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New Pyrochlores of the Charge-Coupled Type

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For $A^{2+}A^{4+}Ti_2O_7$-type compositions, it was found that an upper limit of 0.23 Å for the size difference of the A cations existed for pyrochlore formation. Pyrochlores of the $A^{1+}A^{3+}Ta_2O_7$ type could not be formed. Although pyrochlores of the $A_2^{1+}B_2^{6+}O_7$ type could not be prepared, pyrochlores of the type $A^{1+}A^{3+}B^{4+}B^{6+}O_7$ could be prepared. Compositions of the type $Ca_xGd_{2-x}Sn_{2-x}Sb_xO_7$ ($x = 0$ to 1) showed that the pyrochlore structure could form partial crystalline solutions with compositions of the weberite structure.

Introduction

The object of this investigation was to further the knowledge available concerning the crystal chemistry of pyrochlore-type compositions.

The mineral pyrochlore is a member of a series of isotypic minerals which differ mostly in the type and number of ions present. An approximate formula for the mineral pyrochlore is $(Ca, Na, Ce, Th)_2(Nb, Ta, Ti)_2O_6(OH, F)$ which can be generalized to $A_2B_2X_6Z$ or $A_2B_2X_7$. Many possible cationic and some anionic substitutions are possible in the pyrochlore structure, as is indicated by the more than 300 pyrochlore compositions reported in the literature.

In 1930 the pyrochlore structure was first determined by Gaertner (*1*) to belong to the space group $Fd3m$. The cell edge is approximately 10.4 Å with $Z = 8$. The ions are located as follows:

16 A	in 16 (c)	origin
16 B	in 16 (d)	selected at
8 Z	in 8 (a)	the A
48 X	in 48 (f)	cation site

Symmetry fixes the coordinates of all the ions except for those in position 48(f). This position contains one unknown coordinate, x.

Several different viewpoints have been taken when describing the pyrochlore structure. Byström (*2*) has described it as a network structure consisting of $(BO_6)^{n-}$ octahedra linked corner to corner with the A ions filling the interstices. This viewpoint is especially advantageous when deficiencies exist on the A site, as pointed out by Sleight (*3*), and also when making a comparison

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between pyrochlore and other closely related structures.

Cook and Jaffe (*4*) have described the pyrochlore structure as a fluorite derivative. This relationship between the pyrochlore and the fluorite structures also has been discussed in detail by Barker *et al* (*5*).

Sleight (*3*) compared the pyrochlore structure to two interpenetrating lattices, one being identical with one of the networks of Cu_2O. Since the *A* cations are coordinated by eight anions, six at one distance and two others at a smaller distance, one could ignore the larger bond lengths and assume a linear coordination with the two closest anions. Sleight emphasized that this two network view of the structure was appropriate for pyrochlores which had highly distorted cubic coordination polyhedra around the *A* cations, such as mercury and cadmium pyrochlores.

Various investigators have determined the maximum and minimum ionic radii for the *A* and *B* cations for pyrochlore formation. Based on the oxide compositions prepared at atmospheric pressure reported in the literature one can outline a structure field of stability. The upper radius of the *B* cation has been shown to be that of Pb^{4+} (0.78 Å, Shannon radii (*6*)), although only $La_2Pb_2O_7$ has been reported as a pyrochlore (*7*). The lower limit is that of V^{4+} (0.58 Å) as shown by Bazuev *et al.* (*8*). The upper limit of radius of the *A* cation is that of La^{3+} (1.03 Å) but only for the larger *B* cations (*9*). Once the *B* cation radius drops below that of Sn^{4+} (0.69 Å), the upper limit of the *A* cation radius falls until it reaches about the value of Sm^{3+} (0.96 Å). The lower limit of the *A* cation radius is about 0.83 Å, slightly below that of Lu^{3+}. The lower limit is slightly higher for those pyrochlores with large *B* cations. The smallest *A* cation that still forms a pyrochlore with Hf^{4+} and Zr^{4+} is Gd^{3+} (0.94 Å), although with Zr^{4+} it transforms to the fluorite structure at 1550°C (*10*). These limits were extended to Si^{4+} (*11*) for the *B* cation and Sc^{3+} (*12*) for the *A* cation if one included those compositions prepared at pressures greater than 1 atm. Because of the odd shape of the structure field of stability, it is better to construct the stability field than to rely on radius ratios as an indication of pyrochlore formation. The upper and lower limits for the radius ratio were calculated to be 1.66 and 1.25, respectively. Compositions with a ratio between these two limits need not be pyrochlores, however, as evidenced by $In_2Ti_2O_7$ with a radius ratio of 1.32 which is not a pyrochlore and also lies outside the boundaries of the stability field.

