

Synthesis of Pyrosilicates and Pyrogermanates Having the Thortveitite Structure*

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Synthesis conditions and accurate cell dimensions for the pyrogermanates $\text{In}_2\text{Ge}_2\text{O}_7$, $\text{Sc}_2\text{Ge}_2\text{O}_7$, YInGe_2O_7 , $\text{LuInGe}_2\text{O}_7$, and the pyrosilicates $\text{ScGaSi}_2\text{O}_7$, $\text{ScFeSi}_2\text{O}_7$, and $\text{ScInSi}_2\text{O}_7$ having thortveitite-type structures are reported. Using these compositions and other compositions reported in the literature, approximate stability fields for $\text{A}_2^{3+}\text{B}_2^{4+}\text{O}_7$ and $\text{A}_2^{3+}\text{B}_2^{5+}\text{O}_7$ are outlined.

Introduction

Synthetic thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$) was prepared by Shannon and Sleight (1) and Ito and Johnson (2), and isotypic silicates were prepared by Warsaw and Roy (3), Ito (4), and Ito and Johnson (2). The compound, $\text{In}_2\text{Ge}_2\text{O}_7$, was prepared by Sarkisov, Khozhainov, and Lidin (5), but it was not recognized as belonging to the thortveitite group. The similarity of $\text{Sc}_2\text{Ge}_2\text{O}_7$ to $\text{Sc}_2\text{Si}_2\text{O}_7$ was recognized by Goldschmidt (6) in 1931 but not confirmed. Recently, high-pressure forms of $\text{In}_2\text{Ge}_2\text{O}_7$ and $\text{Sc}_2\text{Ge}_2\text{O}_7$ were found by Shannon and Sleight (1) to be of the pyrochlore type with eight-coordinated Sc^{3+} or In^{3+} and six-coordinated Ge^{4+} . In this paper we report the normal-pressure phases of $\text{In}_2\text{Ge}_2\text{O}_7$ and $\text{Sc}_2\text{Ge}_2\text{O}_7$ to be of the thortveitite type with six-coordinated In^{3+} or Sc^{3+} and four-coordinated Ge^{4+} . A structure refinement of synthetic $\text{Sc}_2\text{Si}_2\text{O}_7$ will be reported in a separate paper.

Experimental Section

The starting materials were high purity oxides. GeO_2 (5-9s %), SiO_2 (6-9s %), Sc_2O_3 (3-9s %), and In_2O_3 (5-9s %) were supplied by Spex Industries, Metuchen, N.J.; Lu_2O_3 (3-9s %), and Y_2O_3 (3-9s %) were supplied by the Lindsay

Chemical Div., American Potash and Chemical Corp., W. Chicago, Ill. The oxides were thoroughly mixed and then heated in one of two ways. $\text{In}_2\text{Ge}_2\text{O}_7$ and $\text{Sc}_2\text{Ge}_2\text{O}_7$, prepared by heating in Pt crucibles under atmospheric conditions at 1300° overnight, were recovered as white powders. The mixed germanates, YInGe_2O_7 and $\text{LuInGe}_2\text{O}_7$, were prepared by sealing the mixture of oxides in Pt tubes, externally pressurizing to 3 kbar, and heating to 1350° for 8 hr.

The silicate compositions were heated at 1500° for 1 hr at 65 kbar and rapidly quenched. The details of the technique were published previously (7). Both $\text{Sc}_2\text{Si}_2\text{O}_7$ and $\text{ScInSi}_2\text{O}_7$ were recovered as transparent colorless crystals about 0.2 mm in diameter. $\text{ScFeSi}_2\text{O}_7$ was obtained as light-green transparent crystals about 0.1 mm in diameter. The $\text{ScGaSi}_2\text{O}_7$ sample was a translucent white pellet.

