ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2010, Vol. 55, No. 1, pp. 6–12. © Pleiades Publishing, Ltd., 2010.
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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Strontium Nickel and Barium Nickel Selenites: Synthesis and X-Ray Diffraction Parameters

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Received July 17, 2008

Abstract—A new strontium nickel selenite, $Sr_2Ni(SeO_3)_3$, was prepared and structurally characterized. The compound crystallizes in triclinic system (space group $P\bar{1}$, $a = 7.2860(10)$ Å, $b = 7.581(2)$ Å, $c = 8.722(2)$ Å, $\alpha = 103.02(2)°$, $\beta = 105.580(10)°$, $\gamma = 95.260(10)°$, $Z = 2$) and is isostructural to cobalt and copper analogues. The structure of $Sr_2Ni(SeO_3)_3$ is a three-dimensional framework built of eight-vertex polyhedra $[SrO_8]$ and distorted octahedra $[NiO_6]$ sharing edges and vertices. The framework channels accommodate selenium atoms bonded to the framework oxygen atoms. The selenite groups SeO_3 are pyramidal, which is indicative of high stereochemical activity of the Se(IV) lone pair. The possibility of replacement of some Ni atoms by Cu in $Sr_2Ni(SeO_3)_3$ was studied. The search for analogous barium phases did not reveal such compounds, but $BaM(SeO_3)_2$ phases were found, where M = Co, Ni, or Cu. The unit cell parameters of the new selenite $BaM(SeO_3)_2$ were determined: space group *Pnma*, $a = 14.989(5)$ Å, $b = 5.439(2)$ Å, $c = 7.161(3)$ Å, $Z = 4$.

DOI: 10.1134/S003602361001002X

Elucidation of relationships between the composition, structure, and physical properties of phases is an important task of modern chemistry. In particular, the lack of a symmetry center in the crystal structure is an obligatory condition for nonlinear-optical and piezoelectric properties in solids. Meanwhile, the probability of formation of acentric structures is postulated to increase upon the introduction of ions with lone pairs, such as Bi^{3+}, Te^{4+}, Se^{4+}, etc., into compounds [1]. According to published data [2], selenite ions should have a pyramidal structure SeO_3E where the lone pair (E) of the Se(IV) atom functions as one ligand; hence, the Se