

Scandiobabingtonite, a new mineral from the Baveno pegmatite, Piedmont, Italy

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ABSTRACT

Scandiobabingtonite, ideally $\text{Ca}_2(\text{Fe}^{2+}, \text{Mn})\text{ScSi}_5\text{O}_{14}(\text{OH})$ is the scandium analogue of babingtonite; it was found in a pegmatitic cavity of the Baveno granite associated with orthoclase, albite, muscovite, stilbite, and fluorite. Its optics are biaxial (+) with $2V = 64(2)^\circ$, $\alpha = 1.686(2)$, $\beta = 1.694(3)$, $\gamma = 1.709(2)$. $D_{\text{meas}} = 3.24(5) \text{ g/cm}^3$, $D_{\text{calc}} = 3.24 \text{ g/cm}^3$, and $Z = 2$. Scandiobabingtonite is colorless or pale gray-green, transparent, with vitreous luster. It occurs as submillimeter sized, short, tabular crystals, slightly elongated on [001], and characterized by the association of forms {010}, {001}, {110}, {1 $\bar{1}$ 0}, and {101}. It occurs also as a thin rim encrusting small crystals of babingtonite. The strongest lines in the X-ray powder pattern are at 2.969 (S), 2.895 (S), 3.14 (mS), and 2.755 (mS) Å. The mineral is triclinic, space group $P\bar{1}$, with $a = 7.536(2)$, $b = 11.734(2)$, $c = 6.748(2)$ Å, $\alpha = 91.70(2)$, $\beta = 93.86(2)$, $\gamma = 104.53(2)^\circ$. Scandiobabingtonite is isostructural with babingtonite, with Sc replacing Fe^{3+} in sixfold coordination, but no substitution of Fe^{2+} by Sc takes place. Due to the lack of a suitably large crystal of the new species, such a replacement has been confirmed by refining the crystal structure of a Sc-rich babingtonite (final $R = 0.047$) using single-crystal X-ray diffraction (XRD) data.

INTRODUCTION

This paper describes the new mineral species scandiobabingtonite. Both the mineral and its name were approved by the IMA Commission on New Minerals and Mineral Names. Scandiobabingtonite is the sixth scandium mineral found in nature after bazzite, cascandite, jervisite, kolbeckite, and thortveitite. Two other Sc minerals were recently discovered: the scandium-dominant analogue of xenotime-(Y) (IMA no. 96-024) and the scandium-dominant analogue of overite and segelerite (IMA no. 96-060) (Mandarino and Grice 1997).

Baveno is the type locality for bazzite (Artini 1915), cascandite, and jervisite (Mellini et al. 1982). Recently thortveitite (Orlandi 1990) was found in this classic locality; therefore, the only scandium mineral not found to date at Baveno is kolbeckite. Due to this peculiarity, the pegmatitic granite of Baveno is unique.

The type material is preserved in the Museo di Storia Naturale e del Territorio, University of Pisa. A small crystal is also stored in the Royal Ontario Museum, University of Toronto.

OCCURRENCE, PHYSICAL, AND OPTICAL PROPERTIES

Scandiobabingtonite was found in the “Montecatini” granite quarry near Baveno (Novara, Piedmont, Italy), within a $10 \times 10 \times 20$ cm cavity, associated with snow-like orthoclase crystals, smoky quartz, light sky-blue albite, stilbite, fluorite, and light green-yellow rosettes of

mica (probably zinnwaldite) on which scandiobabingtonite crystals were implanted (Fig. 1). Platy crystals of scandiobabingtonite were also found in epitaxial intergrowth as a thin rim around green-black prismatic crystals of babingtonite (Fig. 2). The few crystals of scandiobabingtonite studied here came from one sample.

Scandiobabingtonite is transparent, with vitreous luster and pale gray-green color. Scandiobabingtonite occurs as submillimeter-sized, short, prismatic crystals, slightly elongated on [001] and characterized by the association of the forms {010}, {001}, {110}, {1 $\bar{1}$ 0}, and {101}, as shown in Figure 3. The faces were indexed using a two-circle optical goniometer, in conjunction with X-ray single-crystal study, to overcome problems associated with a slight distortion and opacity of the faces from a thin crust of mica.

