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Perovskite structure development in (Ba)Ti-substituted $Pb(Zn_{1/2}W_{1/2})O_3$ and dielectric properties

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ABSTRACT

Simultaneous substitution of Ba and/or Ti into $Pb(Zn_{1/2}W_{1/2})O_3$ was attempted in order to investigate the development of a perovskite structure. Precursor powders of the B-site components were separately prepared and post-reacted with the remaining components to assist the perovskite formation. The low formation yields of perovskite at $Pb(Zn_{1/2}W_{1/2})O_3$-rich compositions increased continuously with increasing substituent levels. Dielectric constant and loss values of the sintered ceramics were measured, followed by microstructure examination.

1. Introduction

Lead-based complex perovskites $Pb(B',B'')O_3$ have been widely investigated for a variety of dielectric aspects [1]. Among them, lead iron tungstate $Pb(Fe_{2/3}W_{1/3})O_3$ (abbreviated as PFW [2]) and lead magnesium tungstate $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW [2]) are contrasting tungsten-containing compositions of ferroelectric and antiferroelectric characteristics, respectively. So far, however, lead zinc tungstate $Pb(Zn_{1/2}W_{1/2})O_3$ (PZW) of a perovskite structure has not yet been synthesized, even though the stoichiometry is similar to those of PFW and PMW. The failure in the perovskite development in PZW could be explained by considering tolerance factor (TF) versus electronegativity difference (END) [3]. Meanwhile, lead and barium titanates of $PbTiO_3$ and $BaTiO_3$ (PT and BT, respectively) are normal ferroelectric compounds, exhibiting sharp phase transition modes in the dielectric constant spectra. Moreover, the perovskite structure forms readily by the large values of TF and END.

In an attempt to stabilize the perovskite structure in PZW, PT and BT were substituted [4], but the results were not satisfactory. In the present study, therefore, perovskite development was further attempted by simultaneously incorporating PT and BT in two different ways. In System I, the B-site complex Zn-W was replaced progressively by smaller Ti ions (along with additional substitution of 20 at.% Ba for Pb) in order to improve the factors of END as well as TF. In System II, by contrast, the A-site Pb ions were replaced by larger Ba (with simultaneous introduction of Ti into the lattice sites of the $Zn_{1/2}W_{1/2}$ complex) and the results were compared.

2. Experimental

The two pseudobinary composition sets under study were $(0.8\text{-}x)Pb(Zn_{1/2}W_{1/2})O_3$-$x$PbTiO3-0.2BaTiO3 and $(0.8\text{-}PbTiO_3$-$0.2BaTiO_3$ and $(0.8\text{-}y)Pb(Zn_{1/2}W_{1/2})O_3-0.2PbTiO_3$-$y$$BaTiO_3$, i.e., $(Pb_{0.8}Ba_{0.2})(Zn_{(0.8-x)/2}W_{(0.8-x)/2}Ti_{0.2+x})O_3$ and $(Pb_{1-y}Ba_y)(Zn_{(0.8-y)/2}W_{(0.8-y)/2}Ti_{0.2+y})O_3$ (Systems I and II, respectively). The values of x and y were selected between 0.0 and 0.8 at regular intervals of 0.2 (Fig. 1). Composition ranges between 0.0 and 0.2 were subdivided further in order to closely explore the results in the vicinity of PZW. It should be noted that the compositions of $x = 0.2$ and $y = 0.2$ are inherently identical, 0.6PZW-0.2PT-0.2BT. Ceramic powders of the two systems were prepared via a B-site precursor route [5–7] in order to enhance the perovskite formation yields. Raw materials used were reagent-grade chemicals of PbO (99.5% purity), $BaCO_3$ (99.9%), ZnO (99.8%), WO_3 (99.8%), and TiO_2 (99.9%). Moisture contents of the raw materials and of the separately prepared precursor powders were measured and introduced into the batch calculation to maintain the compositions as closely to the nominal values as possible.

