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Phase developments in $Pb(Mg_{1/2}W_{1/2})O_3$ and $Pb(Zn_{1/2}W_{1/2})O_3$ via B-site precursor route

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Abstract Phase formation stages of $MgWO_4$ and $ZnWO_4$ (precursor compositions for following steps) were investigated by monitoring the reactions of oxide chemicals at various temperatures. Developed phases were examined by using X-ray diffraction (XRD). Successive attempts were also conducted for $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW) and $Pb(Zn_{1/2}W_{1/2})O_3$ (PZW) by reacting PbO with the precursor compounds. Stages of phase development in the two compositions were also analyzed. The results are compared with those of another tungsten-containing perovskite $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) and its B-site precursor Fe_2WO_6. After PbO addition to the precursor powders, a perovskite phase formed directly (i.e., without any intermediate phases) in the case of PMW. For PbO + ½$ZnWO_4$, in contrast, the decomposition of $ZnWO_4$ and preferential reaction with PbO resulted in Pb_2WO_5 and ZnO, instead of the perovskite PZW.

Introduction

Lead magnesium tungstate $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW) is an antiferroelectric orthorhombic perovskite with a Curie temperature of 38 °C [1], in which the B-site sublattice cations of Mg^{2+} and W^{2+} have been reported to be 1:1 ordered [2, 3]. In contrast, $Pb(Zn_{1/2}W_{1/2})O_3$ (PZW), although an identical stoichiometry to PMW, has not as yet been formed into a perovskite structure. It should be noted that the expression of PZW in the present paper does not necessarily indicate formation of a perovskite structure.

Several reaction sequences regarding the formation of $Pb(B',B'')O_3$-type complex perovskite have been previously reported, e.g., $Pb(Mg_{1/3}Nb_{2/3})O_3$ [4–11], $Pb(Ni_{1/3}Nb_{2/3})O_3$ [12], $Pb(Fe_{1/2}Nb_{1/2})O_3$ [5, 11, 13–16], $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) [13, 14, 16–18], $Pb(Fe_{1/2}Ta_{1/2})O_3$ [19], $Pb(Mg_{1/3}Ta_{2/3})O_3$ [20], etc. However, comparable results for PMW and PZW have rarely been reported. Therefore, reaction stages of $MgWO_4$ and $ZnWO_4$ from constituent oxide chemicals were investigated in detail in the present study. Phase developments of perovskite in PMW and PZW were also examined and the results are compared with those of another W-containing compound PFW. In the powder preparation of PMW and PZW, a B-site precursor method [16, 21] was utilized, which is conceptually identical to the columbite process [6], but is a more comprehensive expression.

Experimental

Starting materials were high-purity oxide chemicals of PbO (99.5%), MgO (99.9%), ZnO (99.8%), and WO_3 (>99%). In order to preclude the effects of moisture (adsorbed to the raw chemicals), moisture contents of the chemicals and of the synthesized precursor powders ($MgWO_4$ and $ZnWO_4$) were measured and introduced into the batch calculations.

MgO + WO_3 and ZnO + WO_3 (by 1:1 molar ratio) powders were mixed in ethyl alcohol for 12 h with ZrO_2 milling media in polyethylene bottles. To form B-site precursor compounds, the slurries were dried overnight and reacted in alumina crucible (heating rate = 5 °C/min) with 2 h soaking at terminal temperatures of 450–1,000 °C at 50 °C increments. The heat-treated powders were examined by means of X-ray diffraction (XRD, MO3X-HF

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Model 1031, MacScience Co., Ltd, Japan) using a Cu target (30 kV, 30 mA) with a monochromator at a scanning speed of 4°2θ/min to monitor the formed phases. B-site precursor powders were then mixed with stoichiometric proportions of PbO, followed by similar steps of drying and reactions from somewhat lower temperatures of 400 °C up to 1,000 °C (also at 50 °C increments). Fractions of the final products (B-site precursor, perovskite, as well as other compositions) were determined by intensity comparison among the constituent phases.

Results and discussion

XRD results of MgO + WO_3 after different reaction temperatures are contrasted in Fig. 1a. MgO and WO_3 did not react at temperatures up to 550 °C and diffraction spectra of 450 and 500 °C were virtually identical to that at 550 °C (mixed state of the two reactants). The two oxides started to react at 550–600 °C, resulting in the development of $MgWO_4$ (wolframite structure, ICDD No. 27-789). With further increase in temperatures, the $MgWO_4$ peaks increased in relative heights by consuming the two reactants, reached full intensities at 750 °C, and remained virtually unchanged at higher reaction temperatures of up to 1,000 °C. For ZnO + WO_3 (Fig. 1b), phase developmental stages were similar, with the exception of $ZnWO_4$ formation (wolframite structure, ICDD No. 15-774) starting at substantially lower temperatures. Once the formation of $ZnWO_4$ was completed at 600 °C, the diffractograms remained virtually unchanged at higher temperatures of up to 1,000 °C.