Experimental

All compositions were prepared from chemically pure reagents by mixing under acetone and then treating at various temperatures and times with intermediate mixings under acetone.

Compositions which involved volatile materials (Cd^{2+}, Mo^{6+}, etc.) were heat treated by one or more of the following methods:

(1) as pellets in evacuated sealed fused silica tubes,

(2) as powder in sealed platinum or platinum–10% rhodium tubes,

(3) as pellets or powder in covered platinum crucibles,

(4) as pellets on platinum foil.

The actual methods used were determined by the ease of volatilization of the chemical species in question, the temperature of reaction, and the possibility of oxidizing or reducing other chemical species contained within the composition. In each case the compositions were heat treated initially from 200 to 500°C.

Nonvolatile compositions were in some cases pelletized to improve the degree of reaction. All other heat treatments were conducted on powders.

Compositions which required high temperatures (1600 to 1800°C) for complete reaction were heat treated either in a Selas (gas fired) or in an induction furnace and were therefore sealed into platinum–20% rhodium tubes. All other heat treatments were conducted in a Globar furnace. Samples heat treated to 1500°C or higher were cooled in the furnace; all others were air quenched.

The final heat treatment of each sample was believed to be such that essentially an equilibrium phase or phase assemblage was obtained.

A Norelco X-ray diffractometer using nickel-filtered Cu$K\alpha$ radiation and a scanning rate of 1° 2θ/min was used for routine phase analyses. For lattice parameter measurements a scanning rate of $\frac{1}{4}$° 2θ/min and a silicon external standard were employed. The silicon reflections between (311) and (620) and those produced from both $K\alpha_1$ and $K\alpha_2$ radiation were scanned both before and after at least every third unknown. The average values of these two runs were used to find the 2θ correction factors. A computer program which accepted the silicon 2θ values, the unknown (hkl), and 2θ values was used to calculate the lattice parameters and standard deviations. The pyrochlore reflections used were those with a 2θ equal to or greater than the (622) reflection and those by both $K\alpha_1$ and $K\alpha_2$ radiation. For each unknown at least 12 reflections were used. Formation of the pyrochlore structure was based on a comparison of systematic absences of reflections and on qualitative agreement of relative intensities with those expected for the pyrochlore structure.

Discussion of Results

$A^{2+}A^{4+}Ti_2O_7$ Compositions

Of the more than 300 pyrochlores reported in the literature none of the $A^{2+}A^{4+}B_2O_7$ type have been synthesized. Coughanour *et al.* (*13*) reported $CaZrTi_2O_7$ as a distorted pyrochlore with orthorhombic or lower symmetry. Pyatenko and Pudovkina (*14*) reported it as monoclinic but concluded that it was derived from the cubic CaF_2–CeO_2 structure. These data indicate that $CaZrTi_2O_7$ should not be considered as even a distorted pyrochlore. To determine if other compositions of the $A^{2+}A^{4+}B_2O_7$ type did indeed exist as pyrochlores, the compositions listed in Table I were prepared.

Those compositions with an average radius for the two A-type cations which are larger than about 0.98 Å and smaller than 0.83 Å, when coupled with Ti^{4+} can be assumed to be nonpyrochlore formers. This was confirmed experimentally. Of the compositions with average radii between these two limits a dependence upon the difference in radii of the two cations was apparent. A difference (Δr) of approximately 0.23 Å or greater apparently induced too high a distortion for formation of the pyrochlore structure. Differences in charge, electronic configuration, and polarization also play a part but, in most cases, size plays the major role. Compositions with $A^{2+}A^{4+}$ as SrHf, SrSn, PbHf, and PbSn, although having average radii in the pyrochlore range, were not prepared since they all had a Δr larger than either of the combinations SrZr or PbZr, which did not form as pyrochlores.

