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PREPARATION AND LATTICE DISTORTION OF PEROVSKITE-TYPE COMPOUNDS $A^{2+}R^{4+}O_3$ (A = Ba,Sr R = Ce,Pr,Tb)

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Preparation and lattice distortion of perovskite-type compounds $A^{2+}R^{4+}O_3$ were studied. All of them belong to the same lattice symmetry of orthorhombic Pbnm,that is,they have monoclinic perovskite cells. The magnitude of the monoclinic distortion increases mainly along the diagonal axis of the b-plane of the perovskite cell with the decrease of "tolerance factor".

The crystal structures and physical properties of many perovskite-type oxides have been studied. The compounds in the title except $SrPrO_3$ have been also studied, and their lattice constants were determined as a = 4.354 Å(1) or 8.708 Å(2) for $BaPrO_3$, a = 4.28₅ Å for $BaTbO_3$(3),a = 4.18 Å for $SrTbO_3$(3),and a = 4.397 Å for $BaCeO_3$(4). These values were calculated assuming that these compounds have cubic or pseudo-cubic symmetry. Only $SrCeO_3$ was reported to be orthorhombic(4) with a = 5.986,b = 8.531,and c = 6.125 Å.

We have been interested in these compounds from the following points of view: what the real symmetry of these compounds is,and why the quadrivalent state of R-ions (except Ce) is stable in these compounds while there are few oxides which have stable R^{4+} ions ? In this report,the preparation of these compounds by way of the solid state reactions between A-carbonates(A = Ba,Sr) and CeO_2 or R-oxides(R = Pr,Tb) and their lattice distortions are described.

Both CeO_2 and $ACeO_3$ were stable at any conditions used in this work,but other compounds were not necessarily stable. Since the composition of R-oxides varies with temperatures and oxygen pressures,the initial composition of R-oxides was determined by means of TGA method. They had a stoichiometric composition of $R_2O_{3.000\pm0.002}$ in a hydrogen atmosphere at 800°C. Appropriate mixtures of A-carbonates and R-oxides were heated at 1150 - 1300°C for 10 - 12 hr in 1 atm oxygen,and were reground and then reheated at 1000 - 1280°C for 12 - 16 hr in 1 atm oxygen. In the case of $APrO_3$,an additional treatment of annealing at 750°C or 1000°C in 1 atm oxygen was carried out, because $APrO_3$ began to decompose to the mixture of AO and Pr-oxides containing Pr^{3+} ion above these temperatures. Since $ATbO_3$ also tend to decompose to AO and Tb-oxides above 1300°C in air,the heating and annealing conditions given in Table 2 were chosen on the basis of TGA data(5). No compounds were prepared in the case of A = Ca.

$ACeO_3$ were white, $APrO_3$ were brown-yellow and $ATbO_3$ were bright yellow. The chemical formula of these compounds was confirmed to be $AR^{4+}O_{3.000\pm0.002}$ from the result that they were reduced completely to $R^{3+}{}_2O_3$ and AO in hydrogen. Magnetic analyses also showed that R-ions were quadrivalent in these compounds.

The lattice constants were measured for the stoichiometric compounds at a room temperature as indicated in Table 2. These perovskites were not cubic, because some superstructure lines and characteristic splitting in many diffraction lines could be observed. These splittings were apparent for $SrRO_3$ as seen in Fig. 1. These splittings, i.e., the triplet of (040), (224) and (400) with the intensity ratio 1 : 4 : 1, the doublet of (044) and (404) of the same intensity, and the doublet of (440) and (008) with the intensity ratio 2 : 1, indicate that $SrRO_3$ has the orthorhombic symmetry of the space group Pbnm. Although the splitting for $BaRO_3$ was insufficient in the low angle region of 2θ, it was large enough in the high-angle region as seen in the X-ray

