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SYNTHESIS AND STUDY OF YTTRIALITE

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ABSTRACT

The rare earth pyrosilicates, $R_2^{3+}Si_2O_7$ (R^{3+}=Sc,In,RE; where RE=Lu,Yb,Tm,Er, Ho,Y,Dy, and Gd) were synthesized at temperatures from 900–1600°C in air. A solid-solution series exists between $Sc_2Si_2O_7$ (thortveitite) and β-$Y_2Si_2O_7$ at 1300°C in air and at 700°C under 2.5 kbar. The compositional range from Y_2SiO_5—$Y_2Si_2O_7$—$Y_2Si_3O_9$ was investigated at temperatures from 900 to 1500°C. "High-yttrialite" was identified as α-$(Y,RE)_2Si_2O_7$ from the results of recrystallization of the natural minerals and by direct synthesis from sodium-free gels both in air and under water pressure. The phase described as "low yttrialite" is a complex silicate of approximate formula $R(Y,RE)_5Si_6O_{21}$ where R includes ions of great variety, such as H^+, Na^+, Fe^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} and Zr^{4+}.

INTRODUCTION

This investigation was undertaken in order to give reasonable interpretations to the conflicting experimental results given in the literature and to establish yttrialite as a well defined mineral.

Yttrialite, metamict yttrium silicate, $Y_2Si_2O_7$, was first found at Llano, Texas (Hidden and Mackintosh, 1889). Several other localities were reported subsequently (Hata, 1938; Nishimura and Ueda, 1954; Protosenko, 1962). Despite its early discovery, crystallographic characterization of yttrialite has been delayed because of its occurrence in the metamict state. The formula for yttrialite has been established as $(Y,RE^{3+},Th^{4+},M^{2+})_2Si_2O_7$ by chemical analysis.

Nishimura and Ueda (1954) reported that the yttrialite from Komenono is isostructural with thortveitite, $Sc_2Si_2O_7$, monoclinic $C2/m$; Omori and Hasegawa (1953) indicated that the yttrialite from Suishoyama has a crystal structure similar to pyrochlore, isometric, $Fd3m$; Protosenko (1962) gave X-ray powder data obtained from heated yttrialite from the USSR at 920 and 1000°C. Faria (1964) reported the results of heating of yttrialite from several localities and described two phases, y(low) and α(high). The former is identical with the phase given as yttrialite by Protosenko.

Warshaw and Roy (1964) synthesized α(low) and β(high) $Y_2Si_2O_7$ with a transition temperature at 1240°C. The former is identical with α high temperature phase given by Lima de Faria, but the relation to yttrialite was not mentioned. In his recent review of rare earth silicates Sidorenko (1966) stated that "yttrialite is not isostructural with

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thortveitite because of the limited isomorphism between Sc and Y pyrosilicates and the different behavior during heating". More recently, Bondar and Toropov (1967) reported that a synthetic compound identical with a mineral described as yttrialite by Protosenko can only be produced by the substitution of 13 percent of ThO_2 in a starting mixture of $Y_2Si_2O_7$, and suggested that thorium may be an essential component of yttrialite.

A new experimental study was carried out using yttrialite specimens from the original locality of Baringer Hill, Llano, Texas, and direct synthesis from precipitated hydrous silicates prepared by a new method using a cation exchange resin. The work was later extended to the study of polymorphism of rare-earth pyrosilicates with special emphasis on the lower-temperature region from 900 to 1500°C.

EXPERIMENTAL PROCEDURE

For the synthesis of rare-earth silicates (below 1200°C), preparation of reactive amorphous silicates containing stoichiometric amounts of the elements is needed, because at low temperature certain mixtures of oxides do not react (Toropov, Bondar, Sidorenko and Kololeva, 1965) within a reasonable time of heating. Furthermore, preparation of alkali-free precipitated hydrous silicates is necessary for the accurate determination of phase transition temperatures of rare-earth silicates, because small amounts of sodium (less than 0.1%) can lower the transition temperature as much as 100°C. For this reason, starting materials prepared by the neutralization or hydrolysis of reagents containing alkalies (Luth and Ingamells, 1965; Roy, 1956) could not be used without removing the alkalies by the tedious process of electrodialysis. In this respect, a method given by Crofts and Marshall (1967) using hydrolysis of pure silicon tetrachloride and aluminum chloride for aluminosilicates seemed promising, but there are two inherent difficulties in the technique: (1) volatile liquid must be injected through a diaphragm with a syringe, and (2) not all of the desired chlorides are readily available.

