Synthesis of Binary Complex Perovskite Solid Solution by Application of both Precursor Method and Wet–Dry Combination Method

Yoshiyuki Abe

Graduate School of Science and Technology, Chiba University, Yayoi-Cho, Chiba-Shi 260, Japan

Kazuyuki Kakegawa* & Yoshinori Sasaki

Faculty of Engineering, Chiba University, Yayoi-Cho, Chiba-Shi 260, Japan

Abstract

A binary complex perovskite solid solution, $Sr(Cu,Zn)_{1/2}W_{1/2}O_3$ (SCZW), was synthesized using a precursor of $(Cu,Zn)WO_4$ (CZW) prepared by a combination of wet and dry methods. Compositional fluctuations in the resulting material were investigated. The new method includes three steps. The first step is a preparation of an oxide mixture of CuO and ZnO (CZ) by the decomposition of a coprecipitate of Cu^{2+} and Zn^{2+} (wet process). The second step is a solid-state reaction between CZ and WO_3 (dry process) to form a precursor, CZW. The third step is a solid-state reaction between $SrCO_3$ and CZW to form SCZW. Powder X-ray diffraction analysis revealed that the SCZW was free from the compositional fluctuation which could not be eliminated by application of the precursor method alone.

*Ein binärer Komplex-Perowskit-Mischkristall der Zusammensetzung $Sr(Cu,Zn)_{1/2}W_{1/2}O_3$ (SCZW), wurde aus $(Cu,Zn)WO_4$-Prekursormaterial synthetisiert, welches durch die Kombination einer nassen und einer trockenen Methode gewonnen wurde. Das sich ergebende Material wurde auf Zusammensetzungsschwankungen hin untersucht. Das neue Verfahren besteht aus drei Schritten. Als erstes wird ein Oxidgemisch aus CuO und ZnO (CZ) durch die Zersetzung des Fällungsproduktes von Cu^{2+} und Zn^{2+} (nasser Prozeß) hergestellt. Der zweite Schritt beinhaltet eine Festphasenreaktion zwischen CZ und WO_3 (trockener Prozeß), wobei das Prekursor-*material CZW gebildet wird. Im dritten Schritt wird dann durch eine Festphasenreaktion zwischen $SrCO_3$ und CZW das SCZW-Material gebildet. Wie Pulver-Röntgenbeugungsuntersuchungen ergaben, ist das hergestellte SCZW frei von Zusammensetzungsschwankungen, welche durch die alleinige Anwendung der Prekursor-Methode nicht hätten beseitigt werden können.*

Une solution solide d'un perovskite binaire complexe, $Sr(Cu,Zn)_{1/2}W_{1/2}O_3$ (SCZW) a été synthétisée à partir d'un précurseur de $(Cu,Zn)WO_4$ (CZW), préparé en combinant des méthodes humides et séches. Les fluctuations dans la composition du matériau obtenu ont été étudiées. La nouvelle méthode comprend trois étapes. La première étape est la préparation d'un mélange d'oxides, CuO et ZnO (CZ), par décomposition d'un coprécipité de Cu^{2+} et Zn^{2+} (procédé humide). La deuxième étape est une réaction en phase solide entre CZ et WO_3 (procédé sec) pour former un précurseur, CZW. La troisième étape est une réaction en phase solide entre $SrCO_3$ et CZW pour former SCZW. L'analyse de poudre par diffraction de rayon X a révélé que le SCZW ne présentait pas de fluctuation de composition, ce qui ne pouvait pas être évité en appliquant uniquement une méthode utilisant un précurseur.

1 Introduction

Many Pb-based complex perovskite compounds having

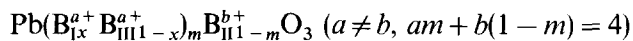$$Pb(B^{a+}_{I\,m} B^{b+}_{II\,1-m})O_3 \quad (a \neq b, \; am + b(1-m) = 4)$$
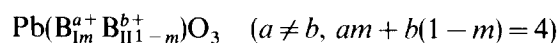
* To whom correspondence should be addressed.

type formula exhibit interesting properties, e.g. the high dielectric constant at the Curie temperature, and the diffuse phase transition between the ferroelectric and paraelectric phases. Difficulties are often encountered in synthesizing these perovskite compounds without the coexistence of pyrochlore phase(s). The second phase pyrochlore is very harmful to the dielectric properties. The columbite (wolframite) precursor method, which was proposed by Shrout and co-workers,[1,2] is effective to avoid the second phase. In this method, a precursor of columbite ($B_I^{a+} B_{II2}^{b+} O_6$) or wolframite ($B_I^{a+} B_{II}^{b+} O_4$) is prepared by a reaction between the constituent oxides before the reaction with PbO. This method is so simple and effective as to have been often used in the preparation of the Pb-based complex perovskite.

