Formation Conditions for a Pyrochlore Structure with Two Different Cations at the A Site

NAOKI WAKIYA, ATSUSHI SAIKI, NOBUO KIEDA,
KAZUO SHINOZAKI, AND NOBUYASU MIZUTANI[1]

*Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute
of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan*

Upon consideration of the crystallographic features of pyrochlore-type compounds, the following two new conditions are proposed for the formation of a mixed cation type at the A site: $\Delta d\,(A^{2+}-O_I) = d\,(A^{2+}-O_I) - (r_A + r_O) > 0$ and $\Delta d\,(A^{4+}-O_{II}) = d\,(A^{4+}-O_{II}) - (r_A + r_O) < 0$. Applying these two conditions, three new compounds $(Sr, Ce)_2Sn_2O_7$, $(Cd,Ce)_2Sn_2O_7$, and $(Ca,Ce)_2Hf_2O_7$, are synthesized. However, they are not phase-pure. Although these conditions are prerequisites, they will serve as a guide for designing new compounds of this structure. © 1992 Academic Press, Inc.

Introduction

In a previous paper (*1*), a new compound, $Ca_{2x}Ce_{2-2x}Sn_2O_7(0.35 \leq x \leq 0.43)$, with a cubic pyrochlore structure was reported. This compound can be written as $(Ca,Ce)_2Sn_2O_7$ for short and can be classified as a mixed cation type at the A site. Such pyrochlore-type compounds were first prepared by McCauley *et al.* (*2*). They fixed Ti^{4+} as the B site ion and tried several combinations of di- and tetravalent cations as the A site ion.

Consequently they reported three new compounds, i.e., $CdZrTi_2O_7$, $CaCeTi_2O_7$, and $CdCeTi_2O_7$. $CaUTi_2O_7$ was also reported by Dickson *et al.* (*3*). In addition to synthesis, McCauley *et al.* reported two formation conditions. One condition is related to the average ionic radius of A^{2+} and A^{4+} ions. For binary titanate pyro-

chlore-type compounds, it is reported that Lu is the smallest cation and Sm is the largest cation among the ions which are able to occupy the A site. Thus, there exists a size range. According to McCauley, none of the combinations whose average ionic radius falls out of this range yield pyrochlore-type compounds. The other condition is that the size difference between A^{2+} and A^{4+} ions should be less than 0.23 Å. However, this latter condition was introduced not from the theoretical but from the experimental point of view. Therefore the geometrical or crystallographic meaning of the latter condition has not been clarified yet. Besides, this condition was derived only from the result of titanate pyrochlores. Presently a more general formation condition from the viewpoint of crystallography will be proposed and supported by the synthesis of new compounds according to the estimation in this report.

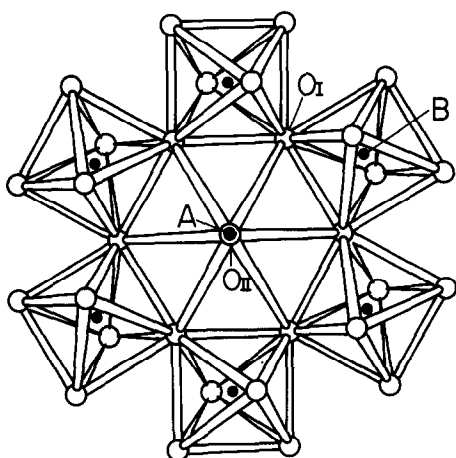[1] To whom correspondence should be addressed.

2. Formation Conditions for a Pyrochlore Structure of the $(A^{2+}, A^{4+})_2 B^{4+} 2O_7$ Type

The general formula of the pyrochlore structure can be written as $A_2B_2O_{16}O_{II}$. The pyrochlore structure was first determined by Gaertner (5). According to Subramanian et al. (6), all atoms occupy special positions in the space group $Fd3m$ (No. 227, origin at the B site); A : 16d, B : 16c, O_I : 48f, and O_{II} : 8b. Symmetry fixes the coordinates of all the ions except for those in 48f. This position has one unknown coordinate, X. Varying the X coordinate changes the shape of the A and B site polyhedra.

