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Preparation of Cubic Perovskites $A(B_{2/5}W_{3/5})O_3$ (A=Ba or Sr, B=Na or Li)

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Pure cubic perovskites $Ba(Na_{2/5}W_{3/5})O_3$, $Sr(Na_{2/5}W_{3/5})O_3$, and $Sr(Li_{2/5}W_{3/5})O_3$ were prepared by solid-state reaction at 600° to 650°C in air, by starting with oxides or carbonates of the various elements. The cubic forms have an ordered arrangement of the B cations in the ABO_3 structure, and the lattice constants are $a=0.8324$ nm [$Ba(Na_{2/5}W_{3/5})O_3$], 0.8136 nm [$Sr(Na_{2/5}W_{3/5})O_3$], and 0.7958 nm [$Sr(Li_{2/5}W_{3/5})O_3$].

OF ALL the ABO_3 phases, the compounds of the perovskite family are the most numerous, the most widely studied, and the most important. Matsuo *et al.*[1,2] first prepared the complex cubic perovskites $Sr(Na_{2/5}W_{3/5})O_3$ and $Sr(Li_{2/5}W_{3/5})O_3$. The tan δ and the dielectric constant of the $Sr(Na_{2/5}W_{3/5})O_3$ ceramics were 0.008 and 260 at −100° to +200°C, and those of the $Sr(Li_{2/5}W_{3/5})O_3$ ceramics 0.0005 and 100 at −100° to +350°C, respectively. These properties may make the $Sr(Na_{2/5}W_{3/5})O_3$ and $Sr(Li_{2/5}W_{3/5})O_3$ ceramics attractive candidates for dielectric applications. No other detailed investigation of new cubic perovskites $A(B_{2/5}W_{3/5})O_3$ (A=Ba or Sr, B=Na or Li, abbreviated ABW) has been reported.

There are several uncertainties regarding these perovskites ABW, including the preparation methods as well as the question of order or disorder among B cations in the ABO_3 structure. Several of these points are discussed in this paper.

EXPERIMENTAL PROCEDURE

The starting materials were reagent-grade $BaCO_3$, $SrCO_3$, Na_2CO_3, Li_2CO_3, and WO_3.* Mixtures of the starting materials to produce stoichiometric $Ba(Na_{2/5}W_{3/5})O_3$ (BNW), $Ba(Li_{2/5}W_{3/5})O_3$ (BLW), $Sr(Na_{2/5}W_{3/5})O_3$ (SNW), and $Sr(Li_{2/5}W_{3/5})O_3$ (SLW) were wet-mixed in a plastic ball mill with ethyl alcohol for 48 h. The mixtures were dried completely in an oven at 105°C for 24 h. After drying, 30 g of the milled powders were heated in air at 500° to 1000°C for 1 to 500 h in an alumina crucible. There was no reaction with the crucible.

A powder X-ray diffractometer using Cu$K\alpha$ radiation at a scanning rate of $1°2\theta$/min and an X-ray fluorescence spectrometer were used for phase identification and for chemical analysis. The results are summarized in Tables I to III.

RESULTS AND DISCUSSION

From the BNW, SNW, and SLW mixtures, cubic forms were obtained above 600°C, but no hexagonal forms were observed in the samples heated at 600° to 1000°C, as shown in Table I. From the BLW mixture, hexagonal BLW ($a=0.576$ nm, $c=2.375$ nm) was obtained above 600°C, but no cubic form was observed in the samples heated at 600° to 1000°C. The structural chemistry of the ABO_3 perovskite type can be described in terms of close-packed AO_3 layers with B cations in octahedral interstices. If the layers are cubic close-packed, the octahedra form a three-dimensional array with corner sharing to give the ideal perovskite structure. Deviations from the ideal structure may be understood in terms of a tolerance factor defined as

$$t=(r_A+r_O)/1.414(r_B+r_O)$$

where r is the ionic radius.[3,4] For the perfect close packing, t has a value of 1.0, whereas for $t>1.0$, structures involving either mixed cubic and hexagonal or pure hexagonal close packing of the AO_3 layers are observed. Tolerance factors of our samples are as follows: BLW, 0.94; BNW, 0.89; SLW, 0.86; and SNW, 0.82. Therefore, BLW has a higher probability of adopting the hexagonal form than do the others. The failure to form hexagonal BNW and SNW is due to the fact that Na is much larger than Li and the absence of hexagonal SLW can be attributed to the smaller size of Sr compared to Ba.