X-ray diffraction patterns of the thortveitite phases prepared in this work and the $\text{RE}_2\text{Si}_2\text{O}_7$ ($\text{RE} = \text{Lu-Ho, Y}$) phases prepared by Ito and Johnson (2) were taken using a Hagg-Guinier camera by a procedure described earlier (7). Table I presents the powder diffraction data for $\text{Sc}_2\text{Si}_2\text{O}_7$, $\text{Sc}_2\text{Ge}_2\text{O}_7$, and $\text{In}_2\text{Ge}_2\text{O}_7$. Cell dimensions, obtained by least-squares refinement of the Guinier data using the extinctions for the monoclinic space group, $C2/m$, are given in Table II.

Discussion

The rare-earth silicates exhibit a high degree of polymorphism; consequently, much confusion over the identity of these phases has arisen in the litera-

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TABLE I

POWDER DIFFRACTION DATA FOR $\text{Sc}_2\text{Si}_2\text{O}_7$, $\text{Sc}_2\text{Ge}_2\text{O}_7$, AND $\text{In}_2\text{Ge}_2\text{O}_7$

$\text{Sc}_2\text{Si}_2\text{O}_7$				$\text{Sc}_2\text{Ge}_2\text{O}_7$				$\text{In}_2\text{Ge}_2\text{O}_7$			
Index	d _{calc}	d _{obs}	I _{obs}	Index	d _{calc}	d _{obs}	I _{obs}	Index	d _{calc}	d _{obs}	I _{obs}
1 1 0	5.0831	5.0822	20	1 1 0	5.1506	5.1460	15	1 1 0	5.2254	5.2240	65
0 0 1	4.5634	4.5612	10	0 0 1	4.7838	4.7854	2	0 0 1	4.8102	4.8117	65
1 1 1	3.1324	3.1333	80	0 2 0	4.3453	4.3419	40	0 2 0			
0 2 1	3.1101	3.1104	100	1 1 -1	3.8569	3.8552	10	1 1 -1			
2 0 -1	2.9225	2.9220	50	1 1 1	3.2350	3.2341	85	1 1 1	3.2675	3.2669	85
1 3 0	2.5869	2.5864	15	0 2 1	3.2165	3.2162	100	0 2 1			
2 2 0	2.5415	2.5415	15	2 0 0	3.1974	3.1966	20	2 0 0	3.2434	3.2445	100
2 0 1	2.3712	2.3713	2	2 0 -1	2.9725	2.9719	70	2 0 -1	3.0120	3.0127	100
0 0 2	2.2817	2.2812	2	1 3 0	2.6387	2.6385	15	1 3 0	2.6697	2.6696	90
1 3 1	2.1686	2.1684	40	2 2 0	2.5753	2.5751	45	2 2 0	2.6127	2.6126	90
0 4 0	2.1250	2.1251	10	2 2 -1	2.4534	2.4534	15	2 2 -1	2.4840	2.4840	2
2 0 2	2.0817	2.0818	20	2 0 1	2.4265	2.4266	10	2 0 1	2.4580	2.4576	50