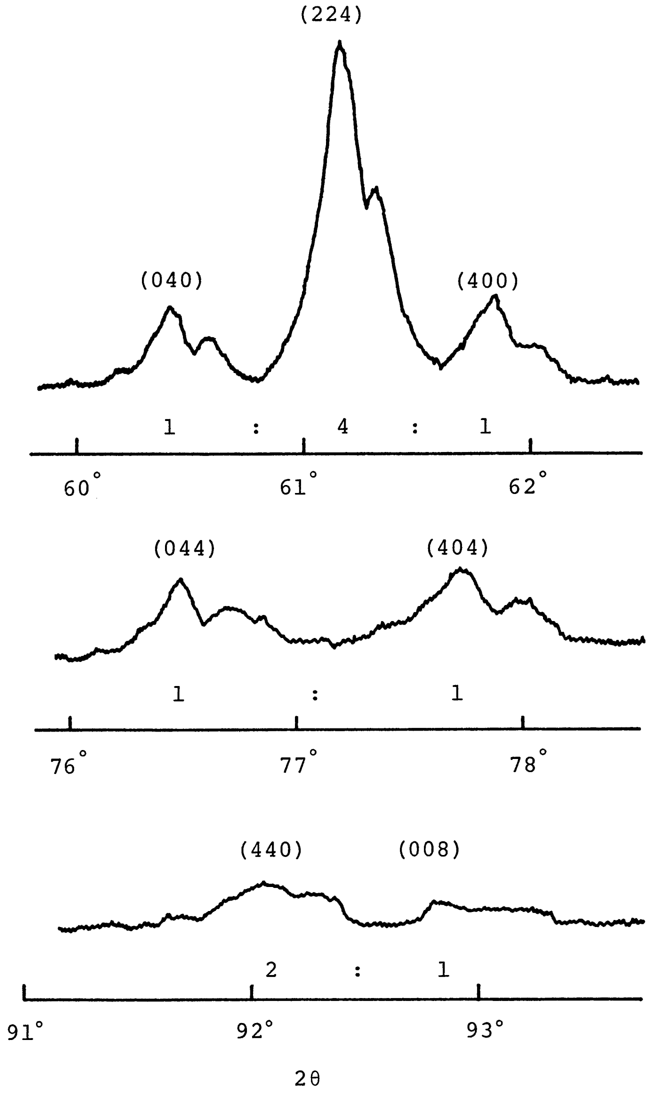

Fig. 1

Typical diffraction profiles of multiplets for $SrPrO_3$ $SrCeO_3$ and $SrTbO_3$ showed similar profiles.
These splittings indicate that these compounds have a monoclinic perovskite cell.

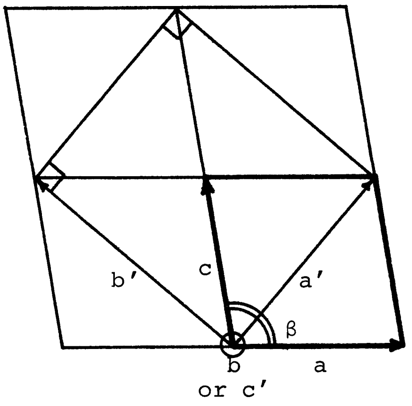

Fig.2

Orthorhombic cell and monoclinic perovskite cell

monoclinic cell $\left\{ \begin{array}{l} a = c > b \\ \beta > 90^\circ \end{array} \right.$

orthorhombic cell $\left\{ \begin{array}{l} a' = a\sqrt{2(1-\cos\beta)} \\ b' = a\sqrt{2(1+\cos\beta)} \\ c' = 2b \end{array} \right.$