$CaCeTi_2O_7$ was unusual since it dissociated above 1300°C to $CaTiO_3$, CeO_2, and an unidentified phase. Knop *et al.* (*15*) claimed that this composition did not form a pyrochlore, but their final heat treatment was 1400°C, well above the dissociation temperature.

The composition $CdThTi_2O_7$, when heat treated at 1250°C/24 hr in a sealed platinum tube, yielded a pyrochlore plus a small amount of thoria. With increasing times of reaction the amount of thoria approached a lower limit and an unknown phase appeared. Apparently a pyrochlore of the type $\square_xCdTh_{1-x}Ti_2O_{7-2x}\square_{2x}$ can be formed easily where x must be slightly greater than

TABLE I

COMPARISON OF $A^{2+}A^{4+}Ti_2O_7$-TYPE COMPOSITIONS

$A^{2+}A^{4+}$	$\bar{r}$ (Å)	$r = r_{A^{2+}} - r_{A^{4+}}$ (Å)	Final heat treatment (°C/hr)	Cubic pyrochlore
CaTh	0.97	0.06	1700/8	No
CaCe	0.94	0.13	1250/144	Yes $a_0 = 10.211 \pm 2$ Å
CaZr	0.86	0.28	1450/48	No
CaHf	0.86	0.29	1450/48	No
CaSn	0.85	0.31	1350/48	No
CaTh	0.95	0.01	1250/96	No
CdCe	0.91	0.08	1150/24	Yes $a_0 = 10.1365 \pm 4$ Å
CdZr	0.84	0.23	1350/48	$a_0 = 10.02 \pm 1$ Å
CdHf	0.83	0.24	1250/96	No
CdSn	0.82	0.26	1250/24	No
SrZr	0.95	0.46	1700/8	No
PbZr	0.96	0.47	1350/48	No

zero. The actual limits of x were not determined but most likely it does not exceed 0.5.

One other interesting composition in this series was $CdHfTi_2O_7$. This composition formed with a powder pattern identical to that of a pyrochlore except that the (222) and (440) reflections were each split into two components, indicating a possible rhombohedral distortion. Splitting of the (311) reflection was not noted possibly due to its low intensity. The average size for Cd^{2+} and Hf^{4+} was very close to the lower limit of the A cation size for titanates, and a distorted pyrochlore was therefore not unexpected.

The composition $CaHfTi_2O_7$ gave an X-ray diffraction pattern similar to that of $CaZrTi_2O_7$, but the reflection at 2.98 Å was missing and the remaining reflections were grouped around those of a pyrochlore more so than the reflections of $CaZrTi_2O_7$. The substitution of Sn^{4+} for Ti^{4+} in $CaZrTi_2O_7$ produced an effect similar to the substitution of Hf^{4+} for Zr^{4+}. The X-ray diffraction pattern of $CaZrSn_2O_7$ was very similar to that of $CaHfTi_2O_7$. This was similar to the indication that larger cations will produce less distorted eightfold coordination polyhedra as reported by McCauley and Hummel (*16*) and by Knop *et al.* (*17*).

$A^{1+}A^{3+}Ta_2O_7$ *Compositions*

A phenomenon similar to that observed in the $A^{2+}A^{4+}Ti_2O_7$ compositions was not found for the $A^{1+}A^{3+}Ta_2O_7$-type compositions. Various combinations of an alkali and a rare earth, Y, Sc, or Bi were prepared with average radii for the A cation ranging from 1.22 to 0.79 Å. The Δr for these compositions ranged from 0.00 to 0.52 Å. Although the A cations of these compositions had the proper average radius for pyrochlore formation and very small differences (Δr), none formed as pyrochlores. All these compositions formed an alkali tantalate plus a rare earth tantalate or an unidentified phase. The actual compositions prepared and the heat treatments can be found in Ref. (*9*). Aleshin and Roy (*18*) reported similar findings for the composition $NaYNb_2O_7$.