Temperature-dependent formation results of the B-site precursor $MgWO_4$ and $ZnWO_4$ are plotted in Fig. 2, where values of another tungstate Fe_2WO_6 (a precursor for the synthesis of perovskite PFW [16]) are also included for comparison purposes. All three precursor compounds developed from constituent oxides without any intermediate phases. Additionally, they did not decompose nor form any other phases at up to 1,000 °C. However, phase fractions of $MgWO_4$ were displaced slightly from those of $ZnWO_4$, indicating that reaction temperatures of the former were 50–70 °C higher than those of the latter. Nevertheless, the two compounds formed at substantially lower temperatures, when compared with Fe_2WO_6.

X-ray diffractograms for the formation of PMW are displayed in Fig. 3a, where the two reactants of PbO and $MgWO_4$ did not react at 400 °C. A PMW perovskite of orthorhombic symmetry (ICDD No. 46-1499) began to form at 450 °C. The intensity levels of perovskite increased with increasing temperatures, while those of the reactants decreased and finally disappeared at 650 °C. At higher temperatures, the patterns of perovskite were solely observed without any development of second phase. In contrast, the reaction results of PbO + ½$ZnWO_4$ (Fig. 3b) were significantly different, where the perovskite did not develop at all throughout the investigated temperature range. Instead, ZnO was decomposed from $ZnWO_4$, resulting in the derivation of WO_3, to which PbO (two times in molar ratio) was combined to form Pb_2WO_5 (ICDD No. 36-1495). The two phases did not react, but persisted up to temperatures of 850 °C, followed by decomposition/melting at higher temperatures. The results indicate that even the B-site precursor method is not effective in the formation of the perovskite PZW. When compared with readily formed PMW, synthesis failure of perovskite PZW is believed to be attributed to the more covalent nature of Zn, which prefers 4-fold coordination [22, 23]. In addition, electronegativity differences [24] of

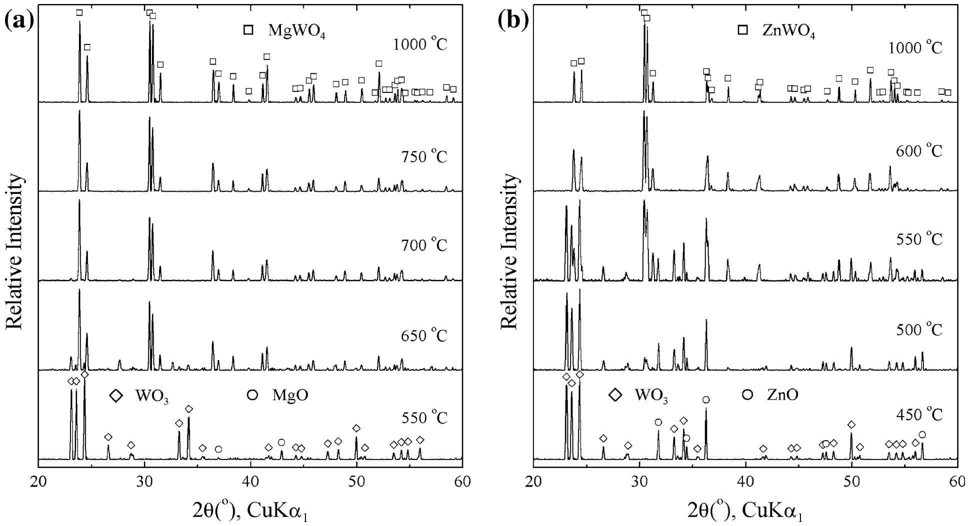


Fig. 1 X-ray diffractograms after reactions of (**a**) MgO + WO_3 and (**b**) ZnO + WO_3

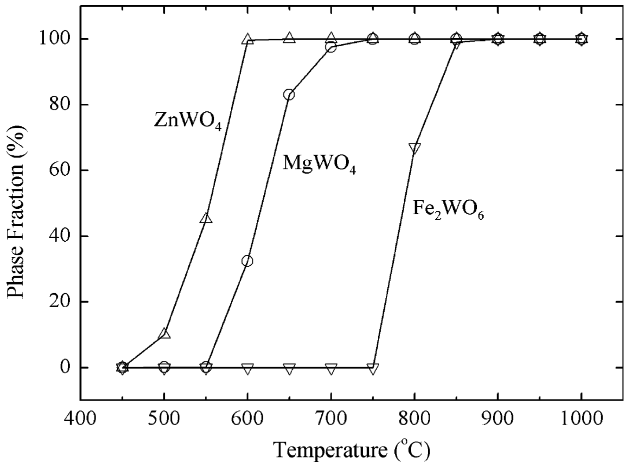


Fig. 2 Phase fractions versus calcination temperature of $MgWO_4$, $ZnWO_4$, and Fe_2WO_6

