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SYNTHESIS OF THE SCANDIUM ANALOGUE OF BERYL[1]

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ABSTRACT

The phase $Be_3Sc_2Si_6O_{18}$ isostructural with beryl $Be_3Al_2Si_6O_{18}$, has been synthesized. Solid solutions with the composition $Be_3(Sc, R^{3+})_2Si_6O_{18}$, where R^{3+} is Fe^{3+}, Cr^{3+}, V^{3+}, Mn^{3+} or Ga, also have been synthesized. The syntheses were effected by the hydrothermal crystallization of precipitated gels of stoichiometric composition at 450°C to 750°C, 2 kbars pressure and run times of 20 to 48 hours. Syntheses of (Sc, Fe^{3+}) and (Sc, Mn^{3+}) beryls also were effected by sintering gels in air at 1020°C. The thermal stability of Sc-beryl under hydrothermal conditions apparently is increased by the presence of R^{3+} ions and of Na.

The substitution of Sc by R^{3+} ions is extensive but does not extend to the Sc-free end-compositions. The (Sc, Fe^{3+}) member corresponds to the mineral bazzite. The Sc and (Sc, R^{3+}) beryls are characterized by a very large increase in a and a small decrease in c as compared to ordinary Al-beryl. The end-composition $Be_3Sc_2Si_6O_{18}$ has a 9.56 Å, c 9.16; the cell volume decreases with increasing substitution of Sc^{3+} by R^{3+}. Sc-beryl has higher birefringence than Al-beryl, caused by a relatively large increase in ω, and the indices of refraction increase with increasing substitution of Sc by R^{3+} ions.

INTRODUCTION

The synthesis of beryl, $Be_3Al_2Si_6O_{18}$, is well known and the Cr-pigmented variety, emerald, has been produced commercially for many years. A summary of the literature has been given by Flanigen *et al.*, (1967). The possibility of synthesizing the scandium analogue of beryl is suggested by the common occurrence of Sc^{3+} as a minor constituent of natural beryl (Table 1) and by the existence of the mineral bazzite. This mineral was first described by Artini (1915) from Baveno, Italy, as a scandium silicate of unknown formula. It was later reported, without quantitative analyses, by Parker, de Quervain and Weber (1940) and by Beck (1954) from four localities in Switzerland. The possibility that the mineral was the scandium analogue of beryl was suggested by Fleischer (1955). This was confirmed by X-ray structural studies of Baveno material by Peyronel (1956) and of Swiss material by Bergerhof and Nowacki (1955). A quantitative electron microprobe analysis of the latter by Nowacki and Phan (1964) established the composition as $Be(Sc_{1.3}Fe_{0.6}Al_{0.1})Si_6O_{18}$. Peyronel (1956) states that the Baveno material contains about 2/3 Sc in the Al position; the presence of Fe and of Y and lanthanides was estab-

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TABLE 1. SCANDIUM CONTENT OF SOME NATURAL BERYLS[a]

Percent Sc_2O_3	Localities	References
1.5	Norway	Oftedal (1943)
0.15 to 0.45	U.S.S.R.	Erdzhanov (1961)
up to 0.2	Various	Borisenko (1961), Borovik (1943)
0.10	Arizona	Schaller, *et al.* (1962)
0.15 max. and 0.015 aver. of 57 anals.	Norway	Neumann (1961)
0.11 max. and 0.04 aver. of 54 anals.	United States	Staatz, *et al.* (1965)

[a] Additional data or summaries given by Eberhard (1908, 1910), Goldschmidt and Peters (1931), Borisenko (1961), Vlasov (1964), Matsuda (1963).

lished qualitatively by Artini (1915) and by Bertolani (1948). Peyronel indicates that considerable Si may be present in the Be positions, and places the rare earths inside the Si_6O_{18} channels. The Swiss material also contains an excess of Si over the requirements of the idealized formula. More recently, Chistyakova *et al.*, (1966) have described bazzite from Kazakhstan, Russia. A complete analysis gave $Be_{3.06}(Sc_{1.26}Fe^{3+}_{0.17}Al_{0.03}Fe^{2+}_{0.31}Mn_{0.12})(Si_{5.93}Be_{0.07})O_{18}\cdot 0.87\ H_2O$ with $(Na_{0.55}K_{0.03}Ca_{0.01})$ in the channels; optical and X-ray data are given in Tables 4 and 5.

