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Synthesis of a New Compound, $Ca_{0.8}Ce_{1.2}Sn_2O_7$, with Pyrochlore Structure

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A new compound of the formula $Ca_{2X}Ce_{2-2X}Sn_2O_7$, wherein $0.35 \leqq X \leqq 0.43$, with cubic pyrochlore structure was synthesized by a solid state reaction at 1450°C. Rietveld analysis based on *A* site substitution gave evidence that this new compound belonged to *Fd*3*m* with cubic pyrochlore structure. It was expected from chemical analysis that some of the Ce ions at the *A* site should be trivalent to maintain electrical neutrality of the whole crystal. This expectation is justified by the description of average ionic radii in the *A* site of this new pyrochlore and the model of Rietveld analysis. © 1991 Academic Press, Inc.

Introduction

The general formula of oxide pyrochlores can be written as $A_2B_2O_7(A^{3+},B^{4+}$ or $A^{2+},B^{5+})$. Various investigators have researched the *A* and *B* cations suitable for pyrochlore formation. They reported that the relative ionic radii or ionic radius ratios governed the formation and stability of the oxide pyrochlores.

In the case of $A_2^{3+}B_2^{4+}O_7$ pyrochlores, the *A* site is occupied by trivalent ions such as Sc, Y, rare earth elements, In, Tl, or Bi, and the *B* site is occupied by tetravalent ions such as group 4 elements (Si, Ge, Sn, Pb), 3*d* elements (Ti, V, Cr, Mn), 4*d* elements (Zr, Mo, Tc, Ru, Rh, Pd), or 5*d* elements (Hf, Os, Ir, Pt) (*1*).

Montmory and Bertaut (*2*) first synthesized pyrochlores with mixed cations at the *B* site, $Ln_2(B\mathrm{Sb})O_7$, (Ln = Pr–Lu or Y; B = Cr, Fe, Ga). Later Golovashchikova *et al.* (*3*) and many other investigators studied the formation of pyrochlores with mixed cations at the *B* site.

Only a few investigators, however, tried to synthesize pyrochlores with two or more different cations at the *A* site. Coughanour *et al.* (*4*) first synthesized $CaZrTi_2O_7$, which had a distorted pyrochlore-type structure with orthorhombic symmetry or other systems of lower symmetry. The structure analysis of $CaZrTi_2O_7$ using a single crystal showed that $CaZrTi_2O_7$ had a monoclinic pyrochlore structure (*5*). Knop *et al.* (*6*) investigated titanate pyrochlores of several *A* site combinations such as CaGe (1200°C), SrGe (1200°C), CaSn (1500°C), CaZr (1400°C), SrZr (1400°C), CaCe (1400°C), and SrCe (1400°C). However, none of the combinations exhibited the cubic pyrochlore structure. McCauley *et al.* (*7*) synthesized $CaCeTi_2O_7$ pyrochlore at 1250°C and showed that the compound decomposed

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into $CaTiO_3$, CeO_2, and an unidentified phase over 1300°C. McCauley *et al.* also tried to synthesize new pyrochlores with various combinations of *A* site cations such as CaTh (1700°C), CaZr (1450°C), CaHf (1450°C), CaSn (1450°C), CdCe (1150°C), CdZr (1350°C), CdHf (1250°C), CdSn (1250°C), SrZr (1700°C), and PbZr (1350°C). However, only three compositions, i.e., CaCe, CdCe, and CdZr, exhibited the cubic pyrochlore structure.

Although Sn^{4+} forms oxide cubic pyrochlores with Y and most of the rare earth elements (*8–10*), no stannate pyrochlore with mixed cations at the A site has been reported. In the present study, a new pyrochlore with formula $(Ca,Ce)_2Sn_2O_7$ was synthesized, and the single phase region of this new pyrochlore was investigated. The crystal structure of this new pyrochlore was refined by means of Rietveld analysis.

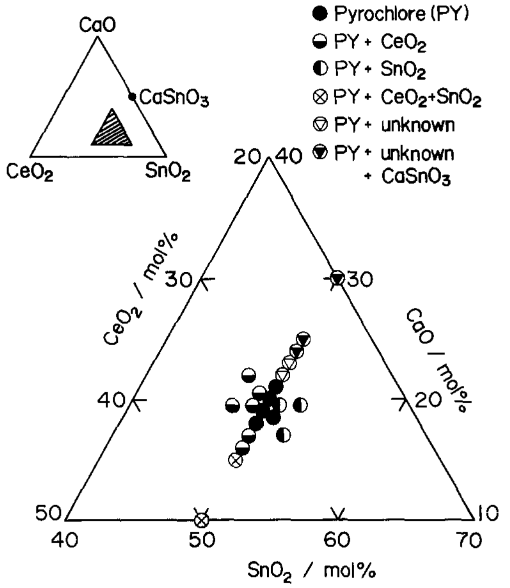

FIG. 1. Relationship between the batch compositions and the resulting phases after firing at 1450°C in air.