Two small crystals used in the optical and chemical study showed a very small black core and a large gray-green transparent rim. It appears that the two crystals of scandiobabingtonite grew starting from a green seed crystal of babingtonite (Fig. 4). Babingtonite, normally associated with minute lamellar crystals of hematite, is a common mineral in the pegmatitic cavities of the Baveno granite. The color of scandiobabingtonite (light gray-green) is however easily distinguishable from that of babingtonite.

Scandiobabingtonite is brittle and shows {001} and {1 $\bar{1}$ 0} perfect cleavage; its hardness is 6. The measured density, obtained by the heavy liquid method on a zoned crystal, is $3.24(5) \text{ g/cm}^3$; the calculated value for the pure

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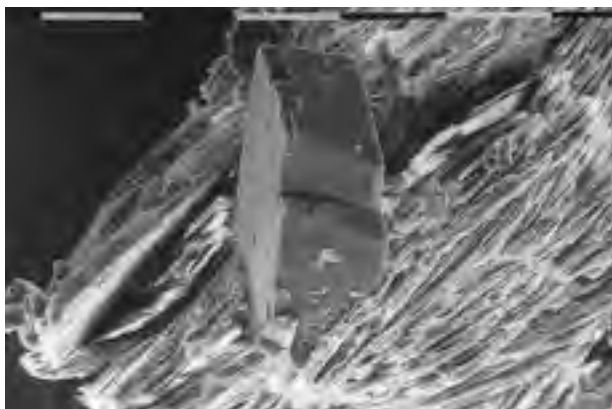


FIGURE 1. SEM photo of scandiobabingtonite crystals on mica from Baveno, Piedmont, Italy. Scale bar = 0.1 mm.

Sc and Fe^{3+} end-members is 3.22 and 3.29 g/cm^3 , respectively.

Optically, scandiobabingtonite is biaxial positive, shows a $2V(\text{meas})$ of $64(2)^\circ$ and a strong dispersion ($r > v$); pleochroism is strong with colors from pink (γ') to green (α'). Refractive indices for Na light are: $\alpha = 1.686(2)$; $\beta = 1.694(3)$; $\gamma = 1.709(2)$.

An evaluation of the optical orientation was done on a thin plate cut perpendicular to $[001]$ with a crystal section delimited by (110) , (010) , $(\bar{1}10)$, $(\bar{1}\bar{1}0)$, $(0\bar{1}0)$, and $(\bar{1}\bar{1}0)$ faces, where an evident cleavage (110) was also present; an extinction angle of approximately 6° was measured on (110) . $Z:\phi = -250^\circ$, $\rho = 47^\circ$; $Y:\phi = 146^\circ$, $\rho = 75^\circ$; $X:\phi = 42^\circ$, $\rho = 47^\circ$. Figure 5 shows the relationship between optical and crystallographic axes in scandiobabingtonite from Baveno.

CHEMICAL DATA

Electron microprobe analyses (Table 1) were collected using a wavelength dispersive ARL-SEM-Q instrument under the following operating conditions: accelerating

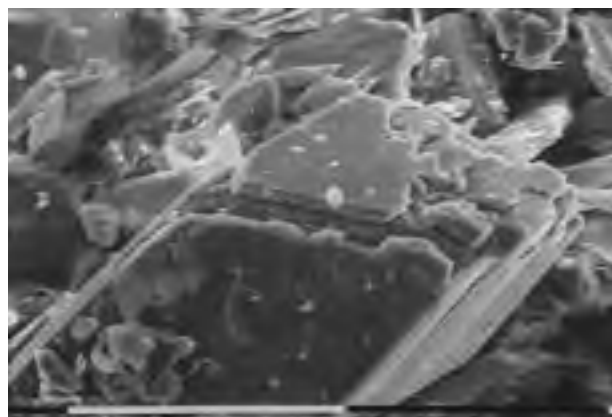


FIGURE 2. Epitaxial growth of tabular scandiobabingtonite crystals on a short prismatic crystal of babingtonite. SEM photo. Scale bar = 0.1 mm.