B-site precursor compositions of $[(Zn_{1/2}W_{1/2})_{0.8-x}Ti_{0.2+x}]O_2$, common to both Systems I and II, were synthesized by wet-milling (ethyl alcohol, ZrO_2 milling media, polyethylene containers) constituent chemicals, drying, and calcination (650 °C for 2 h in air). The milling-to-calcination steps were repeated once in order to promote structure development. Appropriate proportions of PbO and $BaCO_3$ (with the moisture contents considered) were added to the precursor powders and the whole batches were calcined at 850 °C and 950–1200 °C for 2 h each with intermediate milling and drying stages. Phase formation results were investigated by X-ray diffraction (XRD,

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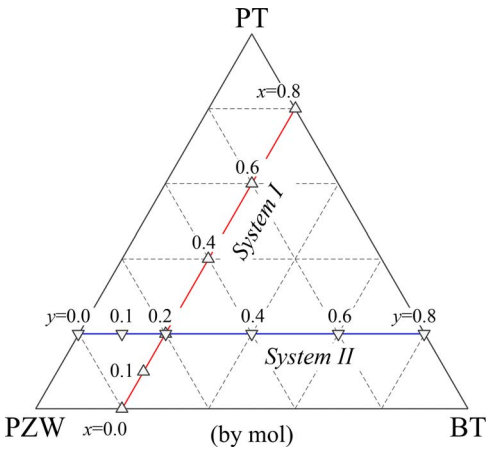

Fig. 1. Selected compositions investigated in the study.

scanning speed = 4°2θ/min, Cu target, monochromator, 30 kV, 30 mA) after each calcination procedure. Two wt.% polyvinyl alcohol was added as a binder into the prepared powders, followed by isostatic pressing (100 MPa) into pellet-type preforms. The powder compacts were then fired at 750–1250 °C for 1 h in a multiple-enclosure inverted-crucible setup [8] to suppress PbO volatilization at high temperatures. Sintered pellets were ground/polished to attain parallel sides, over which gold was sputtered for electrical contacts. Dielectric constant and loss values were measured using an impedance analyzer on cooling, under weak-field (≈1 V_{rms}/mm) low-frequency (1–1000 kHz) conditions. The ceramic samples were fractured, gold-coated, and microstructures were examined using a scanning electron microscope (SEM).

3. Results and discussion

Fig. 2 shows the X-ray diffraction results of the B-site precursor compositions $(0.8\text{-}x)(Zn_{1/2}W_{1/2})O_2\text{-}(0.2+x)TiO_2$, common to both Systems I and II. The pattern of $x = 0.8$ (taken from the TiO_2 chemical) showed only a rutile structure (ICDD No. 21-1276) with a trace amount of anatase (ICDD No. 21-1272). With decreasing values of x (i.e., increasing $(Zn_{1/2}W_{1/2})O_2$ concentration), the intensities of a wolframite structure ($ZnWO_4$, ICDD No. 15-774) increased at the expense of rutile. However, the rutile structure persisted down to $x = 0.0$ of $[(Zn_{1/2}W_{1/2})_{0.8}Ti_{0.2}]O_2$, implying that 20 mol% TiO_2 is beyond the solubility limit of the wolframite structure. It was also observed that reflection angles of the two structures decreased slightly with decreasing x, indicating development of mutual solid solubility (but only to limited extents).

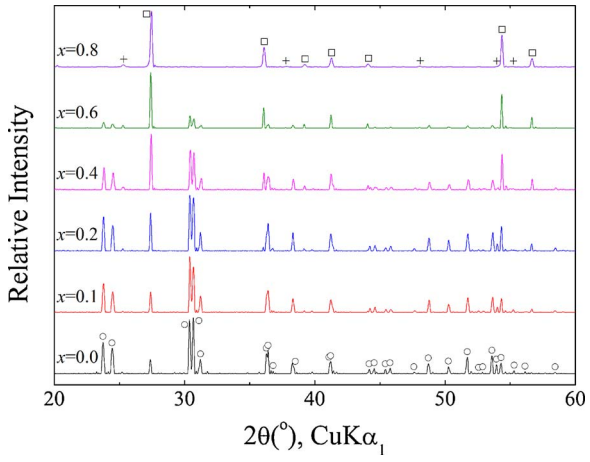

Fig. 2. Developed structures in $(0.8\text{-}x)(Zn_{1/2}W_{1/2})O_2\text{-}(0.2+x)TiO_2$: (○) wolframite, (□) rutile, and (+) anatase.

