

SYNTHESES OF THE SCANDIUM ANALOGUES OF AEGIRINE, SPODUMENE, ANDRADITE AND MELANOTEKITE

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ABSTRACT

Unit-cell dimensions and optical data are given for synthetic $\text{NaScSi}_2\text{O}_6$, $\text{LiScSi}_2\text{O}_6$, $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, and $\text{Pb}_2\text{Sc}_2\text{Si}_2\text{O}_9$. Cell dimensions also are given for intermediate compositions in the solid solution series extending between $\text{NaScSi}_2\text{O}_6$ and the Fe^{3+} analogue aegirine, between $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ and the Fe^{3+} analogue andradite and between $\text{Pb}_2\text{Sc}_2\text{Si}_2\text{O}_9$ and the Fe^{3+} analogue, melanotekite. A series probably also exists between $\text{LiScSi}_2\text{O}_6$ and $\text{LiFeSi}_2\text{O}_6$.

The broad role of Sc as a trace element in ferromagnesian silicates was originally interpreted by Goldschmidt and Peters (1931) as involving a valence-coupled diadochy of Sc^{3+} with Fe^{2+} and Mg. New data on the solid solutions formed by Sc^{3+} and on the size of this ion, however, support an interpretation involving diadochy with Fe^{3+} and Al.

SCANDIUM-AEGIRINE

$\text{NaScSi}_2\text{O}_6$, isostructural with $\text{NaFeSi}_2\text{O}_6$, aegirine, was synthesized by the hydrothermal crystallization of a gel of the same bulk composition. The gel was prepared by precipitating a HCl solution of Sc_2O_3 and Na_2SiO_3 in the molar ratio 1:3 by the addition of ammonia to a final pH of 10. The precipitate was then centrifuged, washed with dilute ammonia, and added to sufficient aqueous solution of Na_2SiO_3 to make the bulk composition correspond to $\text{NaScSi}_2\text{O}_6$. The resulting thin slurry was thoroughly mixed and evaporated slowly to dryness. The final preparation was heated hydrothermally in a cold-seal stainless steel bomb, fitted with a silver liner, at 750°C and 2 kbars for 48 hours. We also have synthesized compositions between $\text{NaScSi}_2\text{O}_6$ and $\text{NaFeSi}_2\text{O}_6$, with the ratios $(\text{Sc}_{0.75}\text{Fe}_{0.25})$, $(\text{Sc}_{0.5}\text{Fe}_{0.5})$ and $(\text{Sc}_{0.25}\text{Fe}_{0.75})$, by a similar procedure using HCl solutions containing Sc_2O_3 and FeCl_3 in the desired ratios. The unit-cell dimensions of these isostructural compositions vary linearly with composition, and solid solution between the Sc^{3+} and Fe^{3+} end-compositions appears to be complete.

$\text{NaScSi}_2\text{O}_6$ also was synthesized by fusion in sodium tungstate as flux. The charge used was Sc_2O_3 0.3g, SiO_2 0.6g and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 50g. The charge was held at 1180°C for 12 hours, cooled at 10°C per hour to 900°C and then quenched. Sodium molybdate also was used as a flux successfully.

The monoclinic crystals of $\text{NaScSi}_2\text{O}_6$ obtained from sodium tungstate fusions were colorless and ranged up to 2 mm in length. They were prismatic on c with $\{100\}$, $\{010\}$, $\{hk0\}$ and complex terminations with

¹ Mineralogical Contribution no. 453.

TABLE 1. UNIT-CELL DIMENSIONS OF SYNTHETIC PRODUCTS

Composition	a , Å	b , Å	c , Å	β
NaScSi ₂ O ₆	9.83 ± 0.02	9.06 ± 0.02	5.37 ± 0.01	107.2° ± 0.1
Na(Sc _{0.75} Fe _{0.25})Si ₂ O ₆	9.77	8.98	5.35	107.0°
Na(Sc _{0.5} Fe _{0.5})Si ₂ O ₆	9.73	8.90	5.33	107.1°
Na(Sc _{0.25} Fe _{0.75})Si ₂ O ₆	9.69	8.84	5.32	107.3°
LiScSi ₂ O ₆	9.83	8.98	5.37	110.4°
LiFeSi ₂ O ₆	9.81	8.73	5.37	111.4°
Pb ₂ Sc ₂ Si ₂ O ₉	7.00 ± 0.01	11.30 ± 0.02	10.44 ± 0.02	
Pb ₂ (Sc ₁ Fe ₁)Si ₂ O ₉	7.00	11.12	10.22	
Pb ₂ Ga ₂ Si ₂ O ₉	6.95	10.90	9.91	
Pb ₂ Cr ₂ Si ₂ O ₉	6.88	10.84	10.01	
Ca ₃ Sc ₃ Si ₃ O ₁₂	12.23 ± 0.01			
Ca ₃ (Sc ₁ Fe ₁)Si ₃ O ₁₂	12.13			
Ca ₃ In ₃ Si ₃ O ₁₂	12.36			
Ca ₃ (In ₁ Fe ₁)Si ₃ O ₁₂	12.20			
Ca ₃ (Sc ₁ In ₁)Si ₃ O ₁₂	12.29			

