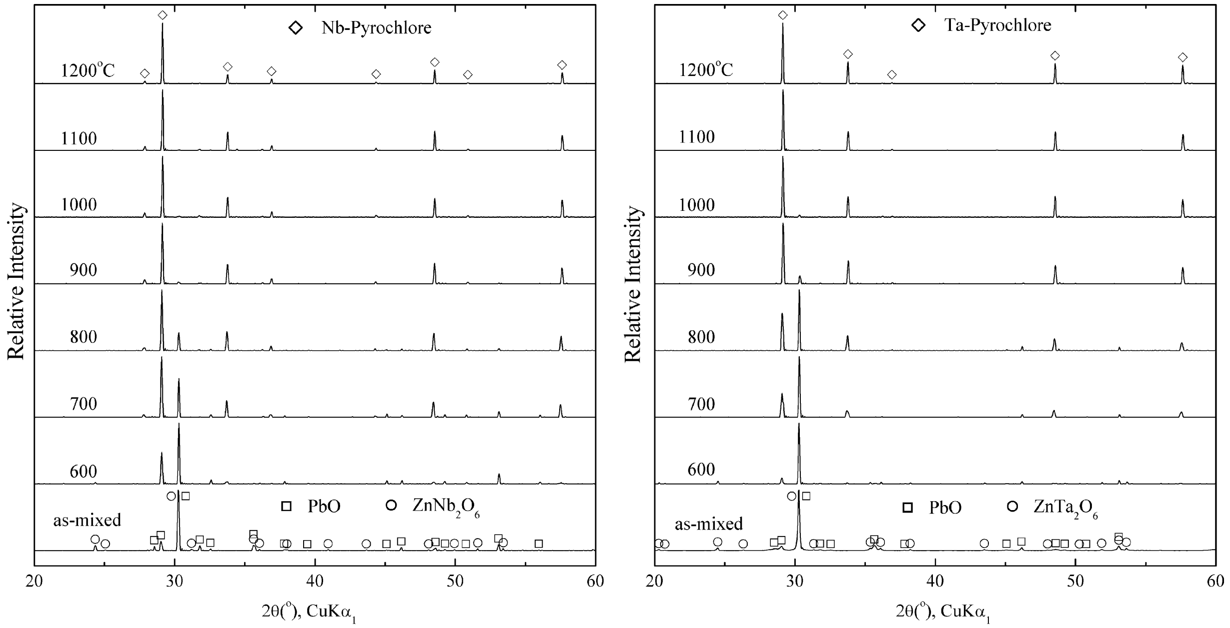

Fig. 3. XRD patterns showing phase developments in (A) PbO + 1/3$ZnNb_2O_6$ and (B) PbO + 1/3$ZnTa_2O_6$.

In $ZnO + Ta_2O_5 \rightarrow ZnTa_2O_6$, by contrast, the developmental stages looked rather complicated and $ZnTa_2O_6$ (tri-αPbO_2 structure, ICDD no. 39–1484) formed indirectly from the reactants via several intermediate phases. Low-$ZnTa_2O_6$ (ICDD no. 49–746) and an unknown phase were developed from 650 °C and became major at 750 °C (relative fractions of 79% and 14%, respectively), followed by gradual decreases up to 1000 °C. It can be speculated, therefore, that the unknown phase seems to be closely associated to low-$ZnTa_2O_6$, as their temperature ranges of stability as well as the temperature-dependency of the formation yields were almost identical. Then, high-$ZnTa_2O_6$ (ICDD no. 39–1484) and $Ta_{0.97}O_2$ (ICDD no. 37–117) started to form with increasing temperature and progressively replaced the previously developed phases. Whereas the intensity values of $Ta_{0.97}O_2$ reached a maximum (35% fraction) at 1000 °C, the values of the high-$ZnTa_2O_6$ phase increased still further. The high-$ZnTa_2O_6$ phase finally became predominant at higher temperatures.

When the phase formation results are compared, the niobate compound $ZnNb_2O_6$ formed directly from ZnO and Nb_2O_5. Such direct formation of the B-site precursors from the reactants was also reported in $MgTa_2O_6$ [17], $MgWO_4$ [24], $ZnWO_4$ [24], and Fe_2WO_6 [8]. By contrast, the tantalum analog $ZnTa_2O_6$ developed indirectly via several intermediate phases. Similar trends can also be found in $MgNb_2O_6$ [16], $FeNbO_4$ [8], and $FeTaO_4$ [21].