We have synthesized compounds isostructural with beryl that lack Al and contain Sc^{3+} alone or together with Cr^{3+}, Fe^{3+}, V^{3+}, Mn^{3+} or Ga in the Al structural site.

METHOD OF SYNTHESIS

The syntheses were effected hydrothermally from precipitated gels of a bulk composition corresponding to the ratio of the beryl type of formula. The reagents employed were 0.2 M solutions of beryllium sulfate (standardized by gravimetric analysis), chromium chloride, manganese chloride, ferric chloride and sodium silicate, and dilute HCl solutions of scandium chloride,[1] ammonium vanadate and gallium chloride. The gels used for the synthesis of material containing Sc with Fe^{3+}, Cr^{3+} or Ga^{3+} were prepared from slightly acid solutions containing these ions together with Be and Si in the desired proportions. The solution was brought to pH 10 by ammonia and was stirred magnetically for 10 minutes. The gelatinous precipitate was then centrifuged, washed with distilled water and dried at 110° in an evacuated oven. The gels containing Mn^{3+} were made similarly but a slight excess of ammonia was added at the time of precipitation and the amount of washing was restricted. The Mn must be divalent during precipitation and then gradually oxidized to Mn^{3+} by heating the gel in air. Gels containing Mn^{4+}, such as through precipitation by a mixture of ammonia and hydrogen peroxide, failed to crystallize as beryl. The gels con-

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[1] Prepared from approximately 75 grams of 99.9 percent Sc_2O_3 (balance chiefly Fe_2O_3) that had been purified by ion exchange resins from crude oxide supplied by the Kawecki Chemical Company and obtained from Fairfield, Utah, crandallite ore.

taining V were prepared by the addition of 0.1 grams of ascorbic acid to the initial HCl solution and then boiling for 3 minutes to reduce the vanadate; ascorbic acid also was added to the bomb charge in order to reduce V^{4+} to V^{3+} when the gels were run hydrothermally. The stability of V^{3+} in the presence of ascorbic acid under hydrothermal conditions has been demonstrated by Ito (1965), in the synthesis of vanadium silicates. The dried gels as prepared above were pulverized and heated in cold-seal stainless steel bombs fitted with silver liners. The temperature, pressure and run times employed and the results obtained are summarized in Table 2.

In the course of the work it became desirable to determine whether beryl-type phases could be obtained from gels lacking traces of Na residual from the sodium silicate employed. Syntheses of $Be_3Sc_2Si_6O_{18}$ and $Be_3(Sc, Fe^{3+})_2Si_6O_{18}$ free from Na were effected from the solution containing the appropriate reagents in 300 ml of dilute HCl solution at a concentra-