The description of this structure was made by Knop et al. (7). The structure is considered a 3D network of corner-shared BO_{16} octahedra. The A cation has eightfold coordination ($6O_I$ ions (48f) arising from the BO_{16} octahedra and $2O_{II}$ atoms (8b)). The projection of a part of the pyrochlore structure along the threefold axis given by Knop et al. is shown in Fig. 1. The centers of the hexagons contain the overlapping projection of one A cation and $2O_{II}$(8b) anions. As shown in Fig. 1, each A cation is located at

the center of a puckered hexagonal ring of six O_I atoms and normal to the mean plane of this hexagon is a pair of O_{II} atoms (7).

Interatomic bond distances of $A-O_I$ and $A-O_{II}$ can be ascertained with X-ray or neutron structural refinement. Knop et al. (7) and Sleight (8) reported these distances for $Er_2Ti_2O_7$, $Hg_2Nb_2O_7$, and $Cd_2Nb_2O_7$.

Comparing the reported $A-O_I$ and $A-O_{II}$ distances (later these distances are described as d ($A-O_I$) and d ($A-O_{II}$), respectively) with the sum of ionic radii, $r_A + r_O$, $d(A-O_I)$ is longer than the sum, and d ($A-O_{II}$) is shorter than it with respect to the refined compounds mentioned above. The values of ionic radii were taken from Shannon (9). These conclusions have already been reported by Nikiforov (10), who made use of these facts to establish two inequality conditions for estimating the X value. Here the facts mentioned above are utilized not to estimate the X value but to propose formation conditions. Namely A and O_I ions are apart from each other and A and O_{II} ions are in contact. From this starting point, a pair of formation conditions about the type of the mixed cation at the A site are derived. For the larger A^{2+} ion, d ($A^{2+}-O_I$) is considered to be longer than $r_A + r_O$, and for the smaller A^{4+} ion, d ($A^{4+}-O_{II}$) is considered to be shorter than the sum. Therefore we propose the following two formation conditions:
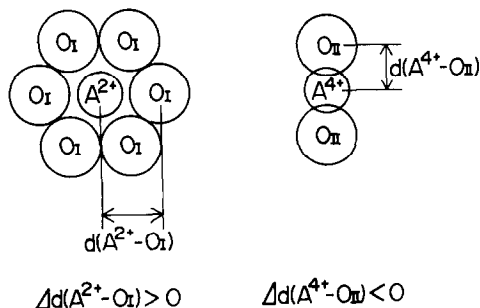

$$\Delta d(A^{2+}-O_I) > 0 \qquad \Delta d(A^{4+}-O_{II}) < 0$$

FIG. 2. Illustration of formation conditions.

$$\Delta d\,(A^{2+}-O_I)$$
$$= d\,(A^{2+}-O_I) - (r_A + r_O) > 0; \quad (1)$$

$$\Delta d\,(A^{4+}-O_{II})$$
$$= d\,(A^{4+}-O_{II}) - (r_A + r_O) < 0. \quad (2)$$

These conditions are illustrated in Fig. 2. The distances of $d\,(A^{2+}-O_I)$ and $d\,(A^{4+}-O_{II})$ are given by the following equations (11),

$$d\,(A^{2+}-O_I) = a\,\sqrt{((X - \tfrac{1}{2})^2 + \tfrac{1}{32})}\;;$$

$$d\,(A^{4+}-O_{II}) = 3a/8,$$

where a is the lattice parameter. Both a and X values must be estimated. The value of lattice parameter was estimated by the following way: When the B site ion was fixed, the linear relationship between the lattice parameter and ionic radii of the A site ion was reported by many authors. Therefore the lattice parameters of new compounds can be estimated with average ionic radii of di- and tetravalent ions which are expected to occupy the A site. Two methods have already been reported to estimate the value of X: One proposed by Nikiforov (10) and the other by Chakoumakos (11). According to Chakoumakos, his method is statistically more accurate than that of Nikiforov. Therefore the X value was estimated using Chakoumakos's method.