Experimental

The specimens were prepared by conventional solid state reaction from starting materials of reagent grade $CaCO_3$, CeO_2, and SnO_2 powders. These powders were mixed with a small amount of ethanol using a porcelain mortar and a pestle for 1 hr. The powder mixture was pressed into pellets and calcined at 980°C for 12 hr in air. Then the pellets were milled, and about 1.5 g of the powders were packed into an alumina Tammann tube attached with an alumina lid and fired at 1450°C for 8 hr in air. After firing, the samples were quickly taken out from the furnace and cooled in air. Firing was repeated once more but the time of the second firing was 18 hr. A furnace with a spiral SiC heating element and an alumina muffle tube was used for the firing. Heating temperature was measured with a Pt–PtRh13% thermocouple which was positioned close to the sample in the furnace.

Powder X-ray diffraction data were collected on a Philips PW-1700 powder diffractometer system operated at 40 kV and 30 mA using graphite-monochromated Cu*Kα* X-rays. The scanning rates for phase analysis and lattice parameter measurement were $\frac{1}{4}$° and $\frac{1}{8}$° 2θ/min, respectively. The cell dimensions were refined by the least-squares method with six separate peaks with the diffraction angles over 90°2θ. In Rietveld analysis, intensity data were collected for 5 s at 0.02°2θ intervals over the range between 15 and 140°2θ. A computer program for pattern-fitting structure refinement named "RIETAN" (*11–12*) was employed and run on a VAX microcomputer.

The densities of the samples around 8 g with particle size between 35 and 60 mesh were measured with a pycnometer.

Results and Discussion

The relationship between the batch compositions and the resulting phases after firing at 1450°C in air is shown in Fig. 1. Along the line corresponding to 50 mol% Sn, the single phase region of the new pyrochlore compound ranged from 18 to 21 mol% Ca. When the Ca content was below 17 mol%, CeO_2 was found in the samples. Furthermore, SnO_2 was also found in the samples of Ca content below 15 mol%. In the samples of Ca content more than 22 mol%, a small amount of an unknown phase coexisted. $CaSnO_3$ was also identified when the Ca content was more than 24 mol%. On the other hand, at any compositions which were not on the line of 50 mol% Sn, single phase pyrochlore was hardly obtained. As shown in Fig. 1, single phases of the new pyrochlore were formed within the range of the cation ratio of Ca : Ce : Sn = X : (1-X) : 1, where $0.35 \leqq X \leqq 0.43$.

The single phase pyrochlore samples were pale gray. This new pyrochlore was fairly inert toward attack by boiling water, most mineral acids such as HCl, H_2SO_4, HNO_3, CH_3COOH, and aqua regia, and NH_3 solution. No change between initial and attacked samples was recognized by powder X-ray diffraction analysis. However, heated concentrated H_2SO_4 affected the pyrochlore, and the color was changed to light green and crystallinity deteriorated.

The weight percentages and molar ratio of each element of two samples were compared with those of the batch compositions in Table I. The metal contents were determined by fluorescent X-ray analysis and the oxygen contents were determined by LECO's oxygen analyzer. The oxygen content of the batches was calculated based on the assumption that the oxygen molar content should be 3.5 times as large as that of tin. The molar ratios of each element were calculated against the molar content of tin which is fixed at 2.00.

TABLE I

THE BATCH COMPOSITIONS AND THE ANALYTICAL COMPOSITIONS OF TWO SAMPLES, A: $Ca_{0.8}Ce_{1.2}Sn_2O_7$ AND B: $Ca_{0.84}Ce_{1.16}Sn_2O_7$

Sample		Ca	Ce	Sn	O
A	Batch compositions (wt%)	5.83	30.6	43.2	20.4[a]
	Analytical compositions (wt%)	6.20	30.3	43.1	20[b]
	Batch compositions (molar ratio)	0.80	1.20	2.00	7.0[a]
	Analytical compositions (molar ratio)	0.85	1.19	2.00	7.0[b]
B	Batch compositions (wt%)	6.17	29.8	43.5	20.5[a]
	Analytical compositions (wt%)	6.49	29.4	43.3	21[b]
	Batch compositions (molar ratio)	0.84	1.16	2.00	7.0[a]
	Analytical compositions (molar ratio)	0.89	1.15	2.00	7.1[b]

[a] It was assumed that the oxygen molar content should be 3.5 times as large as that of tin.