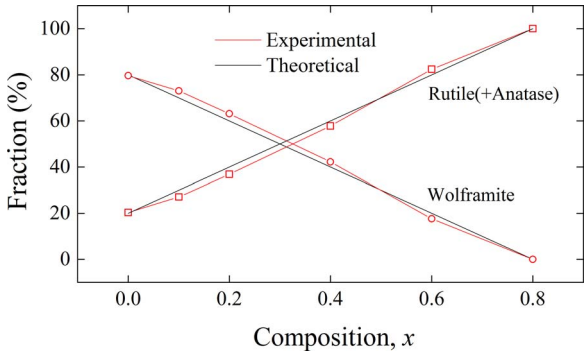

Fig. 3. Fractions of the wolframite and rutile(+anatase) phases with compositional change, along with theoretical values.

The steady shifts in the angular positions can be explained by the gradual replacement of Ti^{4+} by $(Zn_{1/2}W_{1/2})^{4+}$, effective ionic radii [9] of which are 0.0605 and 0.067 nm (weight-averaged value), respectively. Meanwhile, several reflections of anatase (another polymorphic form of TiO_2) were also detected throughout the composition range, though of low intensities. The parasitic anatase phase was only observed in the raw powders of TiO_2 and did not survive when the second components of $(Mg/Zn)(Ta/Nb)_2O_6$ were introduced [10–13]. Therefore, the survival of anatase throughout the entire compositions in the present study seems to be associated with the W component.

Relative fractions of phases present in Fig. 2 were estimated by comparing integrated intensity of the strongest reflections: 2θ≒25.3° (anatase), 27.4° (rutile), and 30.4° (wolframite). The results are presented in Fig. 3, where the values of anatase (as high as 5.5% at $x = 0.8$) were incorporated into rutile. Theoretical phase fractions (assuming no solid solution formation between wolframite and rutile) are also included for comparison. Estimated fractions of rutile(+anatase) were observed to increase quite linearly with increasing x, as discussed above. Besides, the values were quite close to the theoretical ones, indicating that the solid solutions of wolframite and rutile developed only limitedly. The narrow ranges of mutual solubility seem to be resulted from the quite dissimilar nature in their structures.

Structures developed in Systems I and II are compared in Fig. 4(a) and (b). At low to medium values of x and y, several phases of perovskite, $BaWO_4$ (ICDD No. 43-646, BW), as well as two polymorphic forms of Pb_2WO_5 (ICDD Nos. 36-1495 and 37-306, P_2W I and II, respectively) coexisted, except for the absence of BW at $y = 0.0$. It is interesting to note that the P_2W II phase was predominant over P_2W I at $x = 0.0$, whereas P_2W I was prevalent at $y = 0.0$. Nevertheless, the presence of P_2W I and II, along with BW, resulted obviously from the reaction of WO_3 (a decomposed product of the $ZnWO_4$ precursor) with PbO and $BaCO_3$. Hence, the B-site precursor method turned out to be rather ineffective for $Pb(Zn_{1/2}W_{1/2})O_3$, in contrast to other Pb-based complex perovskite compositions [5–7]. Meanwhile, ZnO (ICDD No. 36-1451, another product of the decomposition of $ZnWO_4$) did not form any compound, but remained unreacted instead. Hence, the reflections of ZnO were detected at all compositions of $x,y \leq 0.6$. By comparing the two systems, it was demonstrated that the introduction of Ti (along with additional 20 at.% Ba, System I) and of Ba (with simultaneous substitution of $Zn_{1/2}W_{1/2}$ complex by Ti, System II) steadily promoted the perovskite formation in PZW.

Three compounds in ZnO-TiO_2 have been reported to form: namely in ratios of 2:1 (ICDD Nos. 18-1487, 19-1483, and 30-1493), 1:1 (ICDD Nos. 26-1500 and 39-190), and 2:3 (ICDD No. 38-500). However, none of their profiles matched satisfactorily with those in Fig. 4(a) and (b). Neither any compound formation has been reported in WO_3-TiO_2 [14], nor any polymorphic form of TiO_2 was detected. Hence, all of the TiO_2 component must have reacted with PbO and/or $BaCO_3$ to form perovskite. As a result, the intensity levels of the perovskite structure grew substantially with increasing values of x and y. Besides, reflections of