Table 2 Crystal chemical data of $A^{2+}R^{4+}O_3$ perovskites

Compound	t-factor	Lattice constants(Å)	Perovskite cell dimensions	Preparation conditions
$BaCeO_3$*	0.916	a' = 6.215 b' = 6.233 c' = 8.774	a = c = 4.400 Å b = 4.387 Å β = 90°11'	heating:1350°C,12 hr,in air reheating:1400°C,12 hr,in air
$BaPrO_3$*	0.921	a' = 6.181 b' = 6.210 c' = 8.728	a = c = 4.381 b = 4.364 β = 90° 16'	heating:1150°C,12 hr,in O_2 reheating:1280°C,12 hr,in O_2 annealing:1000°C,43 hr,in O_2
$BaTbO_3$*	0.954	a' = 6.053 b' = 6.068 c' = 8.550	a = c = 4.286 b = 4.275 β = 90° 09'	heating:1300°C,10 hr,in O_2 reheating:1000°C,16 hr,in O_2
$SrCeO_3$**	0.855	a' = 6.003 b' = 6.145 c' = 8.576	a = c = 4.295 b = 4.288 β = 91°20'	heating:1200°C,12 hr,in air reheating:1300°C,12hr,in air
$SrPrO_3$**	0.859	a' = 5.992 b' = 6.120 c' = 8.554	a = c = 4.280 b = 4.277 β = 91° 13'	heating:1300°C,10 hr,in O_2 reheating:1000°C,16 hr,in O_2 annealing:750°C,40 hr,in O_2
$SrTbO_3$**	0.890	a' = 5.879 b' = 5.921 c' = 8.362	a = c = 4.187 b = 4.181 β = 90° 49'	heating:1300°C,10 hr,in O_2 reheating:1000°C,16 hr,in O_2

* accuracy ± 0.001 Å and ± 1'

** accuracy ± 0.002 Å and ± 1'

Table 1 X-ray powder diffraction data for $BaPrO_3$

h k l	$d_{calc.}$	$d_{obs.}$	$(I/I_0)_{obs.}$
1 1 0	4.381	4.37	2
0 0 2	4.364		
0 2 0	3.106	3.092	100
1 1 2	3.092		
2 0 0	3.091		
1 2 1	2.645	2.632	2
2 1 1	2.638		
0 1 3	2.635		
1 0 3	2.632		
0 2 2	2.530	2.520	1
2 0 2	2.522		
2 2 0	2.191	2.190	35
0 0 4	2.182	2.182	18
2 2 1	2.125	2.122	1
0 2 3	2.123		
2 0 3	2.118		
1 3 0	1.963	1.954	1
2 2 2	1.958		
3 1 0	1.956		
1 1 4	1.953		
1 3 1	1.915	1.906	1
3 1 1	1.908		
1 3 2	1.790	1.790	20
0 2 4	1.785	1.785	50
3 1 2	1.785		
2 0 4	1.783		
0 4 0	1.553	1.553	5
2 2 4	1.546	1.546	20
4 0 0	1.545		
2 4 0	1.388	1.385	15
3 3 2	1.385		
4 2 0	1.384		
1 1 6	1.381	1.381	15
0 4 4	1.265	1.265	5
4 0 4	1.261	1.261	5
1 5 2	1.173	1.173	5
2 4 4	1.171	1.171	10
1 3 6	1.169	1.168	20
4 2 4	1.168		
5 1 2	1.168		
3 1 6	1.167		
4 4 0	1.095	1.095	4
0 0 8	1.091	1.091	2

powder diffraction data for $BaPrO_3$(Table 1). The X-ray data for $BaCeO_3$ and $BaTbO_3$ were similar to those for $BaPrO_3$. These splittings which were commonly observed in all ARO_3 indicate that ARO_3 has the same lattice symmetry of Pbnm. This symmetry is common among many ABO_3type perovskites(6),$CaTiO_3$,$CdSnO_3$,$BaPbO_3$,$SrZrO_3$,etc. ARO_3(except $SrCeO_3$ and $SrPrO_3$) were classified in the cubic or pseudo-cubic perovskites by Roth(4),but the results obtained in this work indicate that the cubic region is far narrower and the orthorhombic region is far wider than Roth's result in $A^{2+}B^{4+}O_3$ perovskites. The lattice constants of ARO_3 determined in this work are shown in Table 2.