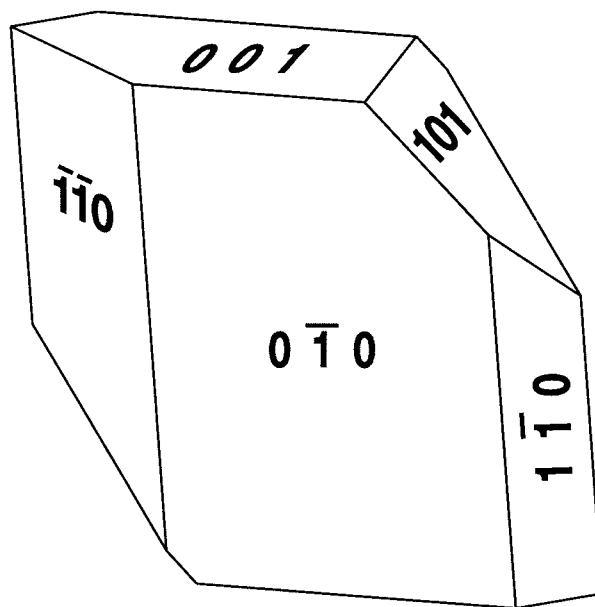


FIGURE 3. Drawing of a single crystal of scandiobabingtonite.

voltage 15 kV, sample current 20 nA, beam size 15 μm . The elements measured were Si, Sn, Sc, Fe, Ca, Mn, and Na. All other elements, including REE and Y, were below detection limit. Spessartine (for Fe and Mn), kaersutite (for Ca, Na, Si), metallic Sn (for Sn), and synthetic $\text{NaScSi}_2\text{O}_6$ (for Sc) were used as standards.

The crystal examined shows a sudden transition from a core with a composition essentially equal to scandium-free babingtonite to a rim with a high and homogeneous scandium content and a composition typical of scandiobabingtonite. These data show that whenever the Fe content is high the Sc content is low and vice-versa, whereas the Mn content remains constant across the two zones.

The H_2O content could not be directly determined because of the scarcity of material, but it was inferred to

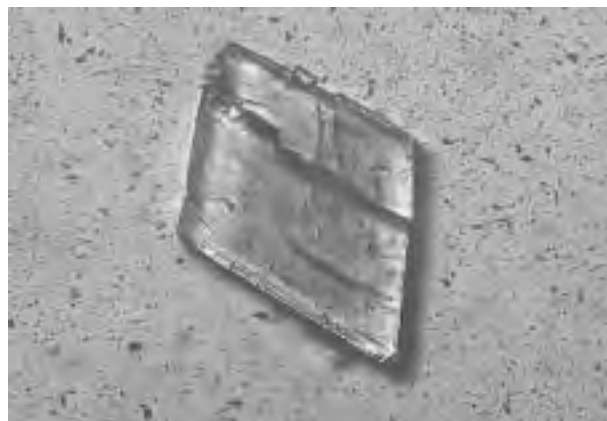


FIGURE 4. Thin section approximately on (001) of a submillimeter sized crystal showing a gray core of babingtonite and a light rim of scandiobabingtonite.

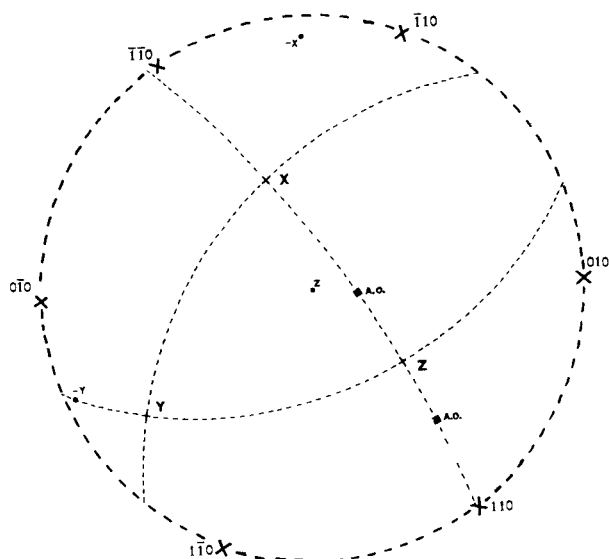


FIGURE 5. Stereographic projection of the optical (X , Y , Z) with respect to the crystallographic (x , y , z) axes in scandiobabingtonite.

possess one (OH) group per 14 O, as in the chemical formula of babingtonite. Fe was recalculated as FeO and Fe₂O₃ based on stoichiometry. On these grounds, the empirical formula of scandiobabingtonite, recalculated on the basis of a total of 15 O, is (Ca_{1.71}Na_{0.25})_{Σ1.96}(Fe_{0.65}²⁺Mn_{0.32})_{Σ0.97}(Sc_{0.91}Sn_{0.04}Fe_{0.03}³⁺)_{Σ0.98}Si_{5.09}O_{14.00}(OH)_{1.00}. The simplified formula is: Ca₂(Fe²⁺,Mn)ScSi₅O₁₄(OH), and thus scandiobabingtonite is the scandium analogue of babingtonite.

