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Crystal structures of the new pseudo-isotypic compounds $NaFe(SeO_3)_2$ and $BaCo(SeO_3)_2$

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Abstract

The new compounds $NaFe(SeO_3)_2$ and $BaCo(SeO_3)_2$ have been synthesized under low hydrothermal conditions. Their crystal structures have been determined using single-crystal X-ray diffraction data and refined to $R_1 = 0.039$, 0.020 and $wR_2 = 0.075$, 0.040 [space group *Pnma*, $Z = 4$; $NaFe(SeO_3)_2$: $a = 12.553(6)$, $b = 5.349(2)$, $c = 7.899(3)$ Å, $V = 530.4$ Å^3; $BaCo(SeO_3)_2$: $a = 15.115(2)$, $b = 5.481(1)$, $c = 7.209(2)$ Å, $V = 597.2$ Å^3]. $NaFe(SeO_3)_2$, which is isotypic with $KFe(SeO_3)_2$, is built up by NaO_8 polyhedra, FeO_6 octahedra and two types of trigonal SeO_3 pyramids to a framework structure. The atomic arrangement in $BaCo(SeO_3)_2$ is pseudo-isotypic to $NaFe(SeO_3)_2$, major differences are observed only in the orientation of half of the selenite groups.

Keywords: Fe(III)–Se(IV) compounds; Co(II)–Se(IV) compounds; Crystal structure; Single crystals

1. Introduction

Within the last few years, a steadily increasing number of Fe(III)–Se(IV) and Co(II)–Se(IV) compounds has been synthesized and structurally investigated. For a survey of these compounds see Refs. [1–5] and references cited therein. The present study describes the preparation and crystal structure of the new compound $NaFe(SeO_3)_2$, which is isotypic to $KFe(SeO_3)_2$ [6], and that of the closely related new phase $BaCo(SeO_3)_2$. These compounds are abbreviated throughout the text as NAFE, KFE and BACO.

2. Experimental and structure refinements

Single crystals of NAFE and BACO were obtained in low hydrothermal synthesis experiments using $Co(OH)_2$, $FeC_2O_4 \cdot 2H_2O$, $Na_2SeO_3 \cdot 5H_2O$, SeO_2 and H_2O as well as $Ba(OH)_2$, $Co(OH)_2$, SeO_2 and H_2O respectively as starting materials. The respective mixtures of these reagents were filled into Teflon-lined steel bombs of 10 cm^3 capacity (filling rates 10–30%), heated to 500 K and kept at this temperature for one week. Finally, the autoclaves were cooled to room temperature within 12 h. The single crystals, obtained in sizes up to 0.5 mm, are yellow (NAFE) and light pink (BACO). They are elongated parallel to [010] with predominant crystallographic forms {100}, {101}, {201} and {111}. The coprecipitates of NAFE were identified as $Fe_2O(SeO_3)_2$ [7] and $Co_3Fe_2(SeO_3)_6 \cdot 2H_2O$ [8], those of BACO have not been investigated so far.

Specimens of NAFE and BACO with dimensions $0.08 \times 0.08 \times 0.3$ mm^3 and $0.05 \times 0.1 \times 0.2$ mm^3 respectively were used for further investigations.

Single-crystal X-ray diffraction intensities as well as accurate 2θ values for the refinement of the lattice parameters were measured on a Stoe AED2 four-circle diffractometer at room temperature. Crystal data and additional details of the data collections and structure refinements are compiled in Table 1; final structural parameters are given in Table 2. The measured intensities were corrected for Lorentz and polarization effects, as well as for absorption by ψ-scans. The crystal structure of BACO was determined by direct methods, while the atomic coordinates of KFE were used as a starting model for NAFE. The full-matrix least-squares refinements on F^2 were carried out with the program SHELXL-93 [9]. Complex scattering curves for neutral atoms were taken from Ref. [10]. The residual electron densities in a final difference Fourier map were less than 2.5 e Å^{-3} in NAFE

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Table 1
Details of crystal data, measurements and refinements for $NaFe(SeO_3)_2$ and $BaCo(SeO_3)_2$