{0kl}, {h0l} and large faces of two {hkl} forms. Contact twins on (100) with reentrant terminations were observed. The substance is optically negative with α 1.683, β 1.715, γ 1.724; $Y = b$, $\alpha \wedge c$ $8.0^\circ \pm 0.2^\circ$, $2V_\gamma$ large. The material synthesized hydrothermally was too fine-grained for satisfactory optical study. The synthetic end-composition NaFeSi₂O₆ had $\alpha \sim 1.765$, and the (Sc₁Fe₁) run had $\alpha \sim 1.71$. All of the runs appeared to be pure. The unit-cell dimensions obtained from X-ray diffractometer charts taken in filtered Cu radiation with Si as internal standard, and indexed following Frondel and Klein (1965), are listed in Table 1. The X-ray power data are given in Table 2.

SCANDIUM-SPODUMENE

The scandium analogue of spodumene, LiScSi₂O₆, was grown from Sc₂O₃ and SiO₂ in lithium molybdate flux. The ratio of charge to flux was 1:10 by weight. The melt was held at 1250°C for 24 hours and then was cooled at 5°C per hour to 950°C and quenched. The crystals obtained were monoclinic, prismatic to needle-like on c , with the forms {100}, {010}, {hk0} and indistinct oblique terminations. The substance is optically negative, with α 1.702, β 1.710, γ 1.716; $\alpha \wedge c$ $37^\circ \pm 0.5^\circ$, $Y = b$, $2V_\gamma$ large. Contact twins on (100) are common, and there is a good prismatic cleavage, presumably (110). The unit-cell dimensions derived from the indexed diffractometer pattern are given in Table 2. We also have obtained crystals containing an undetermined amount of Fe³⁺ in solid solution, with α 1.722, and at least a partial series extends toward LiFeSi₂O₆.

TABLE 2. X-RAY POWDER DATA FOR $\text{NaScSi}_2\text{O}_6$ AND $\text{LiScSi}_2\text{O}_6$
 Cu radiation, Ni filter, in Angstrom units. Relative intensities in arbitrary chart units.

$\text{NaScSi}_2\text{O}_6$			$\text{LiScSi}_2\text{O}_6$		
<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>
110	6.544	25	110	6.43	100
020	4.539	30	020	4.489	40
111	3.680	8	111	3.562	15
220	3.262	10	021	3.348	5
221	3.050	100	220	3.211	20
310	2.963	50	22 $\bar{1}$	3.004	20
13 $\bar{1}$	2.611	10	310	2.902	90
022	2.557	25	130	2.846	10
221	2.525	30	13 $\bar{1}$	2.603	5
311	2.301	3	002	2.507	3
040	2.258	2	221, 401	2.449	10
112	2.230	10	112	2.170	5
33 $\bar{1}$	2.168	10	330, 42 $\bar{1}$	2.140	5
42 $\bar{1}$	2.139	8		1.759	10
240	2.038	2		1.717	5
041	2.071	8		1.641	5
24 $\bar{1}$	2.012	5		1.606	10
51 $\bar{1}$	1.984	3		1.545	5
422	1.885	2		1.493	5
331	1.868	3			
510	1.840	2			
150	1.780	10			
042	1.693	5			
441, 223	1.659	10			
151	1.646	15			
440	1.633	15			
35 $\bar{1}$, 660	1.567	10			
60 $\bar{2}$	1.557	5			
53 $\bar{2}$	1.540	3			
13 $\bar{3}$	1.529	8			
060	1.509	8			