We adopted a relatively simple resin method originally developed for analytical procedure for the separation of pure silicic acid from cations (Shehyn, 1957). Relatively pure and almost alkali-free hydrosilicates are precipitated at pH 9 with ammonia, from solutions containing pure silicic acid and rare-earth chlorides. Comparison of purities of hydrated yttrium silicates prepared from both alkali-free and alkali-containing solutions is given in Table 1. This shows the satisfactory removal of most ions, particularly sodium, to less than 1 ppm by the resin method. The precipitation from sodium silicate solutions left about 100 times more residual sodium. Both sodium values are much less than those reported in the gels (sodium content 0.1%) prepared by Luth and Ingamells (1965) for supposedly sodium-free composition. This resin method may have wide applicability for silicate syntheses; the detailed procedure is therefore described in the following section.

Preparation of the pure silicic acid solutions. Approximately 150 ml of H form resin (Dow X 50, W-X12 200 mesh) was transferred into a beaker containing 200 ml of dilute sodium silicate solution (20 millimole of C.P. $Na_2SiO_3 \cdot 9H_2O$), and stirred by a magnetic stirrer for 2 hours. The pH of the resulting solution was between 2.5 and 3.0. Practically all the cations were removed and most of the CO_2 absorbed in the sodium silicate was evolved. After the resin had settled, the solution was passed through a column, 2″ OD and 10″ in

TABLE 1. SPECTROGRAPHIC ANALYSIS OF THE HYDROSILICATES USED FOR THE SYNTHESES. ANALYST. G. BOMINI, JARREL ASH CO., WALTHAM, MASS. (1967)

Range of concentration	Sample prepared using resin purified silicic acid	Sample prepared using sodium silicate solution
10%	Y, Si	Y, Si
0.01–0.001%	– –	*Na*, Ti, Mn
0.001–0.0001	Ti, Mg	B, Mg, Al
less than–0.0001	B, Al, Ca, Fe, Cu, Be, *Na*, Cr, As, Sn, Pb	Be, Ca, Cr, Cu, Sn, Pb, Ag

length, containing 1″ of the same H-form resin to complete the cation separation. Approximately 400 ml of distilled water was used for the total washing process of the resin. The eluent was transferred to a volumetric flask (1 l.) and standardized by the gravimetric method. This silicate acid solution can be stored safely in a plastic bottle for several weeks without sign of gelatinization.

Preparation of the amorphous hydrous rare-earth silicates. A slightly acid solution containing stoichiometric amounts of silicic acid and rare-earth (including yttrium) chlorides was heated to boiling and conc. ammonia was added gradually to bring the pH to 9. The solution was boiled for five minutes, then cooled to room temperature. The precipitates were then decanted, centrifuged and completely dried in an oven at 110°C. No washing was required, because the solution was essentially free from alkali. The final materials contained approximately 30 percent H_2O, but were nonhygroscopic. They remained reactive for a period of more than one year when kept in a tightly covered vial. Chemical analyses showed that the precipitates contained Si and rare earth ions in the desired ratio. Slight Si deficiency was common, and a small adjustment of starting ratios was required for accurate work.

Synthesis. Heating was carried out in a furnace made of Pt-20 percent Rh winding at temperatures ranging 900–1350°C. Platinum foil was used as a container. An induction heater was used to obtain temperatures above 1400°C. The products were air quenched and examined by X-ray powder diffraction.

The results of the experiments with the original specimens of yttrialite from Llano, Texas, and of thalenite from Suishoyama, Japan, are given in Table 2. Comparison of the X-ray powder data of heated yttrialite and the synthetic α-$Y_2Si_2O_7$ and β-$Y_2Si_2O_7$ of the present study and of the previously reported works are made in Table 3.

The results of partial phase-syntheses of $M_2^{3+}Si_2O_7$ (M^{3+}=Y,Lu,Yb,Tm,Er,Ho,Dy, Gd,In,Sc, $Ho_{50}Dy_{50}$,$Ho_{75}Dy_{25}$), Y_2SiO_5 and $Y_2Si_3O_9$ in air (900–1600°C) and under hydrothermal conditions (550–650°C, 2 kb) are deposited with the National Auxiliary Publications Service, American Society for Information Services.[1] Partly indexed X-ray powder data of the following identified compounds were also submitted to the ASTM powder data file: Z-$Y_2Si_2O_7$, γ-$Y_2Si_2O_7$, γ-$Er_2Si_2O_7$, δ-$Dy_2Si_2O_7$, δ-$Y_2Si_2O_7$, Y_2SiO_5 (X_1) and Y_2SiO_5 (X_2).