	$NaFe(SeO_3)_2$	$BaCo(SeO_3)_2$
Space group	*Pnma*	*Pnma*
a [Å]	12.553(6)	15.115(2)
b [Å]	5.349(2)	5.481(1)
c [Å]	7.899(3)	7.209(2)
V [Å^3]	530.4	597.2
Z	4	4
ρ_{calc}[g cm^{-3}]	4.17	5.01
μ(Mo Kα) [cm^{-1}]	166	215
$h\ k\ l$ (min/max)	−20/0 0/8 −12/12	−24/24 −8/8 0/11
Reflections measured	2699	5616
Unique reflections	1277	1433
Reflections with $F_0 > 4\sigma(F_0)$	952	1029
Extinction coefficient	0.0046(6)	0.0023(1)
Variable parameters	56	56
R_1, wR_2	0.039, 0.075	0.020, 0.040

$R_1 = \Sigma \| F_0| - |F_c\| / \Sigma |F_0|$
$wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w F_0^4]^{1/2}$
$w = 1/[\sigma^2(F_0^2) + a^2 P^2]$
a = 0.038, 0.0138
$P = ([\max(0 \text{ or } F_0^2)] + 2F_c^2)/3$

Graphite monochromated Mo Kα radiation. 2θ–ω scans, 40/38 steps/reflection, increased for α_1–α_2 dispersion, 2*4/5 steps for background correction, 0.03° and 0.5–2.0 s/step, three standard reflections per 120 min. Lattice parameters refined from 48/34 reflections in the range $30° < 2\theta < 41°$.

(close to the positions of the selenium atoms), and less than 0.8 e Å^{-3} in BACO.

3. Discussion

Selected bond lengths and angles in NAFE and BACO are listed in Table 3. For an illustration of the atomic arrangements in the title compounds and their

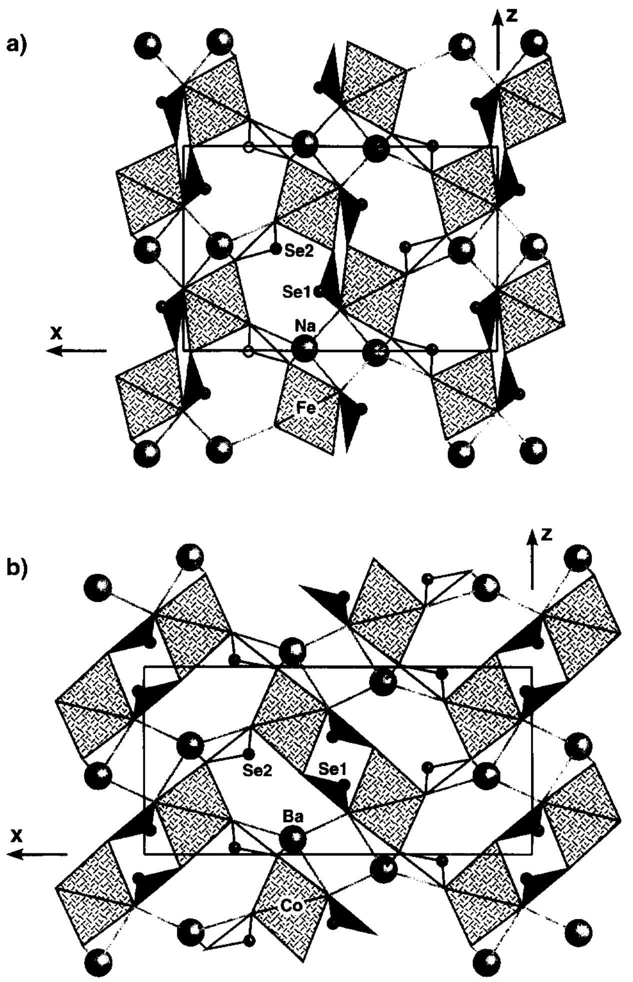

Fig. 1. Crystal structures of (a) $NaFe(SeO_3)_2$ and (b) $BaCo(SeO_3)_2$ in a projection parallel to [010]. The figure was drawn with the program ATOMS [11].