In many perovskite-type compounds,there are several types of distortion from the cubic cell;tetragonal,rhombohedral,monoclinic and triclinic. The former three distortions are connected with three possible deformations of the ideal perovskite cell along the fourfold,threefold and twofold axes,respectively(7). All compounds studied in this work have monoclinic perovskite cells as shown in Fig. 2. Their cell dimensions given in Table 2 indicate that these perovskites belong to the same type of distortion of monoclinic,$a = c > b$ and $\beta > 90$.

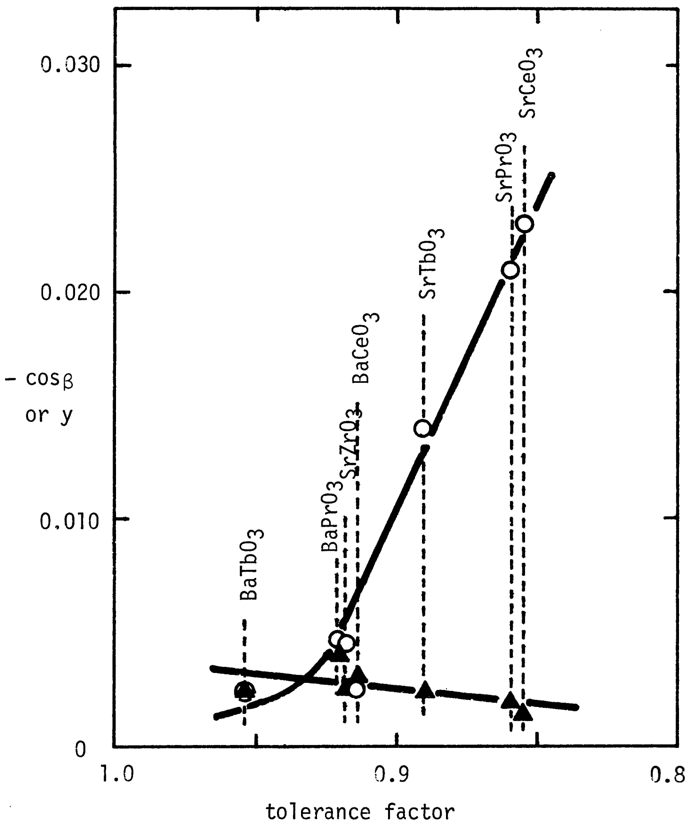

Fig. 3

Lattice distortion of perovskite $A^{2+}R^{4+}O_3$

○ : -cos β

▲ : y = 1 - b/a·sin β

The values for $SrZrO_3$ were calculated from the data given by Roth$^{(4)}$.

The magnitudes of distortion are represented by two parameters of -cosβ and $y = 1 - b/a \cdot \sin\beta$ for the monoclinic perovskites$^{(7)}$. The former is the parameter of angular distortion and the latter is the parameter of axial distortion. Fig. 3 shows the relationship between these parameters and "tolerance factor"$^{(4)}$, $t = (r_A + r_O)/\sqrt{2}(r_R + r_O)$, where r_A, r_R and r_O are ionic radii of A-ion, R-ion and O-ion, respectively. The values of -cosβ increase with the decrease of t-factor, whereas y values are nearly constant or rather decrease gradually. This indicates that the distortion increases in the angles of perovskite cell but does not increase in their edge lengths with the decrease of t-factor. In other words, the deformation of ideal perovskite cell occurs not along the cell axes but along the diagonal axes in the b-plane of perovskite cell as shown in Fig. 2.

This type of distortion (monoclinic, $a = c > b$ and $\beta > 90°$) in ABO_3 perovskites is closely related to the triclinic distortion found in ordered perovskites $A_2B'B''O_6$$^{(8)}$ and $A_3B'B''_2O_9$$^{(9)}$.

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