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# A New Barium Scandium Silicate: $Ba_9Sc_2(SiO_4)_6$

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**We report the synthesis and initial characterization of $Ba_9Sc_2(SiO_4)_6$, the first example of a new oxide structure-type accommodating a large alkaline earth ion, $Ba^{2+}$, a large octahedral ion, $Sc^{3+}$, and tetrahedral silicate units. Transparent crystals which crystallize in the rhombohedral space group, $R\bar{3}$, with $a_H$ = 9.8716(2)Å, $c_H$ = 21.9376(7)Å were grown from a silica-rich eutectic melt. The structure contains layers made up of $ScO_6$ octahedra linked by $SiO_4$ tetrahedra. The $Ba^{2+}$ ions occupy large high-coordination-number interlayer sites.** © 1994 Academic Press, Inc.

## INTRODUCTION

Transparent oxides have a variety of uses such as optical windows or as hosts for active ions in solid state lasers. Many transparent silicates are known from mineral chemistry while still more have been prepared synthetically. A common way for a silicate to accommodate a large divalent ion and an octahedral trivalent ion is the garnet structure (1). The overall stoichiometry of garnets is $A_3^{2+}B_2^{3+}Si_3O_{12}$ and these crystallize in the cubic space group, *Ia*3*d* with lattice constants, *a*, approximately 12–12.5 Å (2). The $A^{2+}$ ions occupy dodecahedral sites with eightfold oxygen coordination. However, the garnet structure in silicates is only stable for certain ranges of cation sizes (3). While a stable garnet phase is formed in e Ca–Sc–Si–O system (4), the ionic radius of the larger $Ba^{2+}$ ion favors a larger coordination sphere which places the corresponding Ba–Sc–Si–O composition outside the garnet stability field. Here we report a new phase of composition $Ba_9Sc_2(SiO_4)_6$, a silicate which accommodates the large divalent barium ion and the octahedral $Sc^{3+}$ in a unique layered structure which represents a new structure-type.

## EXPERIMENTAL

### Sample Preparation

Clear, colorless, euhedral crystals of typical size 0.5 mm were grown from a silica-rich eutectic melt corresponding to the composition 25 mole% BaO (as $BaCO_3$, Johnson Matthew Puratronic, 99.997%), 12.5 mole% $Sc_2O_3$ (Aran Isles, 99.99%), and 25 mole% $SiO_2$ (Alfa, 99.995%). The reagents were ground together using a laboratory mortar grinder (Retsch, Type RM O) with an agate mortar and pestle for 0.5 hr placed in a platinum crucible and subsequently heated at 1100°C for 12 hr. The mixture was then cooled and reground using the autogrinder for an additional 0.5 hr. Finally, the sample was heated to 1500°C at 5°C/min, soaked for 12 hr at this temperature, and slowly cooled at a rate of 1°C/hr to 1200°C. The sample was coarsely crushed in an agate mortar and pestle, and single crystals were selected from the product using a microscope.

A homogeneous powder of the $Ba_9Sc_2(SiO_4)_6$ compound was prepared by grinding together a stoichiometric mixture in an agate mortar and pestle, then firing at 1100°C for 12 hr. The resulting powder was reground, pressed into a pellet and heated to 1400°C for 48 hr.

### Structure Determination

Spherically ground crystals were measured at 23°C on an Enraf–Nonius CAD-4 diffractometer using graphite monochromatized Mo*Kα* radiation and the NRCCAD program package (5). All calculations were carried out on a Sun workstation using the NRCVAX structure package (6). Lattice parameters were determined from the absolute $2\theta$ values of reflections at high angle, 25 reflections with $60° < 2\theta \leq 65°$. A spherical absorption correction was applied to all measured intensities. The initial barium atom positions were determined using the Patterson method. The Sc and Si atoms were located in ensuring Fourier maps and the oxygen positions were obtained from difference maps. Anisotropic temperature factors for all atoms

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TABLE 1
Crystal Data and Intensity Collection for $Ba_9Sc_2(SiO_4)_6$

| | |
|---|---|
| Formula | $Ba_9Sc_2(SiO_4)_6$ |
| Formula weight | 1878.38 |
| Space group | $R\bar{3}$ |
| Crystal size | 0.20 mm-diameter sphere |
| $a_H$ | 9.8716(2) Å |
| $c_H$ | 21.9376(7) Å |
| $V$(Å$^3$) | 1851.38(7) |
| $Z$ | 3 |
| $D_c$(g/cm$^3$) | 5.054 |
| $\mu$(Mo$K\alpha$)(cm$^{-1}$) | 150.1 |
| Diffractometer | Nonius CAD4 |
| Radiation | (Mo$K\alpha$)($\lambda$ = 0.71069 Å) graphite-monochromated |
| Temperature | 23°C |
| $2\theta_{MAX}$ | 80.0° |
| Data collected | 5944 |
| Scan type | $\theta/2\theta$ |
| Independent reflections | 2558 |
| Reflections measured ($I > 2.5\ \sigma(I)$) | 2039 |
| $R$ | 0.071 |
| $R_w$ ($w = 1/\sigma^2(F_o)$) | 0.051 |
| Extinction length ($\mu$m) | 0.023(4) |