Table 2
Structural parameters of $NaFe(SeO_3)_2$ and $BaCo(SeO_3)_2$ with e.s.d.'s in parentheses. The anisotropic displacement factor is defined as $\exp[-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j \boldsymbol{a}_i^* \boldsymbol{a}_j^*]$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.8859(2)	0.25	0.5100(3)	0.0271(4)	0.0324(10)	0.0282(11)	0.0208(9)	0	0.0004(7)	0
Ba	0.882409(12)	0.25	0.58080(3)	0.01910(6)	0.01715(9)	0.01868(9)	0.02147(12)	0	0.00165(7)	0
Fe	0.60059(5)	0.25	0.70197(8)	0.01244(12)	0.0167(2)	0.0112(2)	0.0094(2)	0	−0.0008(2)	0
Co	0.62507(3)	0.25	0.70769(7)	0.01520(9)	0.0156(2)	0.0155(2)	0.0145(2)	0	−0.00105(15)	0
Se1	0.56812(3)	0.25	0.28725(5)	0.01233(10)	0.0153(2)	0.0105(2)	0.0112(2)	0	−0.00032(12)	0
	0.48494(2)	0.25	0.37100(5)	0.01520(7)	0.01600(12)	0.01539(15)	0.0142(2)	0	0.00034(11)	0
Se2	0.29317(3)	0.25	0.50536(5)	0.01439(11)	0.0155(2)	0.0148(2)	0.0128(2)	0	0.00026(12)	0
	0.26850(2)	0.25	0.46502(5)	0.01535(7)	0.01426(12)	0.01609(14)	0.0157(2)	0	0.00012(11)	0
O1	0.4999(2)	0.0080(4)	0.2007(3)	0.0192(4)	0.0315(10)	0.0139(9)	0.0122(8)	−0.0031(9)	0.0011(8)	−0.0076(8)
	0.47484(11)	0.0120(3)	0.2206(3)	0.0195(3)	0.0229(8)	0.0158(8)	0.0199(9)	−0.0029(7)	0.0014(6)	−0.0018(6)
O2	0.5228(2)	0.25	0.4880(3)	0.0153(5)	0.0227(14)	0.0156(13)	0.0077(11)	0	−0.0017(9)	0
	0.5928(2)	0.25	0.4249(4)	0.0243(6)	0.0173(10)	0.038(2)	0.0175(14)	0	−0.0036(10)	0
O3	0.2892(2)	0.0028(5)	0.3717(3)	0.0312(6)	0.0276(11)	0.0272(13)	0.0388(13)	−0.0176(13)	−0.0075(11)	0.0121(10)
	0.27467(11)	0.0104(3)	0.3183(3)	0.0244(4)	0.0221(8)	0.0233(9)	0.0277(11)	−0.0083(8)	−0.0028(8)	0.0054(6)
O4	0.1634(3)	0.25	0.5614(4)	0.0219(7)	0.0173(13)	0.035(2)	0.0137(13)	0	0.0031(10)	0
	0.15769(15)	0.25	0.5094(4)	0.0187(5)	0.0152(10)	0.0231(12)	0.0178(13)	0	0.0020(9)	0

Table 3
Interatomic distances (Å) and bond angles (deg) in $NaFe(SeO_3)_2$ and $BaCo(SeO_3)_2$