TABLE 2. SYNTHESES OF SCANDIUM-BERYLS

No.	Gel composition	Temp. C°	Press., kb	hours	a, Å	c, Å	Phases[a]
1.	$Be_3Sc_2Si_6O_{18}$ (Na-free)	680°	2	20			Phen, crist.
2.	$Be_3Sc_2Si_6O_{18}$ (Na-free)	550°	2	40			Phen, beryl
3.	$Be_3Sc_2Si_6O_{18}$ (Na-free)	450°	2	20	9.56	9.16	Beryl
4.	$Be_3Sc_2Si_6O_{18}$ (Na, tr.)	700°	2	20			Phen, beryl tr.
5.	$Be_3(Sc_{1.98}Fe_{.02})Si_6O_{18}$ (Na, tr.)	700°	2	24	9.56	9.16	Phen. qtz, beryl
6.	$Be_3(Sc_{1.98}Fe_{.02})Si_6O_{18}$ (Na, tr.)	680°	2	20			Phen, qtz, beryl tr.
7.	$Be_3(Sc_{1.94}Fe_{.06})Si_6O_{18}$ (Na, tr.)	700°	2	24	9.56	9.16	Beryl
8.	$Be_3(Sc_{1.88}Fe_{.12})Si_6O_{18}$ (Na 0.1)	680°	2	20	9.56	9.16	Beryl
9.	$Be_3(Sc_{1.87}Fe_{.13})Si_6O_{18}$ (Na, tr.)	700°	2	20	9.56	9.16	Beryl, plus
10.	$Be_3(Sc_{1.75}Fe_{.25})Si_6O_{18}$ (Na, tr.)	700°	2	20	9.552	9.165	Beryl
11.	$Be_3(Sc_{1.6}Fe_{.4})Si_6O_{18}$ (Na-free)	680°	2	20			Phen. crist.
12.	$Be_3(Sc_{1.6}Fe_{.4})Si_6O_{18}$ (Na-free)	620°	2	20	9.53	9.16	Phen, beryl
13.	$Be_3(Sc_{1.6}Fe_{.4})Si_6O_{18}$ (Na free)	550°	2	20	9.53	9.16	Beryl, phen
14.	$Be_3(Sc_{1.5}Fe_{.5})Si_6O_{18}$	680°	2	20	9.53	9.16	Beryl, phen tr.
15.	$Be_3(Sc_{1.5}Fe_{.5})Si_6O_{18}$	650°	2	20	9.53	9.16	Beryl, phen tr.
16.	$Be_3(Sc_{1.5}Fe_{.5})Si_6O_{18}$	550°	2	20	9.53	9.16	Beryl, phen tr.
17.	$Be_3(Sc_{1.33}Fe_{.67})Si_6O_{18}$	650°	2	20	9.52	9.15	Beryl, hem
18.	$Be_3(Sc_{1.33}Fe_{.67})Si_6O_{18}$	1200°	air	10		9.15	Beryl, crist, hem
19.	$Be_3(Sc_1Fe_1)Si_6O_{18}$	650°	2	40	9.51	9.148	Beryl, hem
20.	$Be_3(Sc_{.5}Fe_{1.5})Si_6O_{18}$	680°	2	20	~9.50	~9.15	Crist, hem, beryl weak
21.	$Be_3Fe_2Si_6O_{18}$	650°	2	20			No beryl; hem, qtz
22.	$Be_3(Sc_{1.66}Cr_{.34})Si_6O_{18}$	680°	2	48	9.54	9.15	Beryl, qtz, phen
23.	$Be_3(Sc_{1.5}Cr_{.5})Si_6O_8$	680°	2	48	9.54	~9.15	Beryl, qtz, phen
24	$Be_3(Sc_{1.33}Cr_{.67})Si_6O_{18}$	680°	2	48	9.52	9.15	Beryl, qtz
25.	$Be_3(Sc_1Cr_1)Si_6O_{18}$	650°	2	20	~9.52	~9.15	Beryl, keatite, qtz
26.	$Be(Sc_{1.66}Mn_{.34})Si_6O_{18}$	700°	2	40	9.56	9.16	Beryl, plus
27.	$Be_3(Sc_{1.66}Mn_{.34})Si_6O_{18}$	700°	2	40			Phen
28.	$Be_3(Sc_{1.66}Mn_{.34})Si_6O_{18}$	1020°	air	48	9.54	9.15	Beryl, plus
29.	$Be_3(Sc_1Mn_1)Si_6O_{18}$	1020°	air	48		~9.15	Beryl, plus
30.	$Be_3(Sc_1Mn_1)Si_6O_18$	650°	2	20	~9.54	~9.15	Beryl, phen
31.	$Be_3(Sc_{1.66}V_{1.34})Si_6O_{18}$	680°	2	48	9.53	9.15	Beryl, plus
32.	$Be_3(Sc_{1.5}V_{.5})Si_6O_{18}$	680°	2	48	9.51	9.15	Beryl, plus
33.	$Be_3(Sc_1V_1)Si_6O_{18}$	650°	2	20	9.51	9.15	Beryl, plus
34.	$Be_3(Sc_{1.66}Ga_{.34})Si_6O_{18})$	700°	2	48			Phen, qtz
35.	$Be_3(Sc_{1.66}Ga_{.34})Si_6O_{18}$	550°	2	40	9.49	9.16	Beryl
36	$Be_3(Sc_{1.5}Ga_{.5})Si_6O_{18}$	700°	2	48			Phen. qtz
37.	$Be_3(Sc_{1.5}Ga_{.5})Si_6O_{18}$	550°	2	40	9.46	9.15	Beryl, plus
38.	$Be_3(Sc_1Ga_1)Si_6O_{18}$	650°	2	20	~9.43	9.15	Beryl, qtz

[a] Abbreviations: phen = phenacite, qtz = quartz, crist = cristobalite, hem = hematite, tr = trace.

tion of 1 millimol per formula unit. Precipitation was effected by ammonia at pH 10. After centrifuging, the acid-soluble hydrosilicate gels were dissolved in sufficient HCl, the volume increased to 300 ml H_2O, and again precipitated by ammonia and centrifuged. This entire operation was repeated three times. The Na-free gels finally were crystallized hydrothermally (Table 2).