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[1] Order NAPS Document 00100 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N.Y. 10001; remitting in advance $1.00 for microfiche or $3.00 for photocopies.

TABLE 2. RESULTS OF THE HEATING EXPERIMENTS OF YTTRIALITE FROM LLANO, TEXAS, AND THALENITE FROM SUISHOYAMA, JAPAN

Minerals and Locality	Temp. of heating (C°)	Duration (hr.)	Pressure	Phase identified
Yttrialite Llano County, Texas	900	24	1 bar	amorphous
	1,000	24	1 bar	y
	1,200	24	1 bar	α
	1,350	3	1 bar	α
	1,400	1/2	1 bar	α
	1,400	1/2	1 bar	α & melt
	450	24	2 kb	α (v. weak)
	500	24	2 kb	α
	620	24	1 kb	α
	680	24	2.5 kb	α
Thalenite Suishoyama, Japan	900	24	1 bar	
	1,050	62	1 bar	β & thalenite (weak)
	1,465	1/2	1 bar	γ
	1,600	1/2	1 bar	γ
	520	24	1 kb	thalenite
	630	24	2 kb	thalenite

NOMENCLATURE

Yttrialite. Our heating experiments on the original yttrialite samples gave the same two crystalline phases as reported by Lima de Faria (1964) (Table 3) the low form, y, stable at 900–1000°C and the high form, α, stable between 1200 and 1450°C. The former phase was suggested by Protosenko (1962) to be ytrrialite. Lima de Faria also assumed that the lower y-phase may be an original crystalline yttrialite, because it develops first on heating. However, in the compositional range of the Y_2O_3-SiO_2 system studied, we found that a single y-phase is stable only at a chemical composition richer in SiO_2 than that of yttrialite $Y_2Si_2O_7$ at temperatures between 900 and 1050°C in air, with the possible formula: $H_{3n}Y_{6-n}Si_6O_{21}$ ($n<1$). This phase was often found as a metastable or intermittent phase in the lower temperature equilibrium range for the α-phase of composition $(Y,Ho,Er)_2Si_2O_7$ synthesized from gel at temperatures below 1100°C. The presence of small amounts of sodium seems to stabilize this phase even up to 1200°C in air. Ferrous or ferric iron also stabilizes this phase up to 650°C under 2 kbar pressure. Under both conditions, the compounds of this range containing only yttrium and silicate ions are converted to the higher α- or β-phases. Recrystallized "low yttrialite" (y-phase), therefore, may be a complex silicate with approximate chemical formula $R(Y,RE)_5Si_6O_{21}$ where R includes H^+, Na^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} (Bondar and Toropov, 1967) and Zr^{4+}.

The α-phase formed from natural yttrialite above 1200°C is isomorphous with α-$Y_2Si_2O_7$ and α-$(Gd,Tb,Dy)_2Si_2O_7$ (both low temperature forms), found by Warshaw and Roy (1964). However, the α-phase obtained from natural mineral displays no transitions to higher temperature phases such as those described in the following section for synthetic compounds ranging from Tm to Gd including Y. The natural specimens melt at approximately 1450°C and the α-phase still persists at that temperature. This is due to the fact that the greater complexity of the chemical composition of the natural mineral lowers the eutectic melting point considerably, so that the high-temperature phase does not appear. Hydrothermally recrystallized natural specimens gave only the α-phase at temperatures from 450–720°C under 2 kbar of H_2O pressure.

From the results described above, we can state that α-phase, α-$Y_2Si_2O_7$, may exist in a wider range of stability than y-phase, and the original crystalline yttrialite was most likely α-$Y_2Si_2O_7$. Hydrothermally synthesized α-$Y_2Si_2O_7$ at 650°C and 1 kbar showed under the microscope hexagonal prisms with flat $\{0001\}$ faces. This compound probably is of hexagonal symmetry, but indexing of the powder data was not achieved. Very few X-ray diffraction lines were reported for natural unheated yttrialites by Protosenko (1962), Nishimura and Ueda (1954) and Omori and Hasegawa (1953); the limited data recorded in the literature are both inconsistent and inadequate for identifying the species.