3. Experimental

For the combination of di- and tetravalent ions at the A site, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Cd^{2+} were selected as divalent ions and Ti^{4+}, Sn^{4+}, Zr^{4+}, Hf^{4+}, and Ce^{4+} were selected as tetravalent ions. For the B site ions, Ti^{4+}, Sn^{4+}, Zr^{4+}, and Hf^{4+} were selected.

The specimens were prepared by conventional solid state reaction from starting materials of reagent grade $CaCO_3$, $SrCO_3$, $BaCO_3$, CdO, TiO_2, SnO_2, ZrO_2, HfO_2, and CeO_2 powders. Selected combinations of powders were mixed with a small amount of ethanol. The powder mixtures were pressed
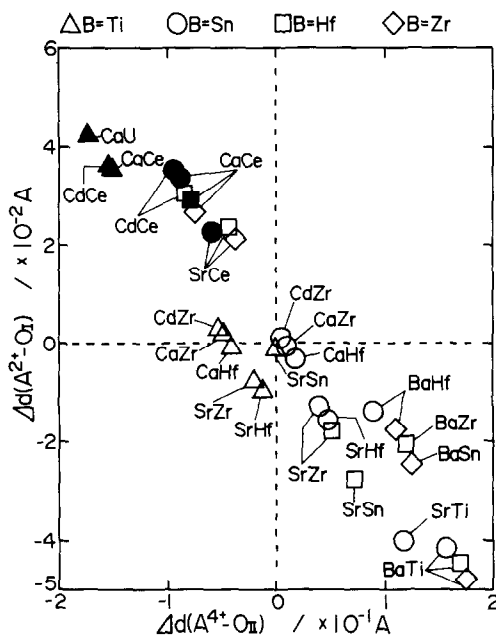

FIG. 3. Formation diagram of $(A^{2-},A^{4-})_2 B^{4+}{}_2 O_7$ pyrochlore-type compounds based on $\Delta d\,(A^{2-}-O_I)$ and Δd $(A^{4+}-O_{II})$. Closed symbols indicate the combinations with which formations of pyrochlore phases were identified.

into pellets and calcined at 800 to 980°C. Then the pellets were milled and pressed again into pellets, and fired at 1250 to 1450°C (the samples containing CdO were fired at 1250°C only). Firing at these temperatures was repeated several times. Resulting phases were identified with powder X-ray diffraction.

4. Results and Discussion

To ascertain the preceding formation conditions, 32 combinations were selected. In these combinations, average ionic radii of A^{2+} and A^{4+} satisfied the radius range of the A site ion with which the formation of binary pyrochlore-type compounds is reported against each B^{4+} ion.

Figure 3 shows the classification of these combinations according to the formation

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TABLE I

Lattice Parameter and X-Ray Diffraction Data for $(Sr,Ce)_2Sn_2O_7$, $(Cd,Ce)_2Sn_2O_7$, and $(Ca,Ce)_2Hf_2O_7$