TABLE 2
Atomic Parameters $x$, $y$, $z$, for $B_{iso}$ for $Ba_9Sc_2(SiO_4)_6$

| | $x$ | $y$ | $z$ | $B_{iso}$[a] |
|---|---|---|---|---|
| Ba 1 | 0 | 0 | 0 | 0.913(24) |
| Ba 2 | 1/3 | 2/3 | 0.00313(4) | 0.640(16) |
| Ba 3 | 0.02691(6) | 0.67043(6) | 0.108739(21) | 0.548(17) |
| Sc | 0 | 0 | 0.16458(11) | 0.39(4) |
| Si | 0.3386(3) | 0.0259(3) | 0.07635(10) | 0.36(7) |
| O 1 | 0.3568(10) | 0.0764(10) | 0.0068(3) | 1.2(3) |
| O 2 | 0.4899(8) | 0.1656(8) | 0.1144(3) | 0.80(20) |
| O 3 | −0.0102(8) | 0.1666(8) | 0.1060(3) | 0.79(21) |
| O 4 | 0.1334(8) | 0.4721(8) | 0.0927(3) | 0.82(21) |

*Note.* ESDs refer to the last digit printed.
[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

were included in the final refinements. Crystallographic data are listed in Table 1, atomic coordinates and isotropic thermal parameters in Table 2, and selected bond lengths in Table 3.[1]

The phase, $Ba_9Sc_2(SiO_4)_6$, crystallizes in a rhombohedral space group, $R\bar{3}$, with $a_H$ = 9.8716(2) Å and $b_H$ = 21.9376 Å. This corresponds well to the powder X-ray diffraction pattern for stoichiometric ceramic material, as shown in Table 4. We note that the powder pattern shows some evidence for preferential orientation; measured and calculated intensities differ for a few reflections.

## DESCRIPTION OF THE STRUCTURE

The $Ba_9Sc_2(SiO_4)_6$ structure contains layers made up of $ScO_6$ octahedra linked by $SiO_4$ tetrahedra as shown in Fig. 1 (7). The $ScO_6$ octahedra are arranged in a nearly hexagonal array. All of the vertices of an $ScO_6$ octahedron are corner-shared with $SiO_4$ tetrahedra, and two pairs of $SiO_4$ tetrahedra link each pair of $ScO_6$ octahedra. The $SiO_4$ tetrahedra are slightly distorted, with Si–O distances varying from 1.588 to 1.664 Å and O–Si–O bond angles from 105.0 to 117.7°. The $ScO_6$ octahedra have a ferroelectric distortion to produce three Sc–O distances of 2.078 Å and three of 2.128 Å. Such a distortion is possible in this centered space group, $R\bar{3}$, because the center of symmetry lies at one of the barium sites. The scandium is not constrained to the center of the octahedron in this structure and instead adopts the offset position.

There are three barium sites in the structure. The $Ba^{2+}$

TABLE 3
Selected Bond Distances for
$Ba_9Sc_2(SiO_4)_6$

| Bond | Distance (Å) | |
|---|---|---|
| Ba 1–O 1 | 3.215(8) | 6× |
| Ba 1–O 3 | 2.879(6) | 6× |
| Ba 2–O 1 | 2.841(8) | 3× |
| Ba 2–O 2 | 3.089(7) | 3× |
| Ba 2–O 4 | 2.767(7) | 3× |
| Ba 3–O 1 | 2.580(6) | |
| Ba 3–O 2 | 2.963(11) | |
| Ba 3–O 2 | 2.968(11) | |
| Ba 3–O 2 | 3.009(12) | |
| Ba 3–O 3 | 2.912(8) | |
| Ba 3–O 3 | 2.968(19) | |
| Ba 3–O 3 | 3.146(5) | |
| Ba 3–O 4 | 2.668(7) | |
| Ba 3–O 4 | 2.718(10) | |
| Ba 3–O 4 | 3.093(8) | |
| Sc–O 2 | 2.078(6) | 3× |
| Sc–O 3 | 2.128(7) | 3× |
| Si–O 1 | 1.588(7) | |
| Si–O 2 | 1.664(7) | |
| Si–O 3 | 1.659(17) | |
| Si–O 4 | 1.613(14) | |

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[1] See NAPS document No. 05113 for 33 pages of supplementary material. This is not a multiarticle document. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163-3513. Remit in advance $11.65 for photocopies or $4.00 for microfiche. There is a $15.00 invoicing charge on all orders filled before payment. Foreign orders add $4.50 for postage and handling for the first 20 pages, and $1.00 for additional 10 pages of material, or $1.75 for the first microfiche and $.50 for each fiche thereafter.