Thalenite. Another yttrium pyrosilicate known in nature is thalenite. The attempted synthesis of thalenite, $Y_2Si_2O_7$ was not successful. The natural specimen of thalenite from Suishoyama described by Nagashima and Kato (1966), was heated hydrothermally and in air. Under hydrothermal conditions from 450–700°C and 2–3 kbar, thalenite remained unchanged, and gave an X-ray powder pattern of the typical thalenite. In air at 1050°C, thalenite converted to β-$Y_2Si_2O_7$, but a few strong lines of thalenite still remained after 62 hours at that temperature. At 1400°C it was further converted to the γ-phase (see following section), and it remained unchanged up to 1600°C. No higher phase was obtained. The β- and γ-phases have been identified recently as phase II and I respectively in two-phase thalenite found at Österby, Sweden (Vatelieva, Krivokoneva and Pyatenko, 1967).

The above experimental results indicate that thalenite is definitely a low-temperature phase and most probably hydrous, as was shown by Proton Magnetic Resonance studies (Nagashima and Kato, 1966). We suspect that the mineral described as thalenite may not be in its original crystalline form. It may have been altered to a hydrous phase during the later stage of crystallization. The X-ray powder data given for the synthetic thalenite by Lazarev, Tenisheva and Bondar (1965) showed some similarity to the data of the natural specimen (Neuman *et al.*, 1957; Adams *et al.*, 1962), but their conditions for the synthesis (1300°C in air) may be questioned on the basis of the present experiments. A mineral described as thalenite from Anneröd Vaaler, Norway, by Sabina and Traill (1960), subsequently identified by Warshaw and Roy (1964) as β-$Y_2Si_2O_7$ (isomorphous with thortveitite; Strunz, 1957) should be given a new name. If an yttrialite described by Nishimura and Ueda (1954) also is truly isostructural with thortveitite, it must be the same mineral. Rowlandite (Frondel, 1960) and Iimoriite (Nagashima and Nagashima, 1960) are different yttria-earth silicates and have not been identified in this study.

On the polymorphism of $(Y,Ln,In,Sc)_2Si_2O_7$. In addition to the characterization of the mineral yttrialite, our study was extended to the polymorphism of rare-earth pyrosilicates, $(Y,Ln,In,Sc)_2Si_2O_7$ (Ln = Lu,Yb, Tm,Er,Ho,Dy, and Gd), because some discrepancies exist in the results and interpretation of the polymorphism of rare-earth pyrosilicates in the literature.

Warshaw and Roy (1964) reported that lower temperature α-$Y_2Si_2O_7$ is structurally similar to the lower polymorph of the so-called intermediate rare-earth pyrosilicates, α-$(Gd,Tb,Dy)_2Si_2O_7$. At 1240°C, the α-phase $Y_2Si_2O_7$ was converted into a higher polymorph β-$Y_2Si_2O_7$, isostructural with so-called smaller rare-earth pyrosilicates $(Lu,Yb)_2Si_2O_7$ which shows only one phase up to the melting point.

Toropov and Bondar (1960) reported phase equilibria studies of the systems Ln_2O_3-SiO_2. They found only one type of $Ln_2Si_2O_7$ at temperatures above 1600°C for each rare-earth oxide-SiO_2 system. Their X-ray powder data of $Y_2Si_2O_7$ are completely unrelated to those of α- or β-$Y_2Si_2O_7$, but show isomorphism with β-$Tb_2Si_2O_7$ reported by Warshaw and Roy (1964).

Lazarev, Tenisheva and Bondar (1965) obtained one compound $Y_2Si_2O_7$ which was spectroscopically isostructural with $Sc_2Si_2O_7$ and $(Lu,Yb)_2Si_2O_7$ by sintering mixed oxides at temperatures between 1300–1400°C. They also reported a high temperature polymorph of $Y_2Si_2O_7$ prepared by arc fusion at over 1450°C. It has the same infrared spectrum as $(Sm,Gd,Dy)_2Si_2O_7$. This phase is apparently the same compound as that given by Toropov and Bondar (1960). Vatelieva, Bondar and Sidorenko (1965) reported one more polymorph of $Y_2Si_2O_7$, grown in KF flux by slow cooling from 1400–1200°C; they obtained good X-ray data.