h k l	$(Sr,Ce)_2Sn_2O_7$ $a = 10.580(5)$Å d(Å)	I/I_0	$(Cd,Ce)_2Sn_2O_7$ $a = 10.449(6)$Å d(Å)	I/I_0	$(Ca,Ce)_2Hf_2O_7$ $a = 10.493(8)$Å d(Å)	I/I_0
1 1 1	6.109	0.3	6.033	0.0	6.059	5.5
2 2 0	3.741	0.0	3.694	0.2	3.710	0.0
3 1 1	3.190	1.1	3.151	0.0	3.164	3.4
2 2 2	3.054	100.0	3.017	100.0	3.029	100.0
4 0 0	2.645	25.3	2.612	32.6	2.623	29.1
3 3 1	2.427	0.5	2.397	1.2	2.407	0.5
4 2 2	2.160	0.0	2.133	0.3	2.142	0.0
5 1 1	2.036	0.6	2.011	0.1	2.020	1.4
3 3 3	2.036		2.011		2.020	
4 4 0	1.870	43.8	1.847	41.2	1.855	36.5
5 3 1	1.788	0.4	1.766	0.0	1.774	0.0
4 4 2	1.763	0.0	1.742	0.0	1.745	0.0
6 2 0	1.673	0.5	1.652	0.0	1.659	0.0
5 3 3	1.614	0.1	1.594	0.0	1.600	0.0
6 2 2	1.595	36.7	1.575	34.2	1.582	26.1
4 4 4	1.527	10.0	1.508	7.6	1.515	5.9
5 5 1	1.482	0.1	1.463	0.2	1.469	0.5
7 1 1	1.482		1.463		1.469	
6 4 2	1.414	0.0	1.396	0.0	1.440	0.0
5 5 3	1.377	0.0	1.360	0.0	1.366	0.6
7 3 1	1.377		1.360		1.366	
8 0 0	1.323	5.3	1.306	4.6	1.312	3.9
7 3 3	1.293	0.0	1.277	0.2	1.282	0.0
6 4 4	1.283	0.0	1.267	0.0	1.273	0.5
8 2 2	1.247	0.4	1.232	0.0	1.237	0.0
6 6 0	1.247		1.232		1.237	
5 5 5	1.222	0.0	1.207	0.0	1.212	0.5
7 5 1	1.222		1.207		1.212	
6 6 2	1.214	15.7	1.199	10.2	1.204	7.3
8 4 0	1.183	12.1	1.168	8.1	1.173	5.2
7 5 3	1.161	0.1	1.147	0.0	1.152	0.0
9 1 1	1.161		1.147		1.152	
8 4 2	1.154	0.0	1.140	0.0	1.145	0.0
6 6 4	1.128	0.1	1.114	0.0	1.119	0.0
9 3 1	1.109	0.1	1.095	0.0	1.100	0.0
8 4 4	1.080	11.5	1.067	7.2	1.071	5.6
7 5 5	1.063	0.0	1.050	0.0	1.055	0.5
7 7 1	1.063		1.050		1.055	
9 3 3	1.063	0.0	1.050		1.055	
8 6 2	1.038	0.1	1.025	0.0	1.029	0.0
10 2 0	1.038		1.025		1.029	
7 7 3	1.023	0.2	1.010	0.2	1.014	0.0
9 5 1	1.023		1.010		1.014	
10 2 2	1.018	12.0	1.006	7.2	1.010	4.1
6 6 6	1.018		1.006		1.010	
9 5 3	0.987	0.0	0.974	0.0	0.979	0.3
8 6 4	0.982	0.0	0.970	0.0	0.974	0.0

TABLE I—*Continued*

h k l	(Sr,Ce)$_2$Sn$_2$O$_7$ a = 10.580(5)Å		(Cd,Ce)$_2$Sn$_2$O$_7$ a = 10.449(6)Å		(Ca,Ce)$_2$Hf$_2$O$_7$ a = 10.493(8)Å	
	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
10 4 2	0.966	0.0	0.954	0.0	0.958	0.0
11 1 1	0.954	0.0	0.942	0.0	0.946	0.0
7 7 5	0.954		0.942		0.946	
8 8 0	0.935	4.4	0.924	2.4	0.928	1.4
11 3 1	0.924	0.1	0.913	0.0	0.917	0.1
9 5 5	0.924		0.913		0.917	
9 7 1	0.924		0.913		0.917	
10 4 4	0.921	0.0	0.910	1.1	0.913	0.0
8 8 2	0.921		0.910		0.913	
10 6 0	0.907	0.2	0.896	0.0	0.900	0.0
8 6 6	0.907		0.896		0.900	
9 7 3	0.897	0.2	0.886	0.0	0.890	0.0
11 3 3	0.987		0.886		0.890	
10 6 2	0.894	18.1	0.883	7.6	0.887	3.8
12 0 0	0.882	12.2	0.871	4.2	0.874	1.8
8 8 4	0.882		0.871		0.874	
11 5 1	0.873	0.1	0.862	0.0	0.866	0.0
7 7 7	0.873		0.862		0.866	
12 2 2	0.858	0.0	0.848	0.0	0.851	0.0
10 6 4	0.858		0.848		0.851	