TABLE 4
Powder Diffraction Pattern for $Ba_9Sc_2(SiO_4)_6$

| $h$ | $k$ | $l$ | $2\theta$(Å) | $d$ | $I/I_0$ |
|---|---|---|---|---|---|
| 1 | 1 | 3 | 21.92 | 4.051 | 19 |
| −1 | 2 | 6 | 30.58 | 2.921 | 45 |
| 3 | 0 | 0 | 31.30 | 2.855 | 100 |
| 0 | 0 | 9 | 37.02 | 2.426 | 18 |
| −2 | 4 | 3 | 38.50 | 2.336 | 28 |
| 2 | 2 | 6 | 44.38 | 2.039 | 74 |
| 0 | 3 | 9 | 49.16 | 1.852 | 18 |
| 1 | 4 | 3 | 50.53 | 1.805 | 16 |
| 1 | 1 | 12 | 53.44 | 1.713 | 16 |
| −4 | 5 | 6 | 55.33 | 1.659 | 47 |
| 3 | 3 | 0 | 55.96 | 1.642 | 10 |

ions occupy large coordination sites. The Ba(1) site is 12-coordinate, Ba(2), 9-coordinate, and Ba(3), 10-coordinate. The 12-coordinate size for Ba(1), which occupies a special position, $\bar{3}$ symmetry, is a slightly distorted cuboctahedron as shown in Fig. 2a. Six oxygens at 2.9 Å form an elongated octahedron with six oxygens at 3.2 Å about the waist of that octahedron forming the coordination sphere. The Ba(1) ions are arrayed in chains in the interlayer gap as shown in Fig. 3. The Ba(2) ion also occupies an intergap site, and is also in a special position, symmetry 3. This ion is 9-coordinate as shown in Fig. 2b. The coordination sphere derives from that of Ba(1), but in this case there are only three oxygens about the waist of the elongated octahedron. This gives rise to triangular faces and large pentagonal faces for the coordination polyhedron. Finally, Ba(3) which is 10-coordinate occupies a general position in the Sc–Si–O layer. The coordination sphere

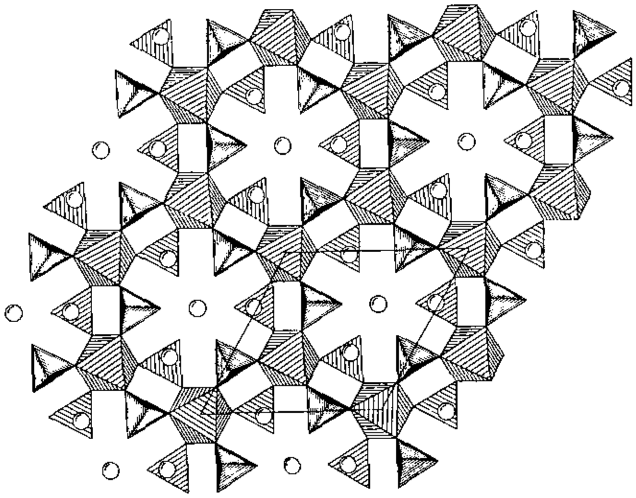

FIG. 1. View of the $Ba_9Sc_2(SiO_4)_6$ structure down the $c_H$ axis showing one layer made up of $ScO_6$ octahedra linked by $SiO_4$ tetrahedra. The open circles represent barium atoms.

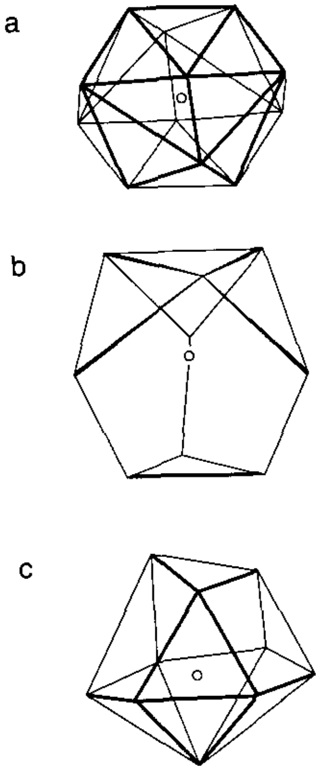

FIG. 2. Coordination polyhedra for the three barium sites in the $Ba_9Sc_2(SiO_4)_6$ structure. (a) The 12-coordinate site for Ba(1) which is a slightly distorted cuboctahedron. (b) The 9-coordinate site occupied by Ba(2) which is the cuboctahedron of (a) minus three oxygens at its waist. (c) The 10-coordinate site for Ba(3) which is half a cuboctahedron is capped by a single oxygen to form a hexagonal pyramid at the bottom.