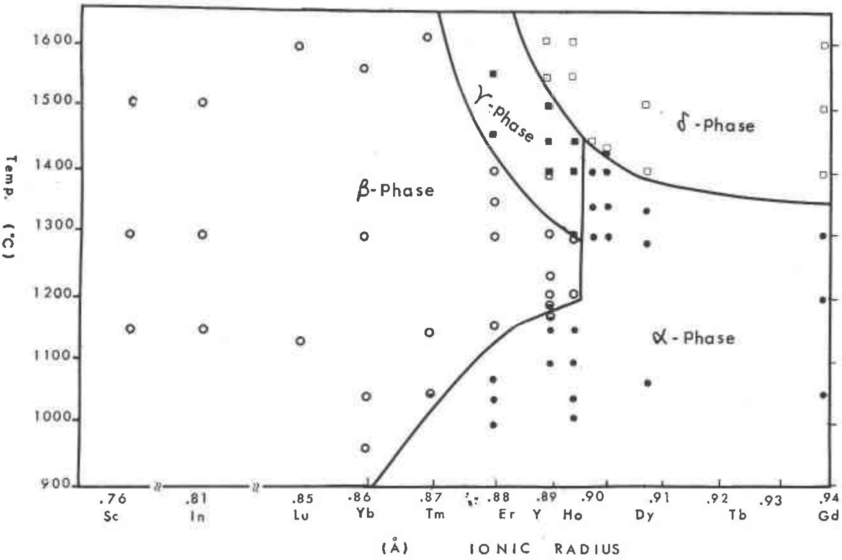

FIG. 1. Schematic presentation of polymorphism of $Y_2Si_2O_7$ in terms of the trivalent ionic radii of rare-earth ions (Templeton and Dauben, 1954), In (0.81 Å by Pauling, 1960) and Sc (0.76 Å by Frondel and Ito, 1967). Black circles $=\alpha$-$Y_2Si_2O_7$; open circles $=\beta$-$Y_2Si_2O_7$; black squares $=\gamma$-$Y_2Si_2O_7$; open squares $=\delta$-$Y_2Si_2O_7$; black and white circles and squares two phases.

We found $Y_2Si_2O_7$ displays at least three first-order polymorphic transitions. These include $\alpha \xrightarrow{1225°C \pm 10°C} \beta$, $\beta \xrightarrow{1445°C \pm 10°C} \gamma$, $\gamma \overset{1535°C \pm 10°C}{\underset{\longleftarrow}{\longrightarrow}} \delta$. The additional lowest temperature Z phase of $Y_2Si_2O_7$ was observed below 1030°C, but its composition was not ascertained. Warshaw and Roy (1964) studied the α and β phases only. The crystals described by Vatelieva, Bondar and Sidorenko (1965) are the γ phase. The compound synthesized by Toropov and Bondar (1960) and also the high temperature phase obtained by Lazarev, Tainisheva and Bondar (1965) are the δ phase. The low temperature phase given by the latter authors probably is the β phase because of its similarity to $Sc_2Si_2O_7$. Our results agree reasonably well with the transition temperatures found by Warshaw and Roy ($\alpha \xrightarrow{1250°C} \beta$) and by Lazarev, Tenisheva and Bondar ($\beta \xrightarrow{1450°C} \gamma$).

$Ho_2Si_2O_7$ also gives the same four-phase polymorphic transitions as $Y_2Si_2O_7$, but the stability ranges and the transition temperatures are slightly different: $\alpha \xrightarrow{1175°C \pm 15°C} \beta$, $\beta \xrightarrow{1330°C \pm 10°C} \gamma$, $\gamma \overset{1475°C \pm 25°C}{\underset{\longleftarrow}{\longrightarrow}} \delta$. $Er_2Si_2O_7$ shows three polymorphs, namely $\alpha \xrightarrow{1050°C \pm 25°C} \beta$, $\beta \xrightarrow{1400°C \pm 10°C} \gamma$. $Tm_2Si_2O_7$ has only two phases, $\alpha \xrightarrow{1050°C \pm 10°C} \beta$. Actually, the α-phase of $Er_2Si_2O_7$ and $Tm_2Si_2O_7$ are accompanied by the y-phase (Protosenko,