conditions mentioned above. Reported pyrochlore-type compounds are also shown in this figure. Closed symbols indicate the combinations with which the formation of pyrochlore phases was identified. According to the proposed formation conditions, Δd (A^{2+}–O$_I$) is expected to be positive and Δd (A^{4+}–O$_{II}$) negative. Consequently combinations in the second quadrant in this plot are expected to form pyrochlore-type compounds. From our results of preparation, besides the (Ca,Ce)$_2$Sn$_2$O$_7$, three new pyrochlore-type compounds, (Sr,Ce)$_2$Sn$_2$O$_7$, (Cd,Ce)$_2$Sn$_2$O$_7$, and (Ca,Ce)$_2$Hf$_2$O$_7$, are successfully synthesized. However, these compounds coexist with slight amounts of other phases, i.e., SrSnO$_3$, CdSnO$_3$, and CaHfO$_3$, respectively. The lattice parameter and powder X-ray diffraction data of the three new compounds are shown in Table I. All these compounds are in the second quadrant in Fig.

3. Furthermore no indication of pyrochlore formation was found against the combinations in other quadrants.

CdZrTi$_2$O$_7$ is reported to be a cubic pyrochlore structure (2). However, the resulting phases prepared in this work had so many diffraction peaks, it was difficult to identify the resulting phase as a pyrochlore-type compound. The resulting phase was rather similar to the CaZrTi$_2$O$_7$ zirconolite structure which has monoclinic symmetry. In Ref. (2), it was not specified that the resulting CdZrTi$_2$O$_7$ was a single-phase pyrochlore-type compound, so there were two possibilities. One is that the resulting phase obtained in Ref. (2) is not pyrochlore but a zirconolite-like compound. Another is that in this work, the pyrochlore-type compound certainly formed but other unknown compounds also formed at the same time. On the other hand, there is the third possibility: the

difference in the firing temperature. In this work, the sample in question was fired at 1250°C, while the sample of Ref. (2) was fired at 1350°C. To clarify this problem, more work is needed.

Getting back to Figure 3, both $CdZrTi_2O_7$ and $CaZrTi_2O_7$ are near the borderline of Δd (A^{2+}–O_I). These facts suggest that the formation conditions considered above are useful. Though these conditions are only prerequisite because not all combinations in the second quadrant form cubic pyrochlore-type compounds, they serve as a guide for designing new compounds of this type. For example actinide ions generated in the nuclear power station would be immobilized as components of A^{4+} ions in $(A^{2+}, A^{4+})_2 B^{4+}{}_2 O_7$ pyrochlores.

5. Conclusions

Upon consideration of the crystallographic features of pyrochlore-type compounds, the following two new conditions are proposed for the formation of a mixed cation type at the A site:

$$\Delta d\ (A^{2+}-O_I)$$
$$= d\ (A^{2+}-O_I) - (r_A + r_O) > 0 \quad (1)$$

$$\Delta d\ (A^{4+}-O_{II})$$
$$= d\ (A^{4+}-O_{II}) - (r_A + r_O) < 0. \quad (2)$$

Applying these conditions, three new compounds, i.e., $(Sr,Ce)_2Sn_2O_7$, $(Cd,Ce)_2Sn_2O_7$, and $(Ca,Ce)_2Hf_2O_7$, are synthesized. Although these conditions are prerequisites, they will serve as a guide for designing new compounds of this structure.

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