This precursor method has been applied not only to such perovskite compounds but also to the solid solutions between them. If

$$(B_{Ix}^{a+} B_{III1-x}^{a+})B_{II2}^{b+}O_6 \quad \text{or} \quad (B_{Ix}^{a+} B_{III1-x}^{a+})B_{II}^{b+}O_4$$
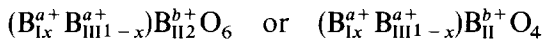
is used for a preparation of

$$Pb(B_{Ix}^{a+} B_{III1-x}^{a+})_m B_{II1-m}^{b+}O_3 \quad (a \neq b, \ am + b(1-m) = 4)$$

as the precursor, a single-phase perovskite solid solution may be obtained. On preparing solid solutions, however, a compositional fluctuation (inhomogeneity of composition) should also be considered. The compositional fluctuation in solid solutions cannot be eliminated easily by the conventional dry method (solid-state reaction of mixed raw powders).[3-6] The precursor solid solution may have the compositional fluctuation by the conventional dry method, that is the fluctuation of value x in

$$(B_{Ix}^{a+} B_{III1-x}^{a+})B_{II2}^{b+}O_6 \quad \text{or} \quad (B_{Ix}^{a+} B_{III1-x}^{a+})B_{II}^{b+}O_4$$
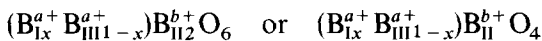
If a precursor solid solution having the compositional fluctuation is used, the obtained perovskite solid solutions may also have the compositional fluctuation. Since the compositional fluctuation affects the electric properties and the crystal structure, it is essential to prepare the solid solutions without the compositional fluctuation.

Kakegawa *et al.*[3] previously reported a method to prepare $Pb(Zr_xTi_{1-x})O_3$ (PZT) having no compositional fluctuation, namely a wet–dry combination method. In PZT, the B-site cations (Zr^{4+} and Ti^{4+}), which have the same valence, are difficult to distribute in B-sites homogeneously. A homogeneous oxide mixture containing Zr^{4+} and Ti^{4+} (ZT) is obtained by a decomposition of a coprecipitate of them (wet process). PZT having no compositional fluctuation is obtained by a solid-state reaction between PbO and ZT (dry process). This
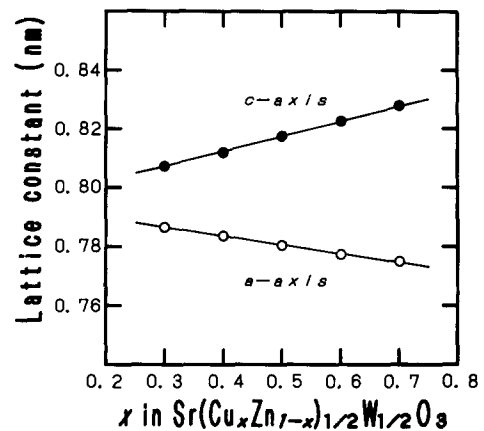

Fig. 1. Relation between lattice constants and composition for $Sr(Cu_xZn_{1-x})_{1/2}W_{1/2}O_3$.

combination method is useful for a preparation of the homogeneous solid solutions. The homogeneous solid solution of the columbite or wolframite precursor can be prepared by the wet–dry combination method. It is expected that use of the precursor solid solution without the compositional fluctuation by the wet–dry combination method leads to the formation of the complex perovskite solid solution without the compositional fluctuation.

If the solid solution has a large dependence of lattice constant on composition, the compositional fluctuation can be easily estimated by a measurement of the widths of powder X-ray diffraction peaks. Unfortunately, a Pb-based solid solution

$$Pb(B_{Ix}^{a+} B_{III1-x}^{a+})_m B_{II1-m}^{b+}O_3$$
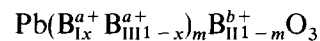
having such a large dependence could not be found. Since an aim of this study is to confirm the effectiveness of this new method,

$$Sr(Cu_xZn_{1-x})_{1/2}W_{1/2}O_3 \quad (SCZW)$$
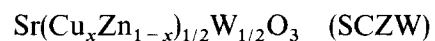
was chosen for this study instead of Pb-based solid solutions. The lattice constants of SCZW vary greatly with the composition, as shown in Fig. 1, and so the degree of compositional fluctuation can be estimated precisely.