[b] Determined by LECO's oxygen analyzer.

As shown in Table I, analytical Ca contents were significantly larger than batch compositions, and analytical Ce and Sn contents were a little smaller than those of the batch compositions. This result probably shows that SnO_2 and CeO_2 were vaporized during heating. It is expected that SnO_2 will dissociate mainly into SnO and O_2 at high temperature. The total gas pressure $\log \Sigma P$ from this dissociation within the range of 1000–1903 K was reported to follow (*13*)

$$\log \Sigma P = -20{,}060/T + 9.029.$$

From this equation, the total gas pressure of this dissociation at 1450°C (1723 K) is estimated to be 2.435×10^{-3} atm. At high temperature, CeO_2 partially dissociates into Ce_2O_3 and O_2. The total gas pressure on the CeO_2–Ce_2O_3 system in the range of 1000–2000 K was reported to follow (*14*)

$$\log \Sigma P = -27{,}580/T + 9.122.$$

The total gas pressure of this dissociation at 1450°C (1723 K) is then estimated to be 1.303×10^{-7} atm. The result of the total gas pressure calculation would suggest that evaporation of CeO_2 was almost negligible but evaporation of SnO_2 was not. Therefore the sample holder was sealed with a tight alumina lid with the intention of suppressing the dissociation. Another possible reason for the result is the errors in fluorescent X-ray analysis. The lightest element, Ca, would be most subject to errors in fluorescent X-ray analysis. Other chemical analysis will be needed to confirm this consideration.

The X-ray diffraction pattern of this new compound could be indexed as a cubic pyrochlore structure of $Fd3m$ symmetry. In general $A_2^{3+}B_2^{4+}O_7$ cubic pyrochlore structures, the trivalent cations occupy an $A(16d)$ site with 8-fold coordination, and the tetravalent ions occupy the $B(16c)$ site with 6-fold coordination. In this new compound, it is considered that Ca and Ce occupy the same site and Sn occupies the other from the result shown in Fig. 1. According to Shannon (*15*), the ionic radius of Sn^{4+} was smaller than those of Ca^{2+} and Ce^{4+} at 6-fold coordination. Consequently, Sn^{4+} may occupy the $B(16c)$ site, and Ca and Ce may occupy the $A(16d)$ sites.

As mentioned above, the number of oxygen in the chemical formula was seven when that of tin was fixed at two, and the single phase pyrochlore was obtained within the range of $0.35 \leqq X \leqq 0.43$ in $Ca_{2X}Ce_{2-2X}Sn_2O_7$. It is believed that part of the Ce or Sn ions should take a lower valence to achieve charge balance, because Ca^{2+} hardly changes the ionic valence. The assumption that part of the Ce ions are trivalent gives good results in the Rietveld analysis and the lattice parameter consideration, which is described later. The cation ratio in the $A(16d)$ site can then be calculated by the relation $Ca^{2+} : Ce^{4+} : Ce^{3+} = X : X : (1\text{-}2X)$ which fixes the restriction of electrical neutrality. It seemed that a reducing atmosphere during preparation did not exist. Due to the stability of CeO_2, it can be considered that Ce^{4+} is more stable than Ce^{3+} in air. However, in this new compound, Ce^{3+} will be needed to achieve crystallographic and/or electrostatic requirements.

Measured densities were 6.385 g/cm^3 and 6.293 g/cm^3 for $X = 0.36$ and 0.42, respectively. Both these values were 99.8% of the theoretical one calculated on the basis of the lattice parameters and the composition. This result shows that the full occupancy of the O site and any other sites can be assumed against all X values in the single phase samples.

TABLE II

REFINED R-FACTORS OF $Ca_{0.8}Ce_{1.2}Sn_2O_7$

R_{wp} (%)	R_p (%)	R_E (%)	R_I (%)	R_F (%)
13.19	10.39	4.61	6.14	6.20

Note. R_{wp}, weighted pattern R-factor; R_p, pattern R-factor; R_E, expected R-factor; R_I, integrated intensity R-factor; and R_F, structure factor R-factor.