X-RAY CRYSTALLOGRAPHY

Preliminary X-ray single-crystal Weissenberg measurements indicate that scandiobabingtonite, similarly to babingtonite, is triclinic with space group $P\bar{1}$ or $P1$. The unit-cell parameters, refined at the four-circle diffractometer, are: $a = 7.536(2)$ Å, $b = 11.734(2)$, $c = 6.748(2)$, $\alpha = 91.70(2)^\circ$, $\beta = 93.86(2)$, $\gamma = 104.53(2)$. The X-ray powder pattern (Table 2), collected with Gandolfi camera and FeK α radiation on a small fragment selected from the rim of a zoned crystal, is almost identical to that of babingtonite.

Chemical dishomogeneity and the evident distortion of some crystals, displayed also by a light curvature of the faces of the crystals, caused all diffracted reflections of the single crystal to be rather broad.

STRUCTURE ANALYSIS

Collection of intensity data were carried out using a small crystal ($0.3 \times 0.2 \times 0.15$ mm) on an Italcristal Structures four-circle automatic diffractometer. The choice of the most suitable crystal for the XRD study represented a compromise between chemical composition and quality. Several crystals were tested by Weissenberg photographs and semiquantitative SEM-EDS chemical analyses. All

TABLE 1. Chemical data for scandiobabingtonite (average of three analyses)

| Oxide | Weight percent | Range |
|--------------------------------|----------------|-------------|
| SiO ₂ | 55.26 | 54.61–55.62 |
| SnO ₂ | 1.21 | 1.09–1.34 |
| Sc ₂ O ₃ | 11.32 | 11.01–11.51 |
| FeO* | 8.93 | 7.74–9.91 |
| CaO | 17.33 | 17.14–17.69 |
| MnO | 4.11 | 3.43–5.18 |
| Na ₂ O | 1.40 | 1.37–1.43 |
| H ₂ O† | 1.63 | |
| Σ | 101.24 | |

* Total Fe: This was recalculated as FeO 8.48 and Fe₂O₃ 0.50.

† Constrained to give 1 hydroxyl pfu.

Sc-rich crystals were unsuitable for a structural study. Therefore, a zoned crystal was used.

Operating conditions were: 48 kV, 28 mA, graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å), 20_{max}

TABLE 2. X-ray powder diffraction pattern for scandiobabingtonite

| l | d_{meas} | d_{calc} | hkl |
|-----|-------------------|-------------------|-------|
| m | 11.37 | 11.34 | 010 |
| mw | 6.96 | 6.98 | 110 |
| w | 6.66 | 6.72 | 001 |
| w | 5.09 | 5.15 | 120 |
| | | 5.14 | 101 |
| w | 4.74 | 4.76 | 101 |
| | | 4.74 | 111 |
| w | 4.44 | 4.45 | 111 |
| mw | 4.11 | 4.11 | 121 |
| w | 3.74 | 3.75 | 210 |
| m | 3.48 | 3.49 | 220 |
| vw | 3.29 | 3.30 | 131 |
| mS | 3.14 | 3.15 | 102 |
| m | 3.03 | 3.04 | 221 |
| S | 2.969 | 2.978 | 112 |
| S | 2.895 | 2.903 | 140 |
| mS | 2.755 | 2.760 | 220 |
| vw | 2.680 | 2.684 | 141 |
| | | 2.679 | 122 |
| w | 2.638 | 2.648 | 141 |
| w | 2.579 | 2.587 | 212 |
| vw | 2.483 | 2.484 | 122 |
| vw | 2.458 | 2.467 | 320 |
| vw | 2.286 | 2.296 | 311 |
| w | 2.244 | 2.247 | 141 |
| vw | 2.216 | 2.219 | 013 |
| w | 2.184 | 2.191 | 250 |
| | | 2.190 | 103 |
| w | 2.156 | 2.158 | 231 |
| vw | 2.120 | 2.120 | 023 |
| mw | 2.084 | 2.089 | 311 |
| | | 2.083 | 251 |
| w | 2.040 | 2.046 | 322 |
| w | 1.900 | 1.899 | 152 |
| | | 1.898 | 302 |
| w | 1.863 | 1.872 | 133 |
| w | 1.813 | 1.814 | 223 |
| w | 1.722 | 1.726 | 160 |
| w | 1.669 | 1.673 | 332 |
| w | 1.648 | 1.648 | 161 |
| w | 1.630 | 1.636 | 450 |
| | | 1.633 | 024 |
| vw | 1.608 | 1.615 | 062 |