2 2 1	2.0707	2.0705	15	1 3 -1	2.4032	2.4031	5	1 3 -1	2.4275	2.4276	60
3 1 1	2.0411	2.0411	30	0 0 2	2.3919	2.3921	5	0 0 2	2.4051	2.4047	55
0 4 1	1.9264	1.9262	10	1 1 -2	2.3303	2.3301	15	1 1 -2	2.3450	2.3445	70
2 2 -2	1.8695	1.8696	20	1 3 1				1 3 1	2.2510	2.2511	60
1 3 -2	1.7928	1.7929	10	0 4 0	2.1726	2.1727	20	0 4 0	2.1960	2.1961	20
2 4 -1				2 0 -2	2.1520	2.1518	5	2 0 -2	2.1706	2.1706	45
3 1 -2	1.7187	1.7184	10	2 2 1				2 2 1	2.1449	2.1447	30
3 3 0	1.6944	1.6947	15	0 2 2				0 2 2	2.1095	2.1093	25
3 3 -1	1.6885	1.6887	15	3 1 0	2.0702	2.0701	5	3 1 0	2.1038	2.1038	20
2 0 2	1.6848	1.6848	10	3 1 -1	2.0649	2.0650	30	3 1 -1	2.0957	2.0957	70
1 3 2	1.6398	1.6398	40	1 1 2	2.0378	2.0378	20	1 1 2	2.0535	2.0537	10
4 0 0	1.5855	1.5854	15	0 4 1	1.9782	1.9783	20	0 4 1	1.9977	1.9976	20
2 2 2	1.5662	1.5664	5	2 2 -2	1.9284	1.9284	30	2 2 -2	1.9459	1.9461	80
1 5 1	1.5178	1.5177	10	1 3 -2				1 3 -2	1.8714	1.8713	20
2 0 -3				3 1 1	1.7691	1.7692	10	3 1 1	1.7943	1.7943	5
4 2 -1	1.5068	1.5068	15	3 1 -2	1.7592	1.7591	10	3 1 -2			
3 3 1	1.5043	1.5041	2	2 4 -1	1.7540	1.7542	20	2 4 -1	1.7744	1.7747	40
3 3 -2	1.4920	1.4919	20	2 0 2	1.7427	1.7424	5	2 0 2	1.7600	1.7601	20
2 4 -2				3 3 0				3 3 0	1.7418	1.7421	40
4 2 0	1.4871	1.4869	5	3 3 -1	1.7169	1.7161	5	3 3 -1	1.7372	1.7374	40
4 0 -2	1.4612	1.4611	5	1 3 2	1.6982	1.6983	50	1 3 2	1.7129	1.7130	90
2 2 -3	1.4201	1.4203	5	1 5 0	1.6773	1.6772	5	1 5 0	1.6959	1.6962	40
0 6 0	1.4167	1.4168	10	4 0 -1				4 0 -1	1.6517	1.6520	5
1 1 3	1.3915	1.3916	10	2 4 1				2 4 1	1.6376	1.6375	2
1 3 -3	1.3659	1.3658	20	2 2 2	1.6175	1.6180	10	2 2 2	1.6337	1.6338	50
4 2 1	1.3340	1.3339	5	1 1 -3	1.6044	1.6043	5	1 5 -1	1.6285	1.6285	15
3 5 -0	1.3248	1.3244	2	4 0 0	1.5987	1.5988	20	4 0 0	1.6252	1.6253	30
3 5 -1	1.3220	1.3221	5	2 0 -3	1.5692	1.5695	5	0 4 2	1.6217	1.6219	2
				1 5 1	1.5554	1.5555	20	0 0 3	1.6034	1.6034	30
				3 3 1	1.5331	1.5333	15	2 0 -3	1.5798	1.5798	30
				3 3 -2	1.5267	1.5269	25	3 3 1	1.5536	1.5536	30
				4 2 -1	1.5228	1.5228	20	4 2 -1	1.5460	1.5455	65