SCANDIUM-MELANOTEKITE

The synthesis of melanotekite ($\text{Pb}_2\text{Fe}_2\text{Si}_2\text{O}_9$), kentrolite ($\text{Pb}_2\text{Mn}_2\text{Si}_2\text{O}_9$) and of intermediate members of this complete solid solution series has been reported elsewhere (Ito and Frondel, 1967). Using similar procedures, we have synthesized the Sc, Ga and Cr analogues of these compounds by the hydrothermal recrystallization of gels at 450°C and 2 kbars. The unit-cell dimensions of these substances, as determined from indexed X-ray powder diffractometer charts, are given in Table 2. The

composition $\text{Pb}_2(\text{Sc}_1\text{Fe}_1)\text{Si}_2\text{O}_9$ also was synthesized and a complete series probably extends between the Fe^{3+} and Sc end-compositions.

SCANDIUM-ANDRADITE

The synthesis of garnets containing Sc in the six-coordinated site has already been reported. These garnets include $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ (Tauber, *et al.* 1961), $\text{Gd}_3\text{Sc}_2\text{Fe}_3\text{O}_{12}$ (Geller, *et al.* 1965), $\text{Y}_3(\text{Sc},\text{Fe}^{3+})_2\text{Fe}_3\text{O}_{12}$ (Cunningham, 1965), $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ (Mill, 1962), and the hydrogarnet $\text{Sr}_3\text{Sc}_2(\text{OH})_{12}$ (Ito and Frondel, 1967b). We have synthesized $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ and also the composition $\text{Ca}_3(\text{Sc}_1\text{Fe}_1)\text{Si}_3\text{O}_{12}$ intermediate between it and $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, andradite. The syntheses were effected by the hydrothermal recrystallization of gels prepared by the general method of Ito and Frondel (1967a). The runs were made at 680°C and 2 kbars for 20 hours. We have similarly synthesized $\text{Ca}_3\text{In}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3(\text{In}_1\text{Fe}_1)\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3(\text{Sc}_1\text{In}_1)\text{Si}_3\text{O}_{12}$. Complete solid solubility probably exists between the Sc, In and Fe^{3+} members. The products were fine-grained but distinct dodecahedra were observed. The unit-cell dimensions cited in Table 1 were obtained from indexed X-ray diffractometer charts taken in filtered Cu radiation with Si as internal standard.

DISCUSSION

The ionic radius of the Sc^{3+} ion in six-coordination with oxygen is generally cited in the literature as 0.83 Å. This value is based on the structural analyses of Sc_2O_3 and $\text{Sc}_2\text{Si}_2\text{O}_7$ by Zachariasen (1927, 1930). The large size of this ion would seemingly preclude any significant degree of solid solution with Al or Fe^{3+} . This view was originally taken by Goldschmidt and Peters (1931) in their survey of the geochemistry of scandium. They interpreted the observed dispersal of Sc as a trace element in solid solution in ferromagnesian silicates as involving the valence-coupled diadochy of Sc^{3+} with Fe^{2+} and Mg rather than the direct substitution for Fe^{3+} or Al. The present study, however, and experimental studies of Sc-beryl (Frondel and Ito, 1968), Sc-garnets (Cunningham, 1965; Villers and Lombard, 1964) and the system $\text{Sc}_2\text{O}_3\text{-Fe}_2\text{O}_3$ (Geller, *et al.* 1961) provide evidence of the extensive mutual substitution of Sc^{3+} and Fe^{3+} . The substitution of Sc^{3+} and Al is shown in the system $\text{Sc}_2\text{O}_3\text{-Al}_2\text{O}_3$ (Toropov and Vasil'eva, 1963) and in natural aluminum phosphates (Frondel, Montgomery and Ito, 1968). This becomes reasonable in view of recent measurements of the Sc-O distances in various compounds, including refinements of the structures of Sc_2O_3 and $\text{Sc}_2\text{Si}_2\text{O}_7$, that show the ionic radius of Sc^{3+} in six-coordination to be much smaller than 0.83 Å. Values have been obtained in the range from 0.69 Å to 0.78 Å, depending on the ionic-covalent proportions in the metal-oxygen

bond and on other factors (Geller, 1957; Geller, *et al.* 1967; Cruickshank, *et al.* 1962). It now appears that the role of Sc^{3+} as a trace element in garnet, allanite and ferromagnesian silicates in general is based on diadochy with Al and in particular Fe^{3+} rather than with Fe^{2+} and Mg. A review of the crystal chemistry of scandium is given elsewhere (FronDEL, 1968).

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Manuscript received, December 1, 1967; accepted for publication, January 22, 1968.