TABLE 3. X-RAY POWDER DATA OF Z-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$, β-$Y_2Si_2O_7$, y-$Y_2Si_2O_7$ OF THIS STUDY AND THOSE DESCRIBED PREVIOUSLY

α-$Y_2Si_2O_7$, 1190°C in air, this study		Warshaw & Roy (1964)		Lima de Faria (1964)		β-$Y_2Si_2O_7$, 1300°C in air, this study			Warshaw & Roy (1964)		y-phase 985°C in air, this study, R $Y_5Si_6O_{21}$?		Protosenko (1962) Sample from USSR 1000°C in air, Yttrialite		Lima de Faria (1964 1000°C in air, Sample from USA, Yttrialite	
d in Å	I/I_0	*d* in Å	I/I_0	*d* in Å	I/I_0	*hkl*	*d* in Å	I/I_0	*d* in Å	I/I_0	*d* in Å	I/I_0	*d* in Å	I/I_0	*d* in Å	I/I_0
6.60	5			6.6	2	110	5.934	50	5.44	20						
5.90	10			5.8	2	001	4.623	40	4.67	30	4.696	50			4.06	4
5.72	10					020	4.494	5	4.51	10	4.050	30			4.05	4
4.807	2					$\bar{1}11$	3.847	5	—		3.463	80	3.500	4		
4.643	2												(3.356)	2	3.50	7
4.480	3					200	3.373	10	3.38	10	3.177	40	3.186	2	3.20	2
4.350	20	4.37	25	4.35	5	111	3.252	60			3.056	100	3.067	6	3.05	10
4.199	3	4.17	10			021	3.222	100	3.23	100	3.003	10	(2.923)	2		
											2.718	5				
4.081	2					$\bar{2}01$	3.025	80	3.04	65	2.627	70	2.647	5	2.64	6
3.905	10					130	2.735	55	2.74	35	2.393	60	2.402	4	2.40	6
3.645	5					220	2.695	60	2.71	30	2.339	10			2.34	1
3.545	10					$\bar{2}21$	2.554	5	—		2.252	5				
3.477	2					201	2.493	10	2.45	10	2.058	65	2.067	9	2.06	7
3.312	20	3.31	20	3.30	4	$\bar{1}31$	2.434	5	—		2.020	20	2.024	6	2.03	6
3.151	20	3.13	10	3.15	2										(1.88)	4
3.005	100	3.01	100	3.00	10	002	2.312	5	2.32	5	1.858	15			1.86	2
2.955	10					131	2.274	50	2.28	30	1.744	25	1.754	7	1.75	9
2.910	80	2.91	50	2.89	76	040	2.252	10			1.690	5	(1.695	2)	(1.71)	1
															1.68	1
2.864	40	2.87	15	2.86	3	310	2.179	20	2.18	15	1.591	15	1.604	4	1.60	6
2.803	50	2.81	20	2.80	5	221, $\bar{1}12$					1.545	20	1.547	10	1.55	10
2.704	30	2.71	18	2.70	7										1.53	2
2.688	5					$\bar{3}11$	2.138	20	2.14	20	1.458	5			1.47	16
2.547	15					$\bar{2}02$	2.117	10	2.12	10	1.368	10	1.379	5	1.380	6
2.434	5										1.322	5	1.323	2	1.325	1
2.273	10										1.292	8	1.297	2	1.298	2
2.194	30	2.20	15	2.20	26	022	2.056	5	2.06	5	1.255	5	1.259	6	1.260	5
2.142	15	2.15	10	2.14	26	$\bar{2}22$	1.916	10	1.918	15	1.235	5	1.233	2	1.240	1
2.106	15	2.11	15	2.10	26	311, 132	1.843	5	1.845	5						
2.065	10	2.06	5			$\bar{2}41$	1.796	15	1.801	10						
1.987	5			1.91	8	312	1.772	10	1.778	10						
1.857	5			1.86	1	302	1.749	10	1.749	10						
				(1.84	1)											
1.806	20			1.81	8	150	1.734	15	1.737	10						
1.776	3			1.78	3	132	1.697	20	1.698	20						
1.760	3					401										
1.729	5			(1.72	1)	400	1.683	15	1.687	10						
				$\bar{9}$1.70	1$\bar{9}$	151	1.651	5	1.656	10						
				$\bar{9}$1.08	1$\bar{9}$											
1.595	10			1.63	9	222	1.635	5	1.631	5						
				1.50	16	331	1.596	15	—							
1.453	10			1.40	16	$\bar{4}21$	1.589	15	—							
						003	1.576	3	—							
						$\bar{1}13$	1.540	3	—							
						$\bar{4}02$	1.518	3	—							
						060	1.487	10	—							