$NaFe(SeO_3)_2$				$BaCo(SeO_3)_2$			
Na–O1	2×		2.496(3)	Ba–O1	2×		2.781(2)
Na–O1	2×		2.548(3)	Ba–O1	2×		2.894(2)
Na–O3	2×		2.745(4)	Ba–O3	2×		2.864(2)
Na–O4	2×		2.803(2)	Ba–O4	2×		2.881(1)
⟨Na–O⟩			⟨2.648⟩	⟨Ba–O⟩			⟨2.855⟩
Fe–O1	2×		2.022(2)	Co–O1	2×		2.147(2)
Fe–O2	1×		1.952(3)	Co–O2	1×		2.096(3)
Fe–O3	2×		2.020(3)	Co–O3	2×		2.090(2)
Fe–O4	1×		2.029(3)	Co–O4	1×		2.098(3)
⟨Fe–O⟩			⟨2.011⟩	⟨Co–O⟩			⟨2.111⟩
O1–Fe–O1	1×	86.1(1)	[2.760(3)]	O1–Co–O1	1×	83.9(1)	[2.872(2)]
O1–Fe–O2	2×	91.0(1)	[2.834(3)]	O1–Co–O2	2×	94.1(1)	[3.105(2)]
O1–Fe–O3	2×	94.6(1)	[2.970(4)]	O1–Co–O3	2×	94.3(1)	[3.106(2)]
O1–Fe–O4	2×	83.8(1)	[2.705(4)]	O1–Co–O4	2×	86.1(1)	[2.897(3)]
O2–Fe–O3	2×	95.4(1)	[2.937(3)]	O2–Co–O3	2×	94.7(1)	[3.078(2)]
O3–Fe–O3	1×	84.0(1)	[2.704(4)]	O3–Co–O3	1×	86.1(1)	[2.855(3)]
O3–Fe–O4	2×	90.0(1)	[2.862(4)]	O3–Co–O4	2×	85.2(1)	[2.836(3)]
			⟨2.840⟩				⟨2.981⟩
Se1–O1	2×		1.695(2)	Se1–O1	2×		1.703(2)
Se1–O2	1×		1.685(3)	Se1–O2	1×		1.677(2)
⟨Se1–O⟩			⟨1.692⟩	⟨Se1–O⟩			⟨1.694⟩
O1–Se1–O1	1×	99.5(1)	[2.589(3)]	O1–Se1–O1	1×	100.0(1)	[2.609(2)]
O1–Se1–O2	2×	102.1(1)	[2.628(3)]	O1–Se1–O2	2×	103.6(1)	[2.656(3)]
⟨O–Se1–O⟩		⟨101.2⟩	⟨2.615⟩	⟨O1–Se1–O⟩		⟨102.4⟩	⟨2.640⟩
Se2–O3	2×		1.693(3)	Se2–O3	2×		1.689(2)
Se2–O4	1×		1.687(3)	Se2–O4	1×		1.705(2)
⟨Se2–O⟩			⟨1.691⟩	⟨Se2–O⟩			⟨1.694⟩
O3–Se2–O3	1×	102.7(2)	2.645(4)	O3–Se2–O3	1×	102.1(2)	2.626(3)
O3–Se2–O4	2×	97.8(1)	2.547(4)	O3–Se2–O4	2×	99.9(1)	2.598(3)
⟨O–Se2–O⟩		⟨99.4⟩	⟨2.580⟩	⟨O–Se2–O⟩		⟨100.6⟩	⟨2.607⟩

structural relationships see Figs. 1(a) and 1(b). The framework structures of both compounds are formed by corner-linkage of MO_6 octahedra ($M = Fe^{3+}$, Co^{2+}) with trigonal pyramidal selenite groups; interstitials are occupied by Na or Ba atoms in eight-fold coordination as well as by lone-pair electrons of the Se(IV) atoms. All cations occupy sites with point symmetry m. Mean M–O distances within the octahedra of Fe and Co are 2.011 and 2.111 Å respectively, values characteristic of ferric iron [12] and divalent cobalt [13]. The sodium atoms are irregular eight-fold coordinated with a separation into four shorter Na–O bonds (2.496 and 2.548 Å, forming a distorted tetragonal pyramid with the sodium atom as apex) and four longer Na–O distances of 2.745 and 2.803 Å. Individual bond lengths within the BaO_8 polyhedra only range from 2.781 to 2.894 Å.

Bond lenghts and angles of the SeO_3 groups in the title compounds comply well with crystal chemical expectations. However, the geometrical arrangement of half of the selenite groups represents the only striking difference between the two structures: while the linkage of the MO_6 octahedra with all the SeO_3 groups is the same in both compounds, the orientation of the $Se(1)O_3$ pyramids is different: in NAFE the Se-apices with their lone-pair electrons point towards the cavities occupied by the sodium atoms, in BACO they are reversed (cf. Figs. 1(a) and 1(b)). This leads to polyhedral shifts and rotations within the mirror planes and, as a consequence, to significant differences of the lattice parameters: the lengths of the *b*-axes are similar, but *c* is enlarged and *a* shortened in NAFE compared with BACO.

The oxygen atoms in both compounds are each bound to one M and one Se atom, Fe–O–Se angles range from 128 to 133°, Co–O–Se angles from 114 to 129°. O3 is further coordinated to one Na/Ba atom, O1 and O4 to two Na/Ba atoms each.

A comparison of NAFE with the isotypic crystal structure of KFE [6] reveals minor differences only. The bond length and angle distortions of the FeO_6 octahedra are almost the same in both compounds.

The most obvious difference is found for the KO_8 poyhedron, with K–O distances ranging from 2.712 to 2.847 Å without [4+4] separation of the bond lengths, in this respect resembling the geometry of the BaO_8 group in BACO.

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