RESULTS OF SYNTHESES

Phases isostructural with beryl were obtained both with the end-composition $Be_3Sc_2Si_6O_{18}$ and with compositions in which the Sc^{3+} was substituted in part by Fe^{3+}, Cr^{3+}, V^{3+}, Mn^{3+} or Ga (Table 2). The composition and properties of the products are discussed beyond. The identification of the run products was established in all instances by X-ray powder diffraction patterns. These were taken in filtered Cu radiation with Si as internal standard. The patterns usually were strong and sharp without line broadening. Under the microscope the products were in general too fine-grained for satisfactory optical study. Some of the (Sc, Cr) and (Sc, V) runs, however, contained a proportion of well-formed crystals up to about 20 microns in size. These were hexagonal prisms terminated by $\{0001\}$. The crystals of (Sc, Cr)-beryl were pale emerald green in color. Most of the runs contained from a few percent up to 10 percent or more of foreign material, but a few were essentially pure. Some runs, of compositions to be noted, yielded little or no beryl phase. The main admixed phases were quartz and phenacite; keatite or cristobalite were identified in some instances, and hematite or compounds of Cr, V, Mn and Ga were generally present in trace amounts or more.

None of the gels afforded beryl-type phases when heated in air at 1 atm with the exception of a few containing Sc^{3+} with Fe^{3+} or Mn^{3+}. Efforts failed to produce Sc-beryl from melts containing appropriate amounts of the oxidic components and the following fluxes: $LiMoO_4$, $LiWO_4$, $NaMoO_4$, $NaWO_4$, V_2O_5, $PbO+V_2O_5$, $BaO+V_2O_5$, Bi_2O_3, PbO, $ScBO_3$, borax or B_2O_3. A factor here is the formation of stable scandium tungstate, molybdate or borate. Transparent blue single-crystals of phenacite up to 0.2 mm in size, colored by V^{4+}, were obtained by slow cooling of saturated melts containing V_2O_5. The possibility still remains that Sc-beryl may crystallize from melts at oxide to flux ratios other than those investigated here. In this connection, Ganguli and Saha (1965a) have drawn attention to the possibility of a small primary field for beryl in the anhydrous system BeO-Al_2O_3-SiO_2. Al-beryl melts incongruently at about 1500°C to phenacite, chrysoberyl and liquid, and complete melting takes place at about 1627°C; beryl glass, however, crystallized to beryl below 1500°C if seeded with beryl (Ganguli and Saha, 1965b). The crystallization of beryl directly from the melt at pressures of over 10 kbars is reported by Wilson (1965).

COMPOSITION OF PRODUCTS

The observed variation in the unit cell dimensions and optical properties of our products, described beyond, establishes that a considerable range of substitution of R^{3+} ions for Sc^{3+} has been effected. Neither the limits of this substitution under our experimental conditions nor the actual $Sc^{3+}:R^{3+}$ ratio in the beryl obtained from stated gel compositions are known. Efforts to obtain satisfactory analyses by electron microprobe techniques failed. It is apparent, however, that only limited series by substitution of R^{3+} ions extend from the end-composition $Be_3Sc_2Si_6O_{18}$. Efforts to synthesize the end-compositions $Be_3R^{3+}Si_6O_{18}$ failed, and in general gel compositions containing more than 25–50 atomic percent R^{3+} gave a decreasing yield of relatively poorly crystallized beryl. There is also some evidence that the unit-cell dimensions remain nearly constant in beryls containing R^{3+} over certain limits. The (Sc, Fe^{3+}) series extend to at least 25 atomic percent Fe^{3+} in the beryl, since a gel of this composition crystallized to beryl without foreign admixture, and it may extend to about 50 percent Fe^{3+} or somewhat over. Natural bazzite, to which this synthetic material essentially corresponds, contains about 2/3 Sc in the 4(*c*) site with the rest chiefly Fe^{3+}.

This matter is complicated by a variation in the thermal stability of the phases. The end-composition $Be_3Sc_2Si_6O_{18}$ has a lower temperature stability than Al-beryl or beryls containing (Sc, R^{3+}). It was obtained in pure form at 450°C and 2 kbars, but not at 680°C and 2 kbars either in the presence or absence of Na. On the other hand, Al-beryl and (Sc, R^{3+})-beryls containing trace amounts of Na are stable at 680°C or 700° and 2 kbars; in the absence of Na these beryls are stable at 550°C to 620°C but not at 680°C and 2 kbars. The stability of scandium-beryls evidently is affected by the presence of both other trivalent ions and of Na.