Note: Gandolfi camera, FeK α radiation were used, d are in angstroms. Eight additional lines were seen.

TABLE 3. Final fractional coordinates and equivalent isotropic displacement parameters for scandian babingtonite

| Site | x | y | z | B (Å ²) |
|----------------------|-----------|-----------|-----------|---------------------|
| Ca1 | 0.7858(2) | 0.9429(1) | 0.1445(2) | 0.98(3) |
| Ca2 | 0.2344(2) | 0.5223(1) | 0.2999(2) | 1.02(3) |
| Fe ²⁺ | 0.5915(1) | 0.6448(1) | 0.0615(1) | 0.71(2) |
| Fe ³⁺ /Sc | 0.0457(1) | 0.2355(1) | 0.1871(1) | 0.60(2) |
| Si1 | 0.2906(2) | 0.0538(1) | 0.3408(2) | 0.66(4) |
| Si2 | 0.4635(2) | 0.3155(1) | 0.4261(2) | 0.60(4) |
| Si3 | 0.8070(2) | 0.4473(1) | 0.2129(3) | 0.61(3) |
| Si4 | 0.9890(2) | 0.7148(1) | 0.3071(3) | 0.58(4) |
| Si5 | 0.3292(2) | 0.8386(1) | 0.1074(3) | 0.66(4) |
| O1 | 0.1993(6) | 0.9898(4) | 0.5342(7) | 1.28(12) |
| O2 | 0.1315(6) | 0.0773(4) | 0.1836(7) | 0.93(10) |
| O3 | 0.4346(6) | 0.1733(4) | 0.4321(7) | 0.90(11) |
| O4 | 0.3230(6) | 0.3416(4) | 0.2478(7) | 0.80(10) |
| O5 | 0.5474(6) | 0.6223(4) | 0.3618(6) | 0.84(10) |
| O6 | 0.6807(6) | 0.3733(4) | 0.3764(6) | 0.85(10) |
| O7 | 0.9670(6) | 0.3864(4) | 0.1589(7) | 0.86(10) |
| O8 | 0.6767(6) | 0.4744(4) | 0.0311(7) | 0.99(11) |
| O9 | 0.9259(6) | 0.5710(4) | 0.3367(6) | 0.80(10) |
| O10 | 0.8694(6) | 0.7534(4) | 0.1242(6) | 0.84(10) |
| O11 | 0.0195(6) | 0.2184(4) | 0.4843(7) | 1.01(11) |
| O12 | 0.2034(6) | 0.7395(4) | 0.2464(6) | 0.84(9) |
| O13 | 0.5106(6) | 0.8003(4) | 0.0577(7) | 1.00(11) |
| O14 | 0.7992(6) | 0.1380(4) | 0.0795(7) | 0.91(10) |
| O15 | 0.3977(6) | 0.9681(4) | 0.2311(7) | 1.08(11) |

= 60°, scan width ± (0.8 + 0.15 tan θ)° symmetrical with respect to the Bragg value, slowest scan speed 2°/min, proportionally raised (up to 25°/min) on the basis of the intensity of the peaks, 0 ≤ h 10, -16 ≤ k ≤ 15, -9 ≤ l ≤ 9.

A set of 2442 independent structure factors were used for the refinement, after correction for Lorentz and polarization effects. The least-squares refinement program SHELX76 was used (Sheldrick 1976). The absorption effects were taken into account by means of DIFABS program (Walker and Stuart 1983; correction factors on F_o 's in the range 0.87–1.30). The structure was refined, using the fractional coordinates of babingtonite (Araki and Zoltai 1972) as starting point, to a conventional R factor of 0.047, and a weighted $R_w = 0.049$ ($w = k/[\sigma^2(F_o) + 0.00046 F_o^2]$).

