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Synthesis of New High-Pressure Pyrochlore Phases

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Compounds with the pyrochlore structure and the formula $A^{III}_2B^{IV}_2O_7$ (where A = rare earth ions and B = Ti, Ru, Ir, Tc, Sn, Hf, Zr, and Pb) have previously been reported by several investigators.¹⁻¹² Hoekstra and Siegel have recently reported the synthesis of

$Tl_2Pt_2O_7$.⁹ In this paper we describe the synthesis of a new series of pyrochlore compounds with the formula $A_2Ge_2O_7$. These compounds, produced at elevated temperatures and pressures, further illustrate the extension of the stability field of a structure by the use of high pressure.

Experimental Section

The starting materials were high-purity oxides. GeO_2 (Spex Industries) of 99.999% purity was thoroughly mixed with In_2O_3 , Tl_2O_3 (Spex Industries, 99.999%), and the rare earth oxides (Lindsay Chemical Division, American Potash and Chemical Corp.) of at least 99.9% purity. These samples were heated at 1100° for 4 hr at a pressure of 65 kbars and rapidly quenched. $In_2Ge_2O_7$ and $Tl_2Ge_2O_7$ were prepared at 1250 and 900°, respectively. The details of the technique have been published previously.^{13,14} The products were recovered as highly dense, sintered pellets with a grain size of ~0.05 mm. An attempt to prepare $Sm_2Ge_2O_7$ resulted in an unidentified product; no trace of a pyrochlore phase could be found in the X-ray pattern.

An X-ray diffraction pattern of $In_2Ge_2O_7$ was taken using a Guinier-de Wolff camera with a KCl internal standard. The films were read on a Mann film reader and d values were calculated using $\lambda(Cu K\alpha_1) = 1.54051 \text{ \AA}$ and $a(KCl) = 6.2931 \text{ \AA}$. A cell dimension of $9.711 \pm 1 \text{ \AA}$ for $In_2Ge_2O_7$ was determined by a least-squares refinement of 10 reflections. X-Ray patterns of other germanates were taken using a Debye-Scherrer camera of 114.6-mm diameter and $Cu K\alpha$ radiation. Cell dimensions of these compounds were obtained by a least-squares refinement using a Nelson-Riley function. Table I presents the powder diffraction data for the new germanates. Observed intensities are given only for $In_2Ge_2O_7$; intensities for the remaining pyrochlores are similar. Although merely indexing powder patterns does not represent proof of structure type, it should be noted

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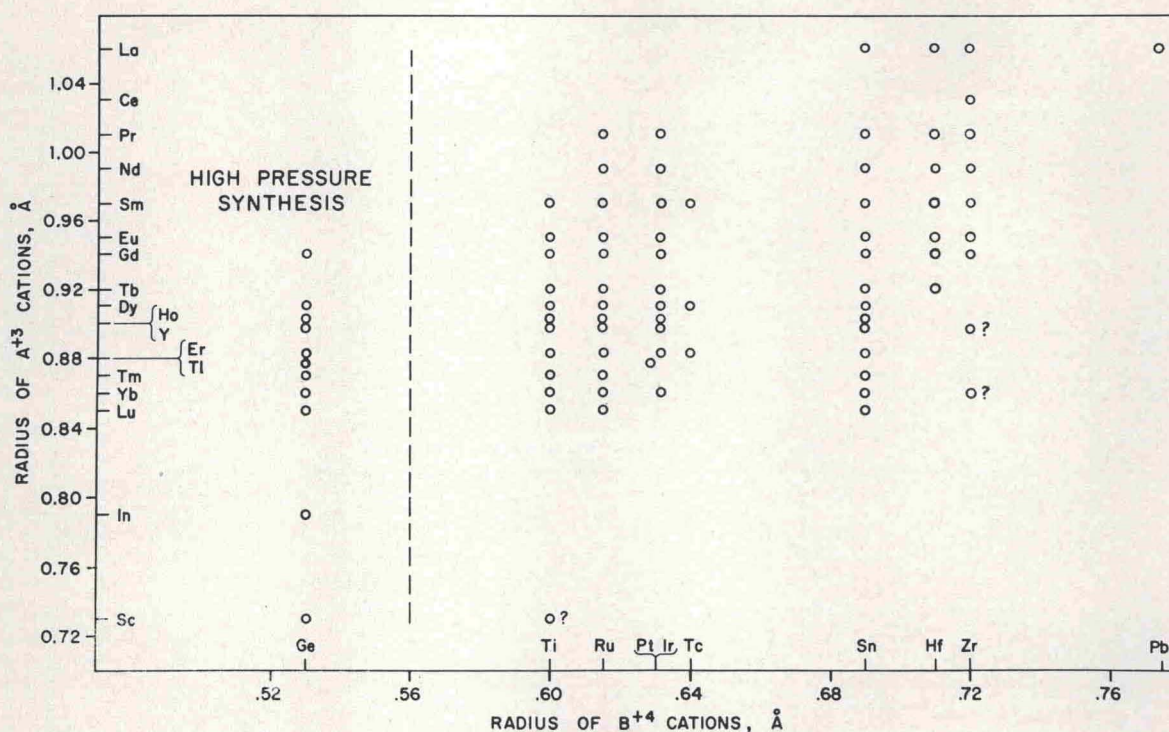
Figure 1.—Stability field for $A^{III}_2B^{IV}_2O_7$ pyrochlores.

TABLE I

$\text{In}_2\text{Ge}_2\text{O}_7$			$\text{Sc}_2\text{Ge}_2\text{O}_7$		$\text{Y}_2\text{Ge}_2\text{O}_7$		$\text{Lu}_2\text{Ge}_2\text{O}_7$		$\text{Yb}_2\text{Ge}_2\text{O}_7$		$\text{Tm}_2\text{Ge}_2\text{O}_7$		$\text{Er}_2\text{Ge}_2\text{O}_7$		$\text{Tl}_2\text{Ge}_2\text{O}_7$		$\text{Ho}_2\text{Ge}_2\text{O}_7$		$\text{Dy}_2\text{Ge}_2\text{O}_7$		$\text{Gd}_2\text{Ge}_2\text{O}_7$		
H	K	L	d	I	d		d		d		d		d		d		d		d		d		
1	1	1	5.604	10	5.540		5.695		5.665		5.623		5.684		5.677		5.753		5.717		5.733		5.753
3	1	1	2.927	10	2.890		2.958		2.956		2.950		2.967		2.966		2.979		2.981		2.991		3.004
2	2	2	2.803	100	2.767		2.856		2.831		2.826		2.842		2.844		2.852		2.857		2.865		2.875
4	0	0	2.427	70	2.396		2.472		2.453		2.449		2.461		2.462		2.470		2.475		2.480		2.492
3	3	1			2.199		2.269		2.249		2.247		2.258		2.258		2.266		2.270		2.278		2.289
4	2	2	1.982	5	1.957		2.017		2.000				2.007		2.007		2.200		2.022				2.039
5	1	1																					
3	3	3	1.869	15	1.845				1.887		1.887		1.894		1.896		1.901		1.904		1.909		1.924
4	4	0	1.717	85	1.695		1.749		1.733		1.734		1.740		1.742		1.746		1.750		1.754		1.763
5	3	1	1.642	10	1.620		1.675		1.657		1.658		1.663		1.666		1.669		1.674		1.675		
5	3	3															1.505						
6	2	2	1.464	80	1.446		1.491		1.478		1.479		1.484		1.487		1.487		1.492		1.496		1.504
4	4	4	1.402	25	1.384		1.428		1.415		1.417		1.421		1.423		1.424		1.428		1.432		1.441
7	1	1			1.343				1.374		1.375		1.377		1.381		1.382		1.385		1.389		1.393
7	3	1			1.249		1.288		1.276		1.278		1.282		1.284		1.285		1.289		1.292		1.300
8	0	0			1.199		1.237		1.226		1.228		1.230		1.232		1.234		1.237		1.240		1.249
7	3	3					1.209		1.198		1.200		1.202		1.204		1.206		1.210		1.212		1.220
6	6	0					1.166								1.161				1.166				
7	5	1							1.132				1.136		1.138		1.140						
6	6	2			1.100		1.134		1.125				1.129		1.131		1.132		1.136		1.138		1.145
8	4	0			1.072		1.106		1.096		1.099				1.103		1.103		1.107		1.109		1.116

TABLE II

CELL DIMENSIONS ($\pm 2 \text{ \AA}$) OF GERMANATE PYROCHLORES

Compound	a, Å	Compound	a, Å
Gd ₂ Ge ₂ O ₇	9.995	Yb ₂ Ge ₂ O ₇	9.829
Dy ₂ Ge ₂ O ₇	9.929	Lu ₂ Ge ₂ O ₇	9.813
Ho ₂ Ge ₂ O ₇	9.903	Y ₂ Ge ₂ O ₇	9.897
Tl ₂ Ge ₂ O ₇	9.872	In ₂ Ge ₂ O ₇	9.711
Er ₂ Ge ₂ O ₇	9.864	Sc ₂ Ge ₂ O ₇	9.600
Tm ₂ Ge ₂ O ₇	9.845		

that all of the compounds reported here did show lines where $h + k + l = 2n + 1$. Consequently, these compounds are not disordered fluorite types which is apparently the case for $Sc_2Ti_2O_7$ ¹¹ and $La_2Ce_2O_7$.¹⁵ Table II gives the refined cell dimensions.

A two-probe resistivity measurement on a sintered piece of $In_2Ge_2O_7$ indicated a room-temperature resistivity greater than $3 \times 10^{10} \text{ ohm-cm}$. Exposure to strong incandescent light reduced the resistivity by a factor of about 100.

Dta experiments performed on the new pyrochlore phases in air showed the transformations to occur irreversibly and endothermically above 1000° for all phases except $Tl_2Ge_2O_7$, $Lu_2Ge_2O_7$, and $Sc_2Ge_2O_7$. $Tl_2Ge_2O_7$ underwent an endothermic change at 525° whereas $Lu_2Ge_2O_7$ and $Sc_2Ge_2O_7$ were not found to transform at temperatures as high as 1200° .

Discussion

The enlargement of structure fields by means of pressure has been demonstrated for rutile,¹⁶ corundum,¹⁷ and perovskite-structure¹³ types. Synthesis of the pyrochlore germanates provides another example of the extension of the stability field of a structure by the use of pressure. In Figure 1 the stability field of 3-4 pyrochlores is illustrated by plotting the radius of A^{3+} vs. the radius of the B^{4+} ions for all reported pyro-

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chlores.¹⁻¹² Sixfold radii of A ions¹⁸ were used because no set of eightfold radii was available. Previously the smallest A and B ions to be found in the pyrochlore structure were Lu^{3+} and Ti^{4+} , respectively. In these new pyrochlores two new A ions, In^{3+} and Sc^{3+} , and one new B ion, Ge^{4+} , have been introduced. Although $\text{Sc}_2\text{Ti}_2\text{O}_7$ was reported to be a pyrochlore, Brisse¹¹ has shown that it is actually a disordered fluorite. The new phases $\text{Sc}_2\text{Ge}_2\text{O}_7$ and $\text{In}_2\text{Ge}_2\text{O}_7$ both have smaller cell dimensions than the value 9.801 quoted by Hoekstra and Siegel⁹ as a "virtual lower limit" for the pyrochlore structure. Brisse and Knop¹⁹ found that the stability of the pyrochlore structure depends upon the ratio of the ionic radii, r_A/r_B , and that the upper limit of this ratio at normal conditions is 1.55. This study indicates that pressure extends this ratio to approximately 1.8 ($r_{\text{Gd}}/r_{\text{Ge}}$).

The germanates are believed to be formed by taking advantage of the difference in compressibility between the oxygen anions and the A and B cations. Pressure

has been used to force a smaller ion into a structure by using compressibility differences in SiO_2 (rutile),²⁰ Lu_2O_3 (B rare earth oxide),²¹ MgGeO_3 (ilmenite),²² and InCrO_3 (perovskite).¹³ It might also be noted that $\text{In}_2\text{Ge}_2\text{O}_7$, InCrO_3 ,¹³ and InRhO_3 ¹³ are the first examples of compounds containing In^{3+} in greater than sixfold coordination.

It seems logical to assume that by the application of sufficient pressure one could make pyrochlores of the type $\text{A}_2\text{Si}_2\text{O}_7$. However, reaction of Sc_2O_3 and SiO_2 at 1500° and 65 kbars resulted only in the well-known $\text{Sc}_2\text{Si}_2\text{O}_7$ thortveitite phase. Apparently, higher pressures are necessary to force Si^{4+} from fourfold to sixfold coordination.

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