It may be noted that all of the R^{3+} elements investigated in our work are well-known as trace or minor constitutents in natural or synthetic Al-beryl (Feklichev, 1963). The content of Fe^{3+} in natural beryl ranges up to at least 3.4 percent Fe_2O_3 (Watters, 1963). The content of Cr in synthetic Al-emerald ranges up to 2.0 percent Cr_2O_3 (Flanigen *et al.*, 1967; Rogers and Sperisen, 1942). Emel'yanova *et al.*, (1965) have verified by absorption spectrophotometry the valence state of V^{3+}, Mn^{3+}, Ni^{3+}, Co^{3+} and Fe^{2+} present in unstated amounts in synthetic Al-beryl grown hydrothermally. Synthetic Al-beryls grown in 1954 by C. F. Chatham, in connection with a projected study of the compositional variation of beryl, were found on quantitative spectrographic analysis by the U. S. Geological Survey to contain Cr 1.5, Co 0.18, Ni 0.74, Mn 0.009 and Ti 1.2 percent (valence states not known) in different crystals.[1]

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[1] Private communication, C. S. Hurlbut, Jr., 1966.

Ordinary beryl, $Be_3Al_2Si_6O_{18}$, is readily synthesized at 680°C and 2 kbars by our method. A run with the composition $Be_3(Sc_{1.66}Al_{0.34})Si_6O_{18}$ under these conditions gave beryl with the cell dimensions of the Al-beryl. A hydrothermal run at 700°C on a gel with the composition $Mg_3Sc_2Si_6O_{18}$ gave an unidentified product.

X-Ray and Optical Data. The unit-cell dimensions of the products are given in Table 2. An indexed pattern of synthetic material obtained from a run in which the starting gel had the composition $Be_3(Sc_{1.75}Fe^3_{0.25})Si_6O_{18}$ is given in Table 3. The cell dimensions cited for this material were obtained by a computer refinement of the spacing data using the program of Burnham (1962). The unit-cell volumes of the Sc and (Sc, R^{3+}) beryls are larger than that of ordinary Al-beryl. The volume change is determined by a very large increase in *a* and a slight decrease in *c* as compared to Al-beryl. This type of variation also is found in the natural Sc-rich beryl bazzite (Table 4). It may also operate in natural Al-beryl. This is suggested by the cell dimensions, cited in Table 4, of Al-beryls from Arizona and Utah containing relatively large amounts of Mg and Fe^{2+} in substitution for Al (Schaller, Stevens and Jahns, 1962; Nassau and Wood, 1968). An opposite change in dimensions is brought about in Al-beryl by the entrance of alkalies into the channelways formed by the Si_6O_{18} rings; here *c* increases and *a* remains essentially unchanged, as seen from Table 4.

TABLE 3. X-RAY POWDER SPACING DATA FOR BERYL FROM RUN-COMPOSITION $Be_3(Sc_{1.75}Fe_{0.25}{}^3)Si_6O_{18}$. PEAK HEIGHTS IN ARBITRARY CHART UNITS. UNIT-CELL DIMENSIONS (*a* 9.552 Å ±0.002, *c* 9.165 Å±0.003) BASED ON REFLECTIONS INDICATED

$hk\bar{i}l$	*d*,calc	*d*,obs	*I*	$hk\bar{i}l$	*d*,calc	*d*,obs	*I*
0001	9.16	9.15	13	*$40\bar{4}0$	2.608	2.068	5
$10\bar{1}0$	8.27	8.27	89	*$31\bar{4}2$	2.051	2.051	8
*0002	4.582	4.578	24	*$20\bar{2}4$	2.004	2.003	10
*$10\bar{1}2$	4.008	4.006	48	*$23\bar{5}1$	1.858	1.857	3
*$11\bar{2}2$	3.306	3.306	100	$31\bar{4}3$	1.833	1.8325	7
*$20\bar{2}2$	3.070	3.072	14	*$41\bar{5}0$	1.8050	1.8045	10
*$21\bar{3}1$	2.959	2.960	75	*$30\bar{3}4$	1.7622	1.7610	15
*$30\bar{3}0$	2.757	2.758	12	*$41\bar{5}2$	1.6794	1.6785	6
*$21\bar{3}2$	2.582	2.577	17	*$22\bar{4}4$	1.6532	1.6520	14
$22\bar{4}0$	2.387	2.383	5	$41\bar{5}2$	1.553	1.5530	6
0004	2.288	2.290	9	*0006	1.5275	1.5250	3
*$31\bar{4}1$	2.225	2.224	4	$33\bar{6}2$	1.503	1.5040	5
$11\bar{2}4$	2.183	2.188	4	$42\bar{6}2$	1.479	1.4780	5
*$22\bar{4}2$	2.117	2.119	5	$11\bar{2}6$	1.453	1.4530	4