Rietveld analysis on the sample of $X = 0.4$ ($Ca_{0.8}Ce_{1.2}Sn_2O_7$) was carried out with the model of the cation site occupation mentioned above. It was also assumed that the anion sites, $8b$ and $48f$, in the cubic pyrochlore structure ($Fd3m$, No. 227) were occupied by O^{2-}. Refinement was done as the occupation factor was fixed and the isotropic thermal parameters changed. Once a solution converged, the occupation factor was changed and fixed at a slightly different value, and then the refinement was repeated.

As the result of Rietveld analysis, the minimum R_{wp} value was obtained when the occupation factor of each site was fixed at 1. Refined R-factors are shown in Table II. The observed d values and intensities of each reflection peak are listed in Table III along with those calculated on the basis of refined data. The observed values are in good agreement with the calculated ones, so the results of Rietveld analysis support the idea that this new compound has cubic pyrochlore structure.

Relationship between the lattice parameter and X in the molar ratio of batch composition Ca : Ce : Sn = $X : (1\text{-}X) : 1$ is shown in

TABLE III

Powder X-Ray Diffraction Data for $Ca_{0.8}Ce_{1.2}Sn_2O_7$

h	k	l	d_{obs}	d_{cal}	I_{obs}	I_{cal}
1	1	1	6.025	6.054	1376	1778
2	2	0	3.706	3.707	847	129
3	1	1	3.154	3.162	3999	2877
2	2	2	3.020	3.027	100000	93505
4	0	0	2.617	2.622	25266	27658
3	3	1	—	2.406	0	89
4	2	2	—	2.140	0	240
5	1	1	2.016	2.018	46	49
3	3	3	2.016	2.018	948	1008
4	4	0	1.852	1.854	44489	44950
5	3	1	1.771	1.772	687	547
4	4	2	—	1.748	0	0
6	2	0	1.648	1.658	473	44
5	3	3	1.597	1.599	483	493
6	2	2	1.579	1.581	36463	37864
4	4	4	1.512	1.514	9025	8314
5	5	1	1.467	1.468	578	540
7	1	1	1.467	1.468	41	38
6	4	2	—	1.401	0	2
7	3	1	1.364	1.365	707	1000
5	5	3	1.364	1.365	48	68
8	0	0	1.310	1.311	5386	5864
7	3	3	—	1.281	5	5
6	4	4	—	1.272	0	0
8	2	2	1.235	1.236	340	83
6	6	0	1.235	1.236	122	30
5	5	5	—	1.211	1	1
7	5	1	—	1.211	274	266
6	6	2	1.202	1.203	14476	14166
8	4	0	1.172	1.172	11486	11068
7	5	3	1.151	1.151	58	50
9	1	1	1.151	1.151	167	143
8	4	2	—	1.144	0	0
6	6	4	—	1.118	0	17
9	3	1	—	1.099	0	184
8	4	4	1.070	1.070	10760	11097
7	5	5	1.053	1.054	93	92
7	7	1	1.053	1.054	5	5
9	3	3	1.053	1.054	33	32
10	2	0	—	1.028	44	31
8	6	2	—	1.028	24	17
9	5	1	1.014	1.014	49	49
7	7	3	1.014	1.014	294	292
10	2	2	1.009	1.009	8780	8782
6	6	6	1.009	1.009	2927	2927
9	5	3	—	0.978	0	191
8	6	4	—	0.974	0	0
10	4	2	—	0.957	0	25
11	1	1	0.945	0.946	7	101
7	7	5	0.945	0.946	10	158
8	8	0	0.927	0.927	4329	4311
11	3	1	0.916	0.916	60	58
9	5	5	0.916	0.916	190	184
9	7	1	0.916	0.916	118	115
10	4	4	—	0.913	0	0
8	8	2	—	0.913	0	0
10	6	0	—	0.899	123	52
8	6	6	—	0.899	0	0
9	7	3	—	0.889	334	310
11	3	3	—	0.889	230	213
10	6	2	0.886	0.886	17966	16631
12	0	0	0.874	0.874	2084	1896
8	8	4	0.874	0.874	9039	8224

Fig. 2. Since the lattice parameter is linear with X between 0.3 and 0.48, it is expected that this pyrochlore is homogeneous within the range. Nevertheless, the single phase region determined by X-ray phase analysis