The X-ray diffraction patterns showing phase developments in the powder mixtures (molar ratio of 3:1) of $PbO + ZnNb_2O_6$ and $PbO + ZnTa_2O_6$ are contrasted in Fig. 3(A) and (B), respectively. The relative fractions of the phases are shown in Fig. 4. In the reactions between PbO and the respective B-site precursor components to develop perovskite PZN and PZT, the formation products were not perovskite. Instead, only the cubic

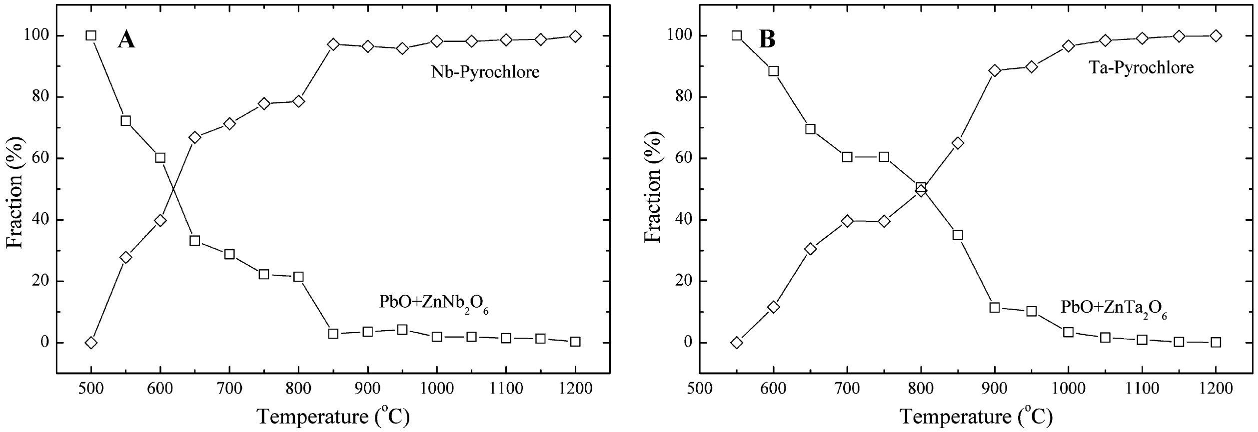

Fig. 4. Fractions of the developed phases in (A) PbO + 1/3$ZnNb_2O_6$ and (B) PbO + 1/3$ZnTa_2O_6$.

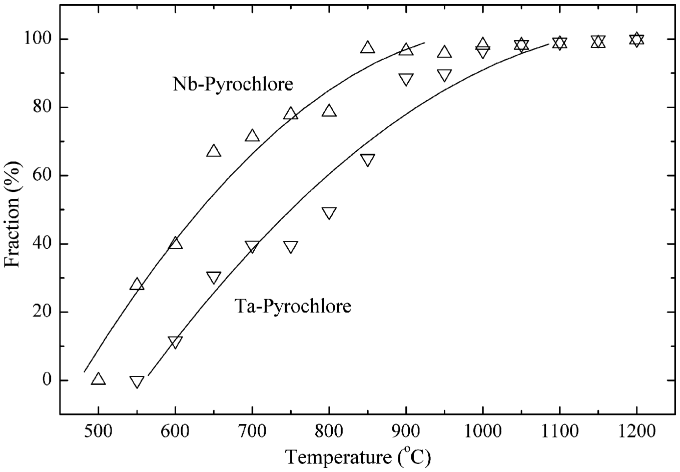

Fig. 5. Fractions of the Nb- and Ta-pyrochlore with fitting curves for ready comparison.

pyrochlore phases of $Pb_{1.83}Zn_{0.29}Nb_{1.71}O_{6.39}$ (ICDD no. 34–374) and $Pb_{1.83}Zn_{0.29}Ta_{1.71}O_{6.39}$ (ICDD no. 34–395) resulted, which were abbreviated as Nb- and Ta-pyrochlore, respectively, in the figures. A similar instance can also be found in $PbO + {}^{1}/_{2}ZnWO_4$ [24], where the final products were Pb_2WO_5 and ZnO, and not perovskite $Pb(Zn_{1/2}W_{1/2})O_3$.