TABLE 4. UNIT-CELL DIMENSIONS OF SC-BERYL, AL-BERYL, AND ALKALI-BERYL

Composition	a(Å)	c (Å)	c/a	Reference
$Be_3Sc_2Si_6O_{18}$ (synthetic)	9.56	9.16	0.9581	Present study
$Be_3(Sc_{1.75}Fe_{0.25}{}^3)Si_6O_{18}$	9.552	9.163	0.9593	Present study
$Be_3(Sc, etc.)_2Si_6O_{18}$ (bazzite, Baveno)	9.51	9.11	0.9579	Peyronel (1956)
$Be_3(Sc,Fe^3,etc.)_2Si_6O_{18}$ (bazzite, U.S.S.R.)	9.521	9.165	0.9626	Chistyakova *et al.* (1966)
$Be_3(Sc,Fe^3,Al)_2Si_6O_{18}$(?) (bazzite, Val Strem)	9.50	9.18	0.9663	Bergerhof and Nowacki (1955)
$Be_3(Al,Mg,Fe^2)_2Si_6O_{18}$ (Arizona)	9.30	9.20	0.9892	Schaller *et al.* (1962)
$Be_3(Al,Fe)_2Si_6O_{18}$ (Utah)	9.23637	9.1972	0.9958	Nassau and Wood (1968)
$Be_3Al_2Si_6O_{18}$ (pure synthetic)	9.210	9.199	0.9988	Evans and Mrose (1966)
$Be_3Al_2Si_6O_{18}$ ("pure" natural)	9.215	9.192	0.9975	Nat. Bur. Standards (1960)
$Be_3Al_2Si_6O_{18}$ ("pure" natural)	9.206	9.205	0.9998	Belov and Matveeva (1951)
$Be_3Al_2Si_6O_{18}$ ("pure" natural)	9.188	9.189	1.001	Norrish (1947)
Alkali-beryl (Cs_2O 4.13)	9.200	9.227	1.0029	Sosedko (1957)
Alkali-beryl (Cs_2O 11.3)	9.208	9.266	1.0062	Evans and Mrose (1966)

There is no evidence of the symmetry of our synthetic products other than the inconclusive facts that the microscopic crystals apparently are hexagonal in shape and optically uniaxial, and that the powder spacing data can be indexed in terms of a hexagonal cell. The structural studies of bazzite by Peyronel (1956) and by Bergerhof and Nowacki (1955), however, both confirm the space group $P6/mcc$. In this connection, it may be noted that the diffraction data for our material includes a weak but distinct reflection that appears to be the first order of (0001), a reflection inconsistent with the stated space group.

A related problem concerns the structural mechanism by which the substitution of Sc and R^{3+} changes the a and c dimensions. The entrance of these large ions solely into the $4(c)$ sites should produce a severe distortion of the ScO_6 polyhedron and of the shared BeO_4 tetrahedron. It may be suggested that the R^{3+} ions also enter the Si_6O_{18} rings in substitution for Si, producing a relative increase in the horizontal dimension and reducing strain in the inter-ring $4(c)$ sites. Valence compensation might then be effected by a concomitant substitution of Na into the channels of the Si_6O_{18} rings by the mechanism $Na_xBe_3Sc_2(Si_{6-x}R_x{}^{3+})O_{18}$. We have established, however, that (Sc, Fe^3) beryls can be formed in the absence of Na. The possibility also exists that valence composition can be effected by a substitution of Si for Be or otherwise. Since the Sc^{3+} ion is