In this study, both the precursor method and the wet–dry combination method were applied to $Sr(Cu_xZn_{1-x})_{1/2}W_{1/2}O_3$ solid solution, and its effectiveness on the homogenization of the composition in the complex perovskite solid solution was examined.

2 Experimental

2.1 Sample preparation

The process using both the precursor method and the wet–dry combination method is illustrated in
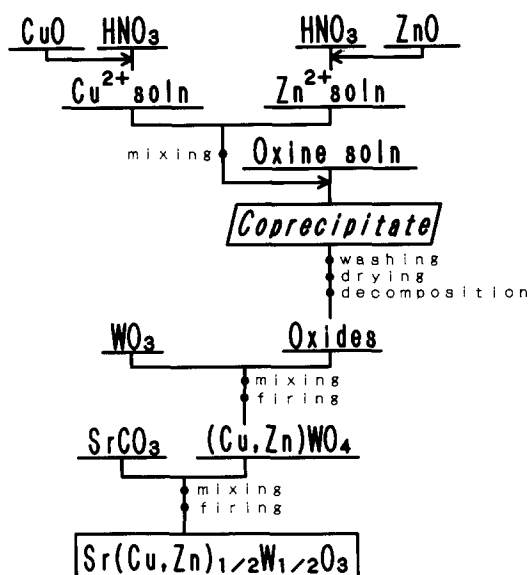
Fig. 2. Process for the preparation of $Sr(Cu,Zn)_{1/2}W_{1/2}O_3$ by an application of both the precursor method and the wet–dry combination method ([S + wdCZW] method).

Fig. 2. Since Cu^{2+} and Zn^{2+} cannot be quantitatively precipitated only by a pH adjustment, the coprecipitation was performed using an organic chelation reagent, 8-hydroxyquinoline (oxine). Powders of CuO and ZnO were dissolved in 2M nitric acid separately. The concentrations of Cu^{2+} and Zn^{2+} were about 0·06M. These solutions were mixed in an appropriate fraction (CZ solution). Oxine was dissolved in 6M aqueous ammonia (0·07M), of which the temperature had been raised to about 60°C because the solubility of oxine is low at room temperature. Then the CZ solution (380 ml) was added into the solution of oxine (1 litre), resulting in a coprecipitate of Cu^{2+} and Zn^{2+}. The amount of oxine used was three times the total amount of Cu^{2+} and Zn^{2+}. The coprecipitate was filtered, washed, dried and brought to decomposition. Since the rate of decomposition of this coprecipitate was slow, a rapid elevation of the temperature caused a predominance of melting. If the coprecipitate melts with little decomposition, it turns immediately into the inhomogeneous state. In order to avoid this melting, the decomposition was performed just below its melting point for several hours, and then the temperature was slowly raised to 700°C. This temperature was kept for 1 h, resulting in copper–zinc oxide powder (CZ). The powders of CZ and WO_3 were mixed thoroughly with an agate mortar and pestle. This mixture was pressed into pellets and fired at 800°C for 1 h. By this process a wolframite precursor solid solution, $(Cu,Zn)WO_4$ (CZW), was obtained.

Pellets of the precursor were ground and mixed

with $SrCO_3$ in stoichiometric proportion in the same way as previously described. The mixture was pressed into pellets and fired at 1200°C for 1 h, resulting in SCZW. This method is herein abbreviated the [S + wdCZW] method, where the notation w means 'wet' and d 'dry'.

For the purpose of comparison, SCZW were prepared by the following two methods with the precursor method only. Powder of CZW was prepared by the solid-state reaction among the constituent oxide powders (conventional dry process). This CZW and $SrCO_3$ were mixed thoroughly and fired to form SCZW. This method is abbreviated the [S + dCZW] method. Another method is as follows. Strontium carbonate, $CuWO_4$ (CW), and $ZnWO_4$ (ZW) were mixed thoroughly and fired to form SCZW. This method is abbreviated the [S + CW + ZW] method. The firing conditions were the same as those in the [S + wdCZW] method.

2.2 X-Ray diffraction (XRD)

Powder X-ray diffraction measurements were performed using a Cu target and a Ni filter. For the qualitative measurement, a divergence slit of 1°, a scattering slit of 1° and a receiving slit of 0·3 mm were used. For the measurement of peak widths and diffraction angles, a receiving slit of 0·15 mm was used. Lattice constants were measured from 004 and 400 diffraction peaks of tetragonal SCZW using Si powder (99·99%) as an internal standard.