Chincholkar (*19*) reported a group of $A^{1+}A^{3+}B_2O_7$ (A^{1+} = Li, Na, or K; A^{3+} = La, Nd, Sm, Gd, Dy, or Y; and B^{5+} = Nb, Ta, or V) pyrochlores using preparation techniques similar to those of the writers except his final heat treatment was 400–500°C lower. Our samples were checked by X-ray diffraction at various intermediate temperatures from 850 up to 1700°C and no indication of pyrochlore formation was found. It was found, however, that a deficient pyrochlore with the composition $\square_x Na_{1-x}SmTa_2O_{7-\frac{1}{2}x}\square_{\frac{1}{2}x}$ could be formed by heat treating in air to 1350°C/24 hr before final treatment at 1700°C/8 hr in a sealed platinum tube ($a_0 = 10.331 \pm 5$ Å). The same initial composition when treated in air to only 1150°C/24 hr and then to 1700°C/8 hr in a sealed platinum tube did not produce a pyrochlore but formed $NaTaO_3$ plus $SmTaO_4$. Using NH_4F as a mineralizer with this composition did not help in the formation of a stoichiometric pyrochlore. It was believed that a portion of the alkali had volatilized at 1350 but not at 1150°C before the final treatment at 1700°C, thus producing a deficient pyrochlore when heated to the higher temperature. A comparison of the lattice parameters of our $\square_x Na_{1-x}SmTa_2O_{7-\frac{1}{2}x}\square_{\frac{1}{2}x}$ and Chincholkar's $LiSmTa_2O_7$ indicates that they are too close for one to contain stoichiometric amounts of Na^{1+} and the other Li^{1+}. If both compositions had lost some alkali, then the lattice parameters (and average A cation size) would approach one another. Thus it is believed that Chincholkar's pyrochlores are probably nonstoichiometric. Sleight (*20*), unsuccessfully, tried to reproduce Chincholkar's results but gave no explanation as to why Chincholkar may have formed pyrochlores.

The composition $NaSbSb_2O_7$ has been reported to be a pyrochlore by Trofimov *et al.* (*21*); however, this composition may also be a deficient pyrochlore according to the work of Stewart and Knop (*22*).

$A^{1+}A^{3+}B^{4+}B^{6+}O_7$ *Compositions*

Compositions of the type $A^{1+}A^{3+}B^{4+}B^{6+}O_7$ were interesting since $A_2^{1+}B_2^{6+}O_7$-type pyrochlores cannot be formed (*18*). $LiSmZrMoO_7$, $NaSmZrMoO_7$, and $NaLaZrMoO_7$ ($a_0 = 10.800 \pm 2$ Å) were all prepared as pyrochlores. This is believed to be the first report of pyrochlores of this type. Due to the multivalent nature of Mo and the volatility of the alkalies, there is a possibility that these compositions were not stoichiometric even though starting compositions were stoichiometric and single-phase pyrochlores resulted.

The combinations LiSm, NaSm, and NaLa span the range of possible average A cation sizes and the combination $Zr^{4+}Mo^{6+}$ places these compositions in the midregion of the pyrochlore stability field. The B cation average size of these compositions places them more toward the region of regular octahedra around the B cations than the corresponding $A^{1+}A^{3+}Ta_2O_7$ compositions. This indicates that the characteristics of the BO_6 polyhedra are more important in determining whether or not a pyrochlore will form.

$A^{2+}A^{3+}B^{4+}B^{5+}O_7$ *Compositions*

The crystalline solubility between the pyrochlore and the weberite structures was investigated and is a good example of the solubility between the pyrochlore and a similar structure. The weberite structure (*2, 23*) is quite similar to the pyrochlore structure in that both are composed of $(BO_6)^{n-}$ polyhedra, but rather than having all the $(BO_6)^{n-}$ groups linked on all corners, as in the pyrochlore, half are linked on all corners and half on four corners. The site symmetry for the larger cations is therefore lowered from D_{3d} in the pyrochlore to C_s in the weberite. A region of pyrochlore crystalline solution was found to extend from 0 to approximately 50 mole% $Ca_2Sb_2O_7$ in a matrix of $Gd_2Sn_2O_7$ prepared at 1200°C (Table II). The region from 50 to 95 mole% $Ca_2Sb_2O_7$ gave an X-ray diffraction pattern similar to that of a pyrochlore but the (311), (222), (400), and (440) reflections were all split into two components. This splitting,