TABLE 5. OPTICAL PROPERTIES OF SC-BERYL AND AL-BERYL

Composition	ε	ω	Biref.	Reference
Synthetic, $Be_3Sc_2Si_6O_{18}$	Mean index = 1.59			Present study
Synthetic, $Be_3(Sc_{1.5}Cr_{0.5})Si_6O_{18}$	1.586	1.606	0.020	Present study
Synthetic, $Be_3(Sc_1Cr_1)Si_6O_{18}$	1.592	1.610	0.018	Present study
Bazzite, Val Strem	1.606	1.622	0.016	Parker, *et al.* (1940)
Bazzite, U.S.S.R.	1.607	1.627	0.020	Chistyakova *et al.* (1966)
Bazzite, Baveno				Artini (1915)
Core	1.608	1.626	0.018	
Outer	1.602	1.623	0.021	
Al-beryl (natural, low alkali, average)	1.573	1.580	0.007	Literature
Al-beryl (synthetic, colorless)	1.563	1.569	0.006	Flanigen *et al.*, (1967)
Al-beryl (synthetic, no Cr or H_2O)	1.560	1.563	0.003	Flanigen *et al.*, (1967)
Alkali-beryl (natural, 11.3 Cs_2O)	1.601	1.608	0.007	Evans and Mrose (1966)

larger than the other R^{3+} ions and presumably occupies the 4(*c*) sites in the synthetic end-composition $Be_3Sc_2Si_6O_{18}$, it seems likely that the R^{3+} ions enter this site. This is the interpretation taken here.

A plot of the unit-cell dimensions of the synthetic $Be_3(Sc, Fe^{3+})_2Si_6O_{18}$ beryls as a function of composition is given in Figure 1. Since there is no direct evidence of the Sc:Fe^3 ratio in these beryls, as earlier discussed, the cited compositions are based on the Sc:Fe^{3+} ratios of the initial gels. The significant variation observed in the cell dimensions clearly indicates

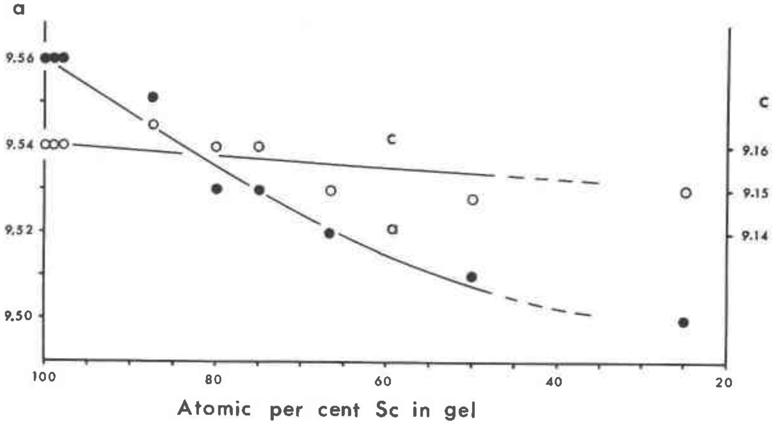

FIG. 1. Variation in the unit-cell dimensions of synthetic (Sc, Fe^3)-beryls as a function of the initial composition of the gels employed.

that there is a substantial amount of substitution of Sc^{3+} by Fe^{3}. The cell volumes of equivalent compositions in the separate (Sc, R^{3+}) series vary in the order $Mn^{3+} > (Cr^{3+}, Fe^{3+}, V^{3+}) > Ga$, as would be expected from the relative ionic sizes.

The indices of refraction of the products could not be measured accurately in most instances because of small particle size. The mean index of refraction of the end-composition $Be_3Sc_2Si_6O_{18}$ is about 1.59 and higher than that of Al-beryl (Table 5). The substitution of Sc^{3+} by R^{3+} ions increases the indices of refraction. In some runs there was a small range of variation in the indices of refraction. In the (Sc_3Cr_1) run, different crystals ranged from ω 1.606, ϵ 1.586 up to at least near ω 1.610. The (Sc_1Cr_1) run was more uniform, with most crystals near ω 1.610, ϵ 1.592. Minute crystals with indices as high as 1.63–1.64, not identified with certainty as beryl, were observed in some high-R^{3+} runs. The (Sc_1Ga_1), (Sc_5Ga_1) and (Sc_5V_1) runs apparently had ω somewhat below 1.61. In comparison to Al-beryl, the birefringence of the (Sc, Cr) beryls is higher, and there is a relatively large increase in ω (Table 5). This correlates with the relatively large increase in the *a* dimension of the unit cell.

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