In all cases, the intermediate products are $BaWO_4$ and $SrWO_4$. X-ray peak intensities of perovskite ABW increased as those of $BaWO_4$ or $SrWO_4$ decreased. ABW seems to be produced by the following reaction:

$$5ACO_3+B_2CO_3+3WO_3=$$

$$3AWO_4+2ACO_3+B_2CO_3+3CO_2=$$

$$5A(B_{2/5}W_{3/5})O_3+6CO_2$$

where A=Ba or Sr, B=Na or Li.

When the mixtures of BNW, SNW, or SLW were fired in the crucible at 600° to 650°C, the amount of cubic form increased with increasing reaction time. Very pure cubic BNW was obtained at 600°C for 400 h, SNW at 650°C for 215 h, and SLW at 600°C for 500 h, without other phases. The resulting powders were not sintered at 600° to 650°C. There was no appreciable difference between the surface and the interior regions of the samples as shown in Fig. 1. However, above 700°C, mixtures began to sinter and a difference in the phases between the surface and the interior of the sintered sample was observed (Fig. 1). Perovskite ABW was richer in the surface than in the interior. Although the surface (mainly ABW phases) of the sintered sample increased gradually with increased heating time or temperature, an interior multiphase region persisted, when starting mixtures were heated above 700°C. When a small amount of starting mixtures, for example 1 g, was heated above 700°C in the crucible, the sample proved to be more homogeneous, but the cubic forms were still accompanied with a small amount of $BaWO_4$ or $SrWO_4$. Matsuo *et al.*[1,2] reported that they prepared sintered ceramics (20 mm by 3 mm, disk), which consisted of cubic SNW or SLW, above 800°C in air. The reason that they got cubic SNW or SLW above 800°C might be due to the small thickness of their disks. The difference in the phases between the surface and the interior of the sintered samples seems to be due to the migration of Na or Li, but we did not analyze the chemical composition of Na or Li in each part. From the viewpoint of mass production and phase purity of cubic ABW, it is preferable to react at 600° to 650°C to avoid sintering and the associated phase inhomogeneities.

Table II shows the chemical compositions (weight percent) of the pure cubic ABW (Nos. 10, 18, and 25 in Table I). The chemical formulas of the cubic forms calculated from the chemical compositions are almost the same as the theoretical BNW, SNW, or SLW.

In order to examine the distribution of B and W cations in ABW, we tried to compare observed intensities of reflections with those calculated on the basis of the assumption that cubic ABW has a perovskite-type superstructure. By trial and error the results of Table III were obtained, and observed intensities were in good agreement with those calculated on the basis of $A(B_1B_2)O_3$, where ⅚ of the W ions are in the B_2 sites and ⅙ of the W ions are randomly distributed with the Na or Li ions in the B_1 sites.

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Table I. Phases Produced

No.	Reaction conditions Temp (°C)	 Time (h)	Phases*
		BLW	
1	500	24	$BaWO_4$, $BaCO_3$
2	600	1	$BaWO_4$, H-BLW, $BaCO_3$
3	600	120	H-BLW, $BaWO_4$, $BaCO_3$
4	700	5	H-BLW, $BaWO_4$, $BaCO_3$
5	900	5	H-BLW, $BaWO_4$, $BaCO_3$
6	1000	5	H-BLW, $BaWO_4$
		BNW	
7	500	24	$BaWO_4$, $BaCO_3$
8	600	24	$BaWO_4$, C-BNW, $BaCO_3$
9	600	96	C-BNW, $BaWO_4$
10	600	400	C-BNW
11	700	90	C-BNW, $BaWO_4$, $BaCO_3$
12	900	5	$BaWO_4$, C-BNW, $BaCO_3$
13	1000	5	$BaWO_4$, C-BNW, $BaCO_3$
		SNW	
14	500	24	$SrWO_4$, $SrCO_3$
15	600	24	$SrWO_4$, $SrCO_3$
16	600	350	C-SNW, $SrWO_4$
17	650	24	$SrWO_4$, $SrCO_3$
18	650	215	C-SNW
19	700	90	C-SNW, $SrWO_4$, $SrCO_3$
20	900	5	$SrWO_4$, C-SNW
21	1000	5	$SrWO_4$, C-SNW, Sr_2WO_5
		SLW	
22	500	24	$SrWO_4$, $SrCO_3$
23	600	24	$SrWO_4$, C-SLW, $SrCO_3$
24	600	150	C-SLW, $SrWO_4$, $SrCO_3$
25	600	500	C-SLW
26	700	90	C-SLW, $SrWO_4$, $SrCO_3$
27	900	5	C-SLW, $SrWO_4$, $SrCO_3$
28	1000	5	C-SLW, $SrWO_4$