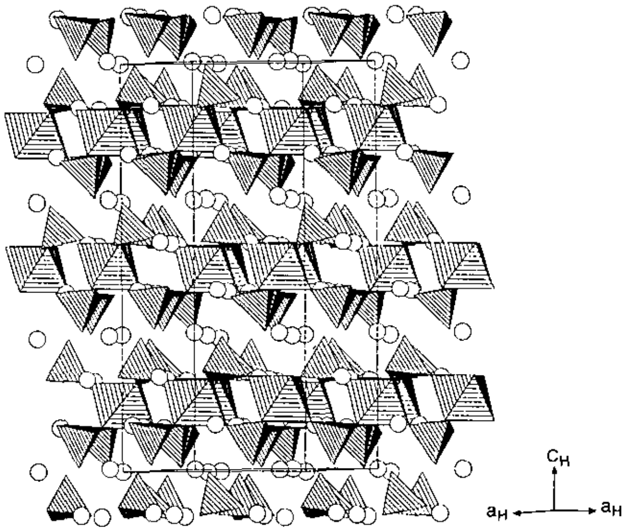

FIG. 3. A view of the structure perpendicular to the $c_H$ axis to emphasize the layered nature of the $Ba_9Sc_2(SiO_4)_6$ structure. The layers are made up of $ScO_6$ octahedra linked by $SiO_4$ tetrahedra. The open circles represent barium atoms. In the chains, Ba(1) and Ba(2) alternate, while Ba(3) is in the Sc–Si–O layer.

again derives from a cuboctahedron like that of Ba(1). As shown in Fig. 2c, half a cuboctahedron is capped by a single oxygen to form a hexagonal pyramid at the bottom. As a consequence of this highly irregular coordination polyhedron, this Ba(3)–O(1) distance is unusually short at 2.580 Å.

The layered nature of $Ba_9Sc_2(SiO_4)_6$ is shown clearly in Fig. 3, a view inclined 5° from the $a_H$ axis. The fact that this material forms in a rhombohedral structure is flagged by the varying orientations of the $SiO_4$ units arrayed along (110).

## DISCUSSION

Like garnets, $Ba_9Sc_2(SiO_4)_6$ is classed as an independent tetrahedral silicate or nesosilicate (also orthosilicate) (8); no two $SiO_4$ units share an oxygen in such structures. In contrast to the garnet structure or other mineral nesosilicates including olivines such as forsterite, $Mg_2SiO_4$ (9), or zircon, $ZrSiO_4$ (10), which have three dimensionally linked structures, the $Ba_9Sc_2(SiO_4)_6$ structure is layered. The Ba–O interlayer links are, however, strong ionic bonds as evidenced by our ability to grind a sphere of this material. Other layered orthosilicates including $Y_2SiO_5$ are also known (11).

The $Ba_9Sc_2(SiO_4)_6$ structure is the first example of a new structure-type; a unique atomic arrangement that accommodates tetrahedral $SiO_4$ units, larger octahedral $ScO_6$ units, and various cuboctahedral-derived high-coordination-number sites for $Ba^{2+}$ ions. This structure can be derived from the structure of $Na_4Zr_2Si_3O_{12}$ (12, 13), a NASICON-related system. NASICON forms with a three-dimensional network of $SiO_4$ tetrahedra and $ZrO_6$ octahedra. The arrangement of tetrahedra around the octahedra is nearly the same in both structures. In the $Na_4Zr_2Si_3O_{12}$ phase, however, the $SiO_4$ tetrahedra share four oxygens with $ZrO_6$ octahedra, while in $Ba_9Sc_2(SiO_4)_6$, the $SiO_4$ tetrahedra have only two vertices linked to $ScO_6$ octahedra. The result is a two-dimensional network which can be obtained from the $Na_4Zr_2Si_3O_{12}$ structure by removing half of the $ZrO_6$ octahedra. The layers in the $Ba_9Sc_2(SiO_4)_6$ are then linked together by large $Ba^{2+}$ ions (Ba(1) and Ba(2)) which occupy high-coordination number sites in between the layers.

The $Ba_9Sc_2(SiO_4)_6$ structure has several unusual aspects. The displacement of the scandium ion from the center of its octahedral coordination polyhedron suggests that this material may have interesting dielectric behavior. Also, in this structure the interlayer gap contains chains of cations (Ba(3)) with relatively low coordination numbers. Significant ionic conductivities may result if this structure can be maintained while substituting a monovalent cation such as potassium or rubidium on the Ba(2) site with appropriate charge compensation, such as the substitution of phosphorus for silicon, elsewhere in the structure. Efforts to characterize this new phase and to prepare related phases are underway.

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