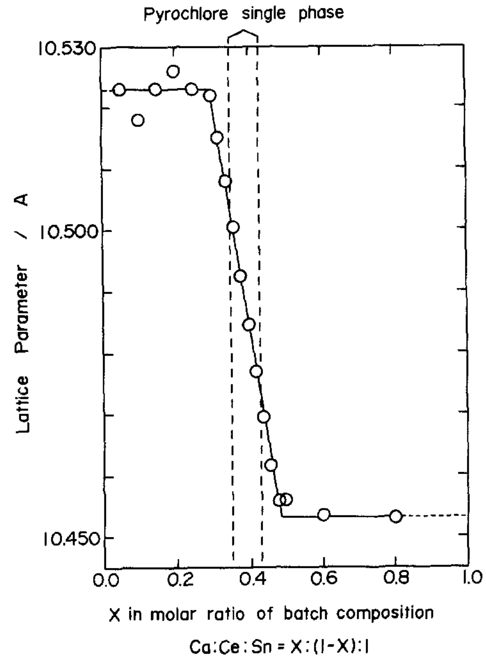

Fig. 2. Relationship between the lattice parameter and X in molar ratio of batch composition Ca : Ce : Sn = X : (1-X) : 1.

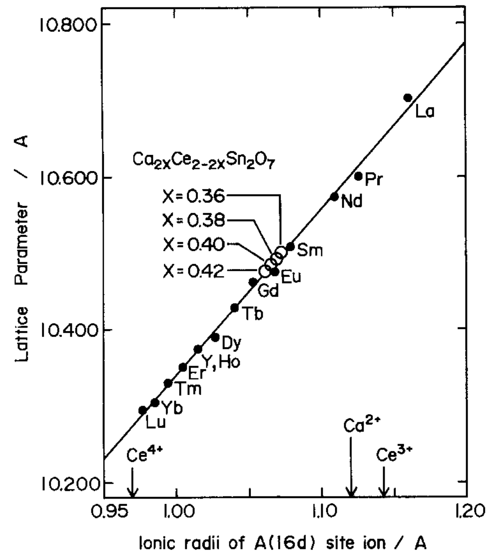

FIG. 3. Relationship between the lattice parameter and the radii of A site ions in stannate pyrochlores.

is $0.35 \leqq X \leqq 0.43$ (See Fig. 1), which is narrower than that expected. The reason has not been made clear yet, but it can be considered that the single phase samples within the full range expected from Fig. 2 are difficult to obtain by conventional solid state reaction. More sophisticated processes such as coprecipitation will be required to confirm the postulation.

It is a bit surprising that the single-phase region does not extend to $X = 0.5$ as the sample was annealed for 12 days in air (every 3 days the sample was milled). However, the resulting phase wasn't changed into a single phase. In this study all samples were fired in air and not in oxygen, but the single-phase region might be extended to $X = 0.5$ by heating in an oxygen atmosphere since Ce^{4+} would be more stable than in air.

Figure 3 shows the relationship between the lattice parameter and the radii of *A* site ions in various stannate pyrochlores. The ionic radii of *A* site ions in this new pyrochlore were calculated from each occupied ratio of those of Ca^{2+}, Ce^{3+}, and Ce^{4+}. All other ionic radii data were taken from Shannon (*15*) and the lattice parameter data were taken from JCPDS powder diffraction file data. As shown in Fig. 3, the plots of this new compound fall on the line connecting the plots of other rare earth stannates. This fact evidences that some of the Ce ions are trivalent at the *A* site and the model of *A* site substitution is proper in this new pyrochlore. From the lattice parameters and ionic radii, this new compound should resemble $Eu_2Sn_2O_7$ in properties. However, the color of $Eu_2Sn_2O_7$ is white while that of this new pyrochlore is pale gray. The difference in color is probably derived from the differences in their electronic structures. Therefore the electronic properties of this new pyrochlore can be different from that of $Eu_2Sn_2O_7$ and other rare earth-stannate pyrochlores, which are now under investigation by us.

Conclusions

A new pyrochlore compound of the formula $Ca_{2X}Ce_{2-2X}Sn_2O_7$ wherein $0.35 \leqq X \leqq 0.43$ was synthesized by a conventional solid state reaction. This compound is fairly inert toward humidity, most mineral acids, and NH_3 solution.

The phase–composition relationship, the chemical analysis data, and the results of Rietveld analysis give evidence that this new compound belongs to space group $Fd3m$ with cubic pyrochlore structure. The *A* site is occupied by Ca and Ce ions, and some of the Ce ions are trivalent to maintain the electrical neutrality in the whole crystal.

The lattice parameter measurements showed that the homogeneous range was $0.30 \leqq X \leqq 0.48$.

From the lattice parameters and ionic radii, this new pyrochlore is closely related to the binary stannate pyrochlores of rare earth elements.

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