TABLE II

VARIATION OF LATTICE PARAMETER IN $Ca_xGd_{2-x}Sn_{2-x}Sb_xO_7$ COMPOSITIONS

Composition (x)	Lattice parameter (Å)
0.0	10.460±1
0.1	10.434±2
0.2	10.428±2
1.0	10.345±5

which increased with increasing amounts of $Ca_2Sb_2O_7$, indicated the possibility of a trend toward the orthorhombic symmetry of the weberite structure. The region from 95 to 100 mole% $Ca_2Sb_2O_7$ was not investigated. Thus a pyrochlore with the composition $Ca_xGd_{2-x}Sn_{2-x}Sb_xO_7$ with $x = 0$ to 1 could be formed. A large number of $A^{2+}A^{3+}B^{4+}B^{5+}O_7$-type pyrochlores have been reported by Belyaev *et al.* (*24–26*) and by Fedorov *et al.* (*27*), not all of which would be expected to readily form pyrochlores and thus the formation of solutions between the pyrochlore and weberite structures is not surprising.

The interesting feature of these compositions was the large amount of calcium they contained. Compositions such as $Ca_2Nb_2O_7$ and $Ca_2Ta_2O_7$ do not form the pyrochlore structure as reported by Brandon and Megaw (*28*) and by Rosén and Westgren (*29*), respectively. Since crystalline solutions, however, can be formed between the pyrochlore and these compositions, they probably have similar structures. An interesting crystal chemical fact is that although $La_2Ti_2O_7$ (*30*) and $Ca_2Ta_2O_7$ both do not form pyrochloes the composition CaLaTiTaO$_7$ does. Apparently the addition of $Ca_2Ta_2O_7$ to $La_2Ti_2O_7$ is sufficient to bring the average A and B cation radii into the pyrochlore range and the addition of $La_2Ti_2O_7$ to $Ca_2Ta_2O_7$ is sufficient to provide the distortion needed for the $Ca_2Ta_2O_7$-structure not to form. This can be explained further if one considers the amount of distortion away from D_{3d} symmetry, the electronic configurations, and the electronegativities of the cations involved. The composition $Ca_2Ta_2O_7$ lies in a region of the pyrochlore stability field that possesses reasonably high distortion of the eightfold coordination polyhedra while still maintaining D_{3d} symmetry. This being the case, the D_{3d} site still desires directional bonding more so than nondirectional bonding. Ca^{2+}, having an Ar electronic configuration and a relatively low electronegativity, tends toward nondirectional or ionic bonding. Thus a structure other than pyrochlore is more favorable for $Ca_2Ta_2O_7$. As $La_2Ti_2O_7$ is added to $Ca_2Ta_2O_7$, however, the average electronic configuration and electronegativity of the $Ca^{2+}La^{3+}$ combination become more favorable to directional bonding and the composition is shifted to a region of the stability field which will accept a more nondirectional bonding. Thus the pyrochlore structure becomes the more favorable.

Summary

For $A^{2+}A^{4+}Ti_2O_7$-type compositions, it was found that an upper limit of 0.23 Å for the size difference of the A cations existed for pyrochlore formation. $A^{1+}A^{3+}Ta_2O_7$-type pyrochlores could not be prepared, in contradiction to the work of Chincholkar. Due to the volatility of alkali it is quite possible that compositions believed to be pyrochlores are actually nonstoichiometric.

LiSmZrMoO$_7$, NaSmZrMoO, and NaLaZrMoO$_7$ were prepared as pyrochlores for the first time.

Combinations of $Gd_2Sn_2O_7$ (pyrochlore) and $Ca_2Sb_2O_7$ (weberite) showed that a pyrochlore partial crystalline solution series formed from 0 to about 50 mole% $Ca_2Sb_2O_7$.

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