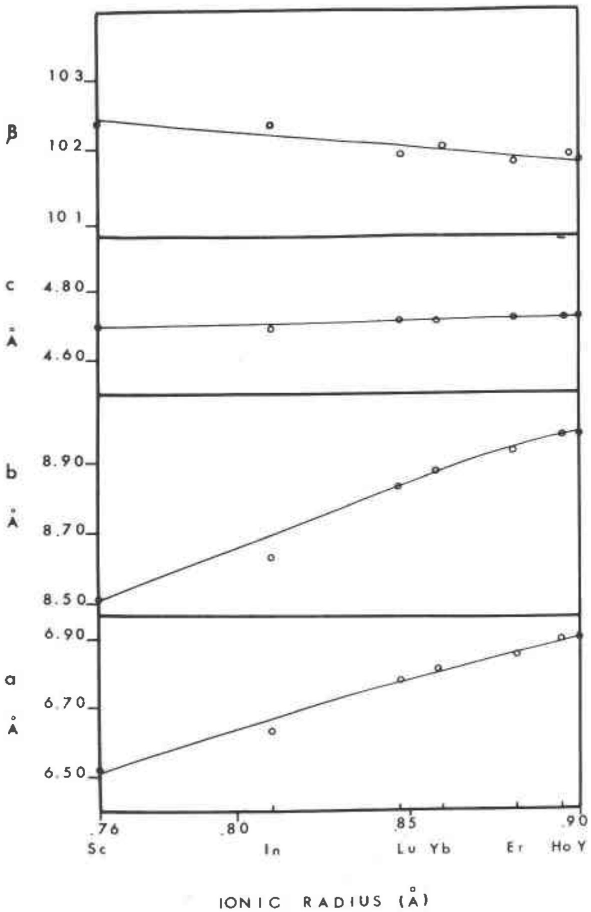

FIG. 2. Unit-cell dimensions of β-$Y_2Si_2O_7$ and its analogues plotted against ionic radii of trivalent rare-earth, Sc and In ions (Templeton and Dauben, 1954; Pauling, 1960; Frondel and Ito, 1967).

1962; Lima de Faria, 1964). Lu and Yb analogues do not display polymorphism. β-$Ln_2Si_2O_7$ is the only phase in the temperature range studied here. The so-called intermediate $(Gd,Tb,Dy)_2Si_2O_7$ shows dimorphism α to δ, which corresponds to (α) and (β) $Tb_2Si_2O_7$ reported by Warshaw and Roy (1964). δ-$Dy_2Si_2O_7$ is the phase found by Toropov and Bondar (1961). Among the four phase transitions, only a reverse reaction from δ to γ takes place within reasonable time of heating at slightly below the transition temperatures.

The polymorphism described above is shown schematically in Figure 1. The experimental results in this diagram were plotted in terms of

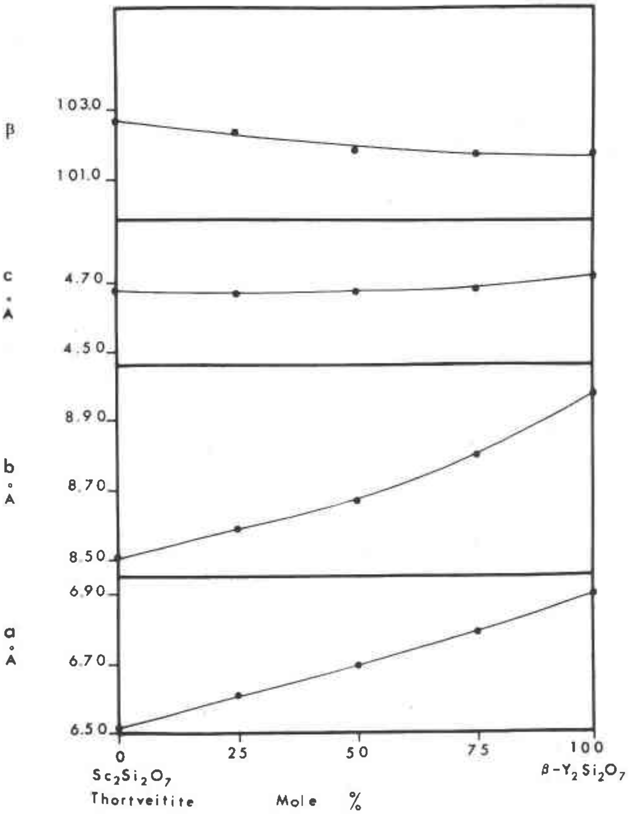

FIG. 3. Unit-cell dimensions for the solid solution series of $Sc_2Si_2O_7$-β-$Y_2Si_2O_7$.