The basic crystal-chemical features of scandiobabingtonite are identical with babingtonite (Araki and Zoltai 1972), and therefore will not be considered in detail. For sake of comparison, only the final fractional coordinates of scandiobabingtonite are reported in Table 3.

The only major difference with respect to babingtonite lies in the peculiar chemical composition of scandiobabingtonite, which causes an increase in the dimensions of the Fe³⁺- (and Sc-) centered octahedron: The <Fe³⁺-O> distance is 2.048 Å in babingtonite but 2.092 Å in scandiobabingtonite. To account for this, during the refinement the occupancy of Fe³⁺ and Sc was allowed to vary, by setting Fe³⁺ + Sc = 1.0 in the site occupied by Fe³⁺ only in babingtonite. The refinement converged to the occupancy of 73% Fe³⁺ + 27% Sc. This result shows that the crystal used for the structural study is not, strictly speaking, a crystal of scandiobabingtonite, but a Sc-rich variety of babingtonite. However, the structural study

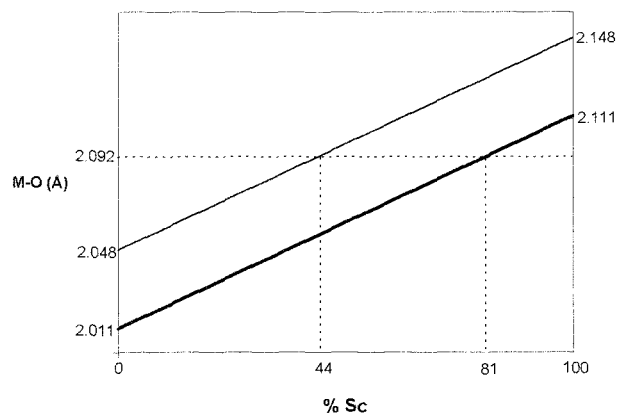


FIGURE 6. Occupancy at the Fe³⁺-Sc octahedral site vs. average M-O distance. The experimental <M-O> value for scandian babingtonite is 2.092 Å (this study). The bold line gives the average M-O distance for any substitution of Fe by Sc based on the values of the ionic radii by Shannon (1976). The thin line has the same significance, but it starts from the observed <Fe³⁺-O> distance (2.048 Å) found in babingtonite (Araki and Zoltai 1972).

demonstrates that all scandium concentrates in one only of the two independent octahedral sites: The average <Fe²⁺-O> distance of 2.169 Å in babingtonite and 2.165 Å in scandian babingtonite excludes any iron-scandium substitution at this site.

The average value of the cation-oxygen distance in the [(Fe³⁺-Sc)O₆] octahedron, 2.092 Å, suggests a site occupancy of Sc_{0.81}Fe_{0.19}, based on linear regression using the ionic radii given by Shannon (1976): 0.645 Å for ¹⁶Fe³⁺, 0.745 Å for ¹⁶Sc, and 1.366 Å for O, for which a coordination number of 3.33 (equal to the average coordination for the six O atoms belonging to the octahedron) was assumed. However, consideration of the difference in ionic radii between iron and scandium (0.10 Å) and the proportional increase in the average <M-O> distance with respect to the almost pure Fe³⁺ crystal of babingtonite refined by Araki and Zoltai (1972), implies an alternate occupancy of Sc_{0.44}Fe_{0.56} (Fig. 6). Both of these analyses, together with the uncertainty in X-ray data deriving from the number of electrons of iron and scandium, which are not too different, suggest that the actual content of scandium in our scandian babingtonite may be somewhat higher than 27%, as is also indicated by semiquantitative SEM-EDS data.

The crystal structure of babingtonite also has been independently refined in the space group $P1$ (Kosoi 1976). Therefore, refinement of the structure of scandian babingtonite in this non-centric space group was also attempted. Such a procedure implied the doubling of all atomic sites. In our case, such a trial could be substantiated by the possible ordering of scandium and trivalent iron in two different sites. However, the occurrence of very high correlation coefficients between positional parameters related to each other by pseudo-inversion centers led us to deny any reliability to such refinement (e.g.,

some non-positive definite atomic displacement parameters are obtained). Therefore, the slight observed deviation from equivalent occupancy of scandium and iron in sites related by a pseudo-inversion center was considered as negligible.

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