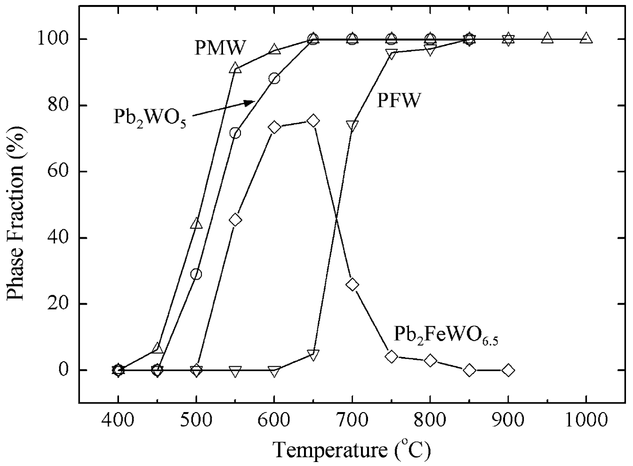


Fig. 4 Phase development yields of PMW, Pb_2WO_5, $Pb_2FeWO_{6.5}$, and PFW versus calcination temperature

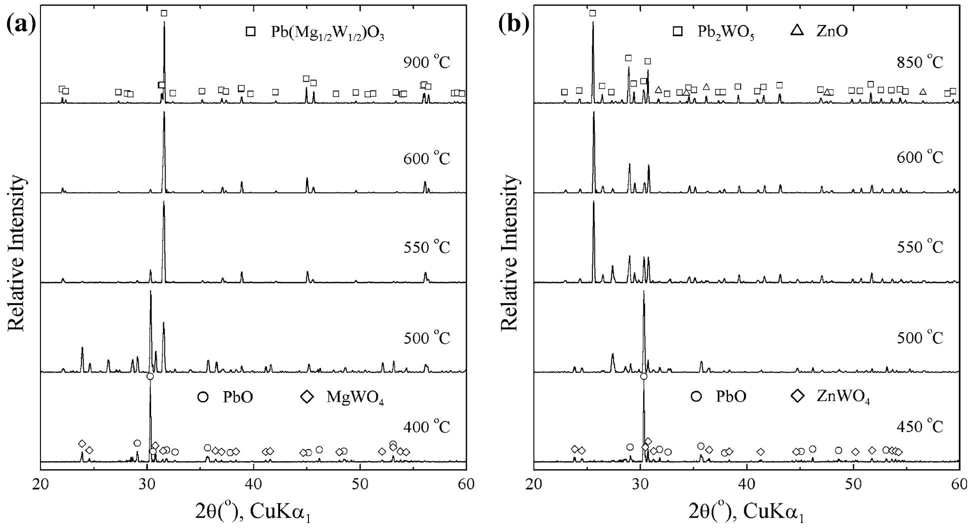
Zn–O and Mg–O are 1.8 and 2.2, respectively, supporting the results. Slightly larger (0.0740 nm) ionic size of Zn [25], as compared with 0.0720 nm [25] of Mg, also appears to be a factor, when considering the perovskite formability in $Pb(Mg_{1/3}Nb_{2/3})O_3$ by the B-site precursor method [6, 9] versus inability in $Pb(Zn_{1/3}Nb_{2/3})O_3$ [22, 23].

Phase yields monitored after the reactions for PMW and PZW are presented in Fig. 4, in conjunction with the results of PFW [16]. As discussed above, perovskite PMW formed directly from the reactants without intermediate phases. In contrast, perovskite PZW did not develop at all; hence, only the fractions of Pb_2WO_5 are plotted. Meanwhile, perovskite PFW formed at much higher temperatures at the expense of the pyrochlore $Pb_2FeWO_{6.5}$, which developed at intermediate temperatures from PbO and B-site precursor Fe_2WO_6 [16, 17]. However, the PFW perovskite persisted at temperatures of only up to 900 °C, followed immediately by melting at 935 °C [26].

Conclusion

B-site precursor compounds $MgWO_4$ and $ZnWO_4$ developed directly from equimolar mixtures of $MgO + WO_3$ and $ZnO + WO_3$, respectively, without any formation of intermediate phases. However, phase formation temperatures of $MgWO_4$ were somewhat higher than those of $ZnWO_4$. After the addition of PbO to precursor powders and subsequent reactions, the formation of perovskite PMW started at 450 °C (directly from the reactants, without intermediate phases) and was completed at 650 °C. For PbO + ½$ZnWO_4$, in contrast, the decomposition of

Fig. 3 X-ray diffraction results of (**a**) PbO + ½$MgWO_4$ and (**b**) PbO + ½$ZnWO_4$



$ZnWO_4$, followed by a subsequent reaction of the WO_3 component with PbO, resulted in a mixed state of Pb_2WO_5 and ZnO, rather than the desired perovskite phase.

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