the temperature and the radius of trivalent rare-earth (Templeton and Dauben, 1954), In (Pauling, 1960) and Sc (Frondel and Ito, 1967) ions. From the results, it is clear that the phase transitions are controlled by ionic radii as well as temperature. The gradual changes of the temperature of the phase transition observed in this diagram are not consistent with a simple classification of rare-earth ions into, for example, small, intermediate, etc., based on the polymorphism of these compounds.

We found that $Sc_2Si_2O_7$ (thortveitite), $In_2Si_2O_7$, $(Lu,Yb)_2Si_2O_7$ and β-$(Er,Ho,Y)_2Si_2O_7$ are isostructural. X-ray powder data for β-$Y_2Si_2O_7$ (Table 3) were indexed according to the space group for thortveitite $C2/m$ monoclinic, and the unit-cell dimensions of all other analogues are tabulated in Table 4. The gradual change of the unit-cell dimensions in terms of trivalent ionic radii of cations is illustrated in Figure 2.

TABLE 4. UNIT CELL DIMENSIONS OF β-$Y_2Si_2O_7$ AND OTHER RARE EARTH ANALOGUES AND OF THE SOLID SOLUTION SERIES OF $Sc_2Si_2O_7$–β-$Y_2Si_2O_7$

Formula	a	b	c	β
β-$Y_2Si_2O_7$	6.90	8.98	4.72	101.7
$Ho_2Si_2O_7$	6.89	8.98	4.72	101.8
$Er_2Si_2O_7$	6.85	8.94	4.72	101.6
$Yb_2Si_2O_7$	6.81	8.88	4.71	102.0
$Lu_2Si_2O_7$	6.78	8.84	4.71	101.9
$Tm_2Si_2O_7$	6.82	8.90	4.71	101.9
$In_2Si_2O_7$	6.63	8.63	4.69	102.8
$Sc_2Si_2O_7$	6.52	8.51	4.68	102.7
β-$(Y_{75}Sc_{25})_2Si_2O_7$	6.79	8.80	4.72	101.7
$(Y_{50}Sc_{50})_2Si_2O_7$	6.69	8.67	4.67	101.6
$(Y_{25}Sc_{75})_2Si_2O_7$	6.61	8.51	4.66	102.4
Thortveitite[a]	6.54	8.52	4.67	102.3

[a] Unit-cell dimensions by Dawson, Harrison, Gallagher and Horne (1966).

Furthermore, complete solid solubility was established between $Sc_2Si_2O_7$ and β-$Y_2Si_2O_7$ at 1300°C in air and at 700°C under 2.5 kb H_2O pressure. Unit-cell dimensions of this series are also given in Table 4 and Figure 3.

Hydrothermally crystallized β-$Y_2Si_2O_7$ prepared from sodium-free gel, yield fine transparent crystals up to 0.5 mm in size with well developed faces. The single crystals of γ-$Y_2Si_2O_7$ were grown in a flux of $Li_2W_2O_7$ at a 1:5 charge/flux ratio by slow cooling from 1250–900°C. Flat crystals of almost square section up to $1\times1\times0.3$ cm were obtained in a fine mass of β-$Y_2Si_2O_7$. Eu and Tb activation of the four different modifications of $Y_2Si_2O_7$ yields mildly fluorescent crystals.

In addition, we studied Y_2SiO_5 using the same experimental techniques of synthesis from gel. We found only one phase (X_2-phase) at temperatures above 1190°C. This is the same compound described by Toropov and Bondar (1961), and Harris and Finch (1965). At temperatures around 1050°C we obtained one low temperature phase (X_1-phase, possibly hydrous), but its stoichiometry is uncertain. These X_1- and X_2-phases are different from that described by Warshaw and Roy (1964).

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