3 Results and Discussion

3.1 Determination of compositional fluctuation

The width of the XRD peak includes three contributions, e.g. the broadening due to the apparatus, the doublet of wavelength and the net broadening. In the XRD peak profiles, being assumed to obey Cauchy-type curves, each observed peak was separated into two peaks originating from $K\alpha_1$ and $K\alpha_2$ lines of the Cu target by a curve-fitting procedure. By this separation widths at half maximum intensity (WHI) for an X-ray of single wavelength of $K\alpha_1$ were obtained. The WHIs of Si were determined similarly, and they can be seen as widths establishing the resolving power of the apparatus. These values were plotted against 2θ (θ: Bragg angle) in order to obtain the resolution width at any angle. The resolution width at the diffraction angle of the sample was taken from the WHI of the sample, resulting in net broadening, β.
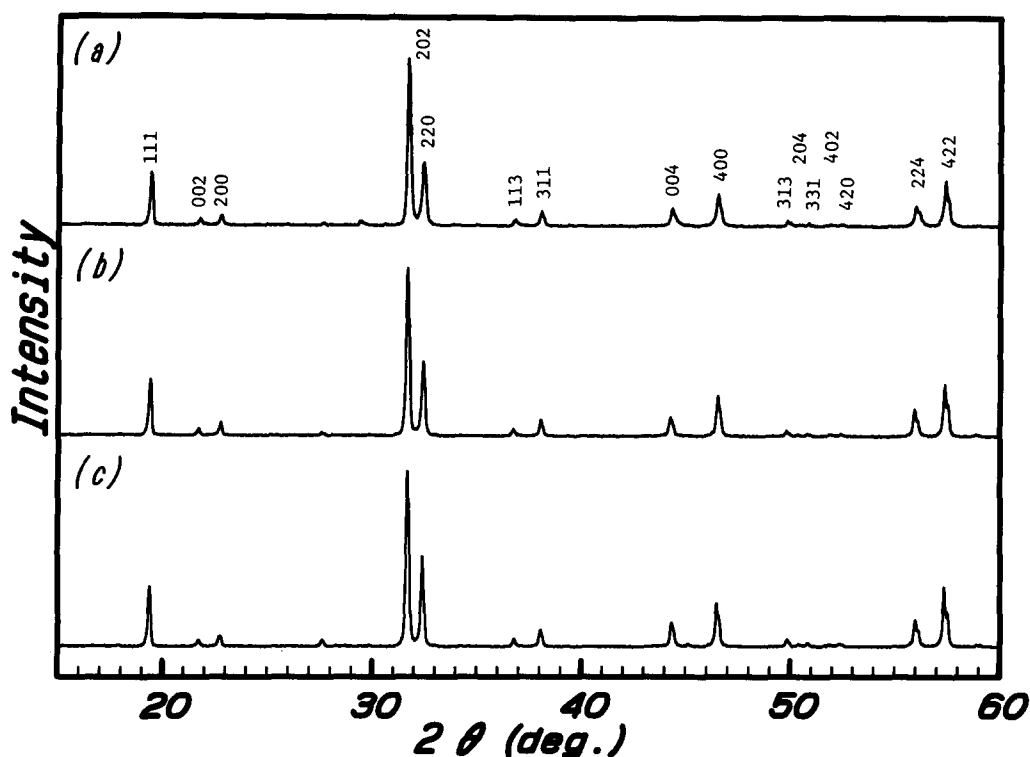
If the lattice spacing varies with composition, the

Fig. 3. Powder X-ray diffraction patterns (CuK_α) for Sr(Cu$_{0.5}$Zn$_{0.5}$)$_{1/2}$W$_{1/2}$O$_3$ prepared by (a) the [S+CW+ZW] method, (b) the [S+dCZW] method and (c) the [S+wdCZW] method (firing conditions: 800°C for 1 h for the precursors and 1200°C for 1 h for SCZW).

lattice spacing fluctuates with the compositional fluctuation. Thus, the degree of the compositional fluctuation can be estimated from the value of the fluctuation of lattice spacing, $\Delta d/d$.[3-6] The fluctuation of the lattice spacings can be determined from the value of β. The plots of $\beta \cos \theta$ versus $\sin \theta$[7] for a diffraction from a certain plane and its higher order diffractions can be theoretically fitted on a straight line. The slope corresponds to $\Delta d/d$ of these lattice planes.

Figure 1 shows the relation between the lattice constants and composition for

$$Sr(Cu_xZn_{1-x})_{1/2}W_{1/2}O_3$$
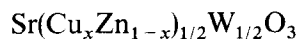
which was derived from the samples by the ordinary dry processing from a mixture of SrCO$_3$, ZnO, CuO and WO$_3$. SCZW has a tetragonal symmetry and a superstructure due to 1:1 ordering of B-site cations in the examined composition range ($x = 0.3$–0.7). Since the lengths of both a and c axes vary with composition, as shown in Fig. 1, the degree of compositional fluctuation can be estimated by the widths of either 00l or hk0 diffractions. However, there were few 00l diffraction peaks whose shape could be measured precisely compared with hk0 diffraction peaks. So hk0 diffractions were used to estimate the compositional fluctuation.

3.2 Compositional fluctuation in samples

The powder XRD patterns for

$$Sr(Cu_{0.5}Zn_{0.5})_{1/2}W_{1/2}O_3$$
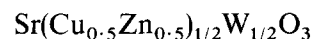
prepared by the three different methods are shown in Fig. 3. In order to determine the fluctuation of the lattice spacings from the observed peaks, the plots of $\beta \cos \theta$ versus $\sin \theta$ already mentioned were carried out.

Figure 4 shows the plots of $\beta \cos \theta$ versus $\sin \theta$ for the hk0 diffractions of Sr(Cu$_{0.5}$Zn$_{0.5}$)$_{1/2}$W$_{1/2}$O$_3$. The
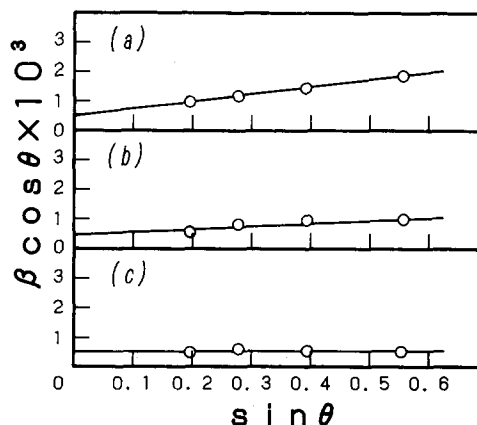
Fig. 4. Plots of $\beta \cos \theta$ versus $\sin \theta$ for Sr(Cu$_{0.5}$Zn$_{0.5}$)$_{1/2}$W$_{1/2}$O$_3$ prepared by (a) the [S+CW+ZW] method, (b) the [S+dCZW] method and (c) the [S+wdCZW] method (firing conditions: 800°C for 1 h for the precursors and 1200°C for 1 h for SCZW).

plots for SCZW prepared by the [S+CW+ZW] method are shown in Fig. 4(a). This set of the plots had a large slope, indicating that SCZW had the large compositional fluctuation. Figure 4(b) shows the plots for SCZW prepared by the [S+dCZW] method. The slope of this set of the plots was smaller than that in Fig. 4(a). This is due to the diffusion of Cu^{2+} and Zn^{2+} during the firing of a mixture of CuO, ZnO and WO_3. However, the small slope indicates that Cu^{2+} and Zn^{2+} could not satisfactorily diffuse during the formation of CZW and SCZW. The results of Fig. 4(a) and (b) revealed a difficulty in preparing SCZW which has no compositional fluctuation by the use of the conventional dry method only. On the other hand, it can be seen from Fig. 4(c) that the plots for SCZW prepared by the [S+wdCZW] method was almost horizontal. So this SCZW had almost no compositional fluctuation. Thus, the use of the precursor CZW prepared by the wet–dry combination method is effective in the preparation of SCZW having no compositional fluctuation.

4 Conclusions

An application of both the precursor method and the wet–dry combination method was effective in the preparation of $Sr(Cu,Zn)_{1/2}W_{1/2}O_3$ having no

compositional fluctuation. This method may also be effective for the preparation of Pb-based binary complex perovskite solid solutions of the type

$$Pb(B^{a+}_{Ix}B^{a+}_{III1-x})_mB^{b+}_{III1-m}O_3 \ (a \neq b, am + b(1 - m) = 4)$$
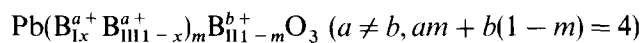
without coexistence of the pyrochlore(s) and without the compositional fluctuation in the perovskite phase.

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