ture. Ito and Johnson (2) found at least four polymorphs of $\text{Ho}_2\text{Si}_2\text{O}_7$ and $\text{Y}_2\text{Si}_2\text{O}_7$. Toropov, et al. (8-13) prepared many $\text{RE}_2\text{Si}_2\text{O}_7$ phases which,

however, were not characterized as to structure. Smolin and Shepelev have determined the structure of $\text{Gd}_2\text{Si}_2\text{O}_7$ (14). Felsche and Hirsiger (15) have

TABLE II
CELL PARAMETERS OF THORTVEITITE PHASES

Compound	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	β°	$V, \text{\AA}^3$
Sc ₂ Ge ₂ O ₇	6.5504 ± 4	8.6905 ± 4	4.9003 ± 3	102.514 ± 4	272.3
In ₂ Ge ₂ O ₇	6.6580 ± 4	8.7840 ± 5	4.9266 ± 3	102.480 ± 5	281.3
YInGe ₂ O ₇	6.830 ± 2	8.881 ± 2	4.910 ± 1	101.67 ± 2	291.7
LuInGe ₂ O ₇	6.764 ± 2	8.859 ± 2	4.916 ± 1	102.02 ± 2	288.1
ScGaSi ₂ O ₇	6.469 ± 1	8.268 ± 1	4.6591 ± 8	104.30 ± 1	241.5
ScFeSi ₂ O ₇	6.4414 ± 9	8.3800 ± 7	4.6697 ± 7	103.06 ± 1	245.6
Sc ₂ Si ₂ O ₇	6.5011 ± 4	8.5000 ± 4	4.6779 ± 2	102.700 ± 4	252.2
ScInSi ₂ O ₇	6.5627 ± 3	8.5499 ± 3	4.6916 ± 2	102.804 ± 3	256.7
In ₂ Si ₂ O ₇	6.6238 ± 9	8.5958 ± 9	4.7023 ± 8	102.94 ± 2	260.9
Lu ₂ Si ₂ O ₇	6.7655 ± 5	8.8369 ± 6	4.7121 ± 3	102.00 ± 6	275.6
Yb ₂ Si ₂ O ₇	6.7978 ± 3	8.8725 ± 4	4.7075 ± 2	101.98 ± 1	277.7
Tm ₂ Si ₂ O ₇	6.8268 ± 5	8.9073 ± 6	4.7058 ± 4	101.85 ± 1	280.0
Er ₂ Si ₂ O ₇	6.8476 ± 9	8.935 ± 1	4.7193 ± 6	101.74 ± 1	282.7
Y ₂ Si ₂ O ₇	6.8722 ± 7	8.9712 ± 8	4.7205 ± 4	101.75 ± 1	284.9
Ho ₂ Si ₂ O ₇	6.8779 ± 6	8.9762 ± 7	4.7235 ± 4	101.69 ± 1	285.6

recently found that the pyrosilicates of the larger rare-earth ions La–Sm have the $\beta\text{Ca}_2\text{P}_2\text{O}_7$ structure at high temperatures (1500°C) and the $\alpha\text{Sr}_2\text{P}_2\text{O}_7$ structure at low temperatures (1200°C). Since the structural relations among all these phases are not yet clear, it is difficult to prepare a reliable structure stability field for $\text{A}_2\text{B}_2\text{O}_7$ compositions.

However, the work of Ito and Johnson (2) and the identification of the pyrogermanates reported here allow us to outline approximately the stability field of the thortveitite structure. Figure 1 shows the fields for both $\text{A}_2^{3+}\text{B}_2^{4+}\text{O}_7$ and $\text{A}_2^{2+}\text{B}_2^{5+}\text{O}_7$ compositions. The pyrochlore field is drawn with solid lines because this field has been carefully determined