*H: Hexagonal form. C: Cubic form.

Table II. Chemical Compositions of (1) Cubic BNW, (2) Cubic SNW, and (3) Cubic SLW

	Composition (wt%) BaO	 SrO	 Na_2O	 Li_2O	 WO_3	Total (wt%)
(1)	50.56		3.96		45.47	99.99
(2)		41.19	4.72		54.10	100.01
(3)		41.36		2.42	56.12	99.90

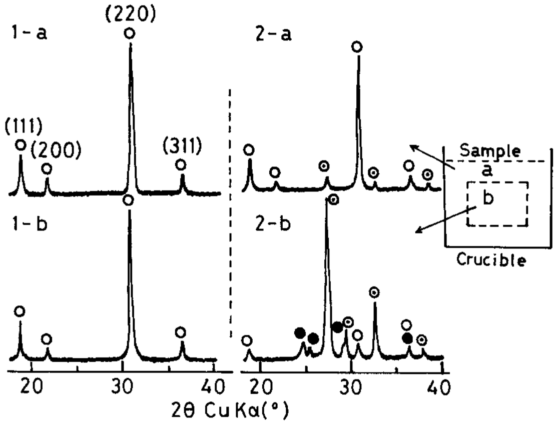

Fig. 1. X-ray diffraction patterns of samples obtained by heating the mixture of SNW at (*1*) 650°C for 215 h and (*2*) 800°C for 24 h: (*a*) surface, (*b*) interior, (○) cubic SNW, (⊙) $SrWO_4$, (●) $SrCO_3$.

Table III. X-ray Diffraction Data for Cubic BNW (*a* =0.8324 nm), SNW (*a* =0.8136 nm), and SLW (*a* =0.7958 nm)

hkl	BNW *d*(obsd)	 *d*(calcd)	 *I*(obsd)	 *I*(calcd)	SNW *d*(obsd)	 *d*(calcd)	 *I*(obsd)	 *I*(calcd)	SLW *d*(obsd)	 *d*(calcd)	 *I*(obsd)	 *I*(calcd)
111	0.480	0.480	16	16	0.469	0.470	33	25	0.460	0.460	37	34
200					0.407	0.407	7	8	0.398	0.398	6	6
220	0.294	0.294	100	100	0.288	0.288	100	100	0.281	0.281	100	100
311	0.2510	0.2510	8	9	0.2453	0.2453	14	14	0.2399	0.2400	16	19
222	0.2401	0.2403	3	3								
400	0.2082	0.2081	27	30	0.2033	0.2034	27	32	0.1989	0.1990	30	33
331	0.1910	0.1910	3	4	0.1866	0.1867	4	6	0.1826	0.1826	6	9
420									0.1780	0.1780	2	3
422	0.1699	0.1699	47	40	0.1661	0.1661	42	39	0.1624	0.1624	39	39
333 511	0.1602	0.1602	4	3	0.1566	0.1566	5	5				

We found only the cubic ordered $A[(B_{2/5}W_{1/10})(W_{1/2})]O_3$, and no other disordered or ordered cubic ABW was observed in the samples heated at temperatures ranging from 600° to 1000°C, even though the heated cubic forms were quenched rapidly or slowly cooled to room temperature.

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