Unlike the B-site precursors, however, the phase developmental modes were identical in both of the Nb- and Ta-containing compositions: direct formation of the final products without the intervention of any intermediate phase(s). The perovskite PMN [16] and PMW [24] also developed directly from the reactants (PbO and respective B-site precursor components), whereas formation of the intermediate phase(s) preceded the perovskite development in PMT [17], PFN [8], PFT [21], and PFW [8,28].

The formation fractions (and the fitting curves as well) of the two species of pyrochlore are directly compared in Fig. 5 against the heat-treatment temperatures. As can be easily seen, the development temperatures of the Nb-pyrochlore were 100–150 °C lower than those of the tantalum counterpart (Ta-pyrochlore). Similarly, the perovskite formation temperatures of PMN [16] and PFN [8] were somewhat lower than those of PMT [17] and PFT [21], respectively, by ≈100 °C. $Pb_3Nb_4O_{13}$ also developed at ≈50 °C lower than $Pb_4Ta_6O_{19}$ (before the perovskite formation) in PFN [8] and PFT [21]. All the instances indicate the comparatively refractory nature of the Ta-containing compositions.

Table 1
Comparison among various compositions of $(B',B'')O_2$ and $Pb(B',B'')O_3$ in terms of phase formation modes.

$(B',B'')O_2$	Mode*	$Pb(B',B'')O_3$	Mode*	Reference
$MgNb_2O_6$	I	$Pb(Mg_{1/3}Nb_{2/3})O_3$	D	[16]
$MgTa_2O_6$	D	$Pb(Mg_{1/3}Ta_{2/3})O_3$	I	[17]
$ZnNb_2O_6$	D	$Pb(Zn_{1/3}Nb_{2/3})O_3$	Pyrochlore	Present work
$ZnTa_2O_6$	I	$Pb(Zn_{1/3}Ta_{2/3})O_3$	Pyrochlore	Present work
$FeNbO_4$	I	$Pb(Fe_{1/2}Nb_{1/2})O_3$	I	[8]
$FeTaO_4$	I	$Pb(Fe_{1/2}Ta_{1/2})O_3$	I	[21]
$MgWO_4$	D	$Pb(Mg_{1/2}W_{1/2})O_3$	D	[24]
$ZnWO_4$	D	$Pb(Zn_{1/2}W_{1/2})O_3$	$Pb_2WO_5 + ZnO$	[24]
Fe_2WO_6	D	$Pb(Fe_{2/3}W_{1/3})O_3$	I	[8,28]

* D: direct; I: indirect.

The overall results are summarized in Table 1. As discussed above, the formation modes of the B-site precursor compositions can be grouped into two cases of (a) direct formation from the reactants ($MgTa_2O_6$, $ZnNb_2O_6$, $MgWO_4$, $ZnWO_4$, and Fe_2WO_6) and (b) indirect formation via intermediate phase(s), as in $MgNb_2O_6$, $ZnTa_2O_6$, $FeNbO_4$, and $FeTaO_4$. By contrast, phase developmental stages after the addition of PbO can be categorized into three groups: (a) direct formation of the final products from the reactants (PMN and PMW), (b) indirect formation (PMT, PFN, PFT, and PFW), and (c) formation failure of the desired perovskite phase, as in PZN, PZT, and PZW (all with Zn^{2+} as the lower valence octahedral cation).

4. Conclusion

In the B-site precursor compositions, $ZnNb_2O_6$ formed at 500–750 °C directly from the reactants, whereas $ZnTa_2O_6$ (high-temperature form) developed indirectly via several intermediate phases. The low-$ZnTa_2O_6$ phase was stable at 650–1000 °C, along with an unknown one at the same temperature range. By contrast, $Ta_{0.97}O_2$ was detected at considerably higher temperatures of 750–1250 °C.

In the formation attempts of $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Ta_{2/3})O_3$ from PbO and the respective B-site precursor components, only the cubic pyrochlore phases (instead of the perovskite) resulted directly from the reactants. There was not any temperature range, where the perovskite formation was detected at all. In addition, the reaction temperatures of the Nb-pyrochlore were 100–150 °C lower than those of Ta-pyrochlore.

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