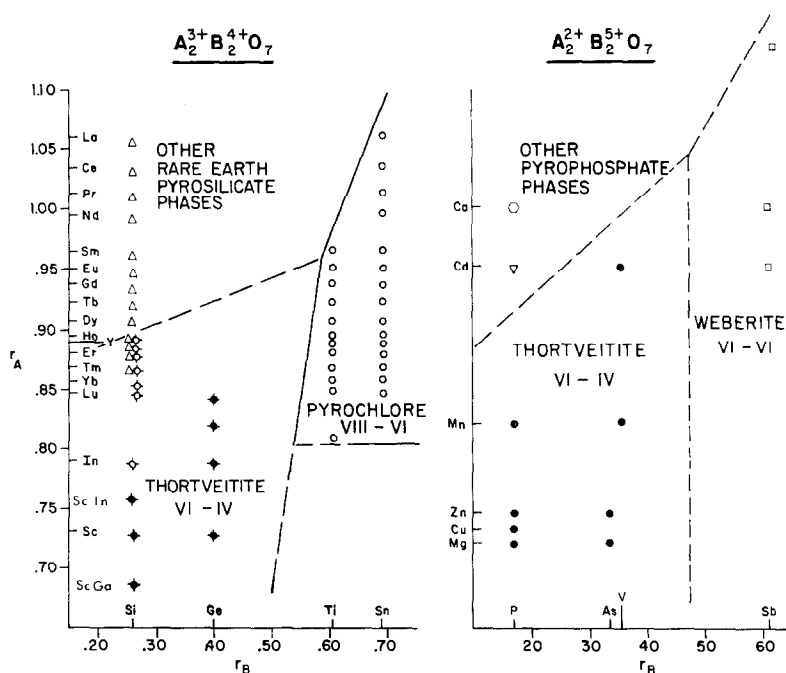


FIG. 1. Stability fields for $\text{A}_2\text{B}_2\text{O}_7$ compositions. Solid crossed circles represent thortveitite phases prepared in this work; open crossed circles represent thortveitite phases prepared by Ito and Johnson (2).

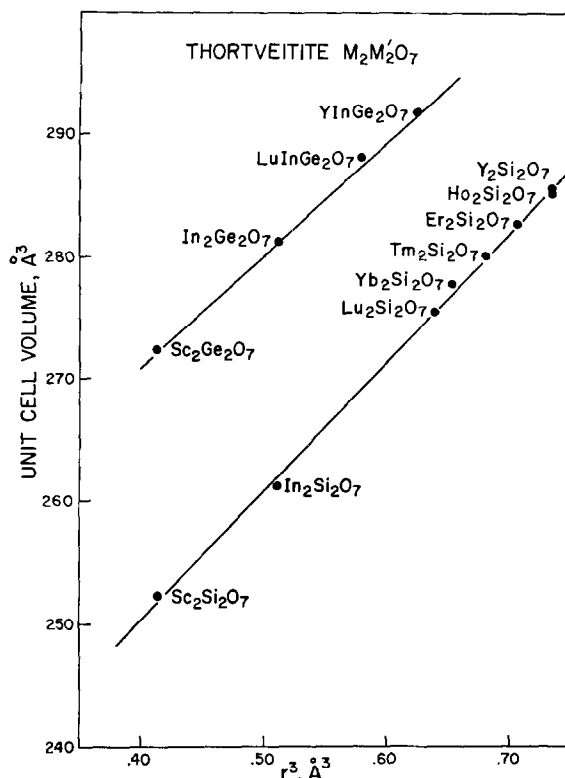


FIG. 2. Unit cell volume vs r^3 for phases having the thortveitite structure.

by Brisse (16). The other fields are more uncertain and are enclosed by dashed lines. The positive slope to the boundary between thortveitite and the larger RE pyrosilicates is assumed by similarity to other structure fields of ternary oxides (7, 16). The two compositions $\text{ScGaSi}_2\text{O}_7$ and $\text{ScFeSi}_2\text{O}_7$, are probably only stable at high pressures and represent a typical high-pressure extension of the field. The 2–5 thortveitites have been characterized structurally by Calvo et al. (17–20) and others (21, 22). The pyrophosphates are similar to the pyrosilicates and show considerable polymorphism. $\text{Cd}_2\text{P}_2\text{O}_7$ appears to have a unique structure (17). Although these stability fields are only approximate, it is possible to make some predictions. Other small rare-earth pyrogermanates as well as $\text{Mn}_2\text{As}_2\text{O}_7$ and $\text{Cd}_2\text{As}_2\text{O}_7$ should have the thortveitite structure. Larger RE pyrogermanates should have either the $\beta\text{Ca}_2\text{P}_2\text{O}_7$ or the $\alpha\text{Sr}_2\text{P}_2\text{O}_7$ structure.

It has been shown elsewhere (23) that plots of r^3 vs V for isotopic series are generally linear. Figure 2 shows that this relationship also holds

quite well for the isotopic pyrosilicates and pyrogermanates. The mixed phases such as $\text{LuInGe}_2\text{O}_7$ and YInGe_2O_7 fit on such plots whereas $\text{ScGaSi}_2\text{O}_7$ and $\text{ScFeSi}_2\text{O}_7$ do not. This may reflect the fact that the latter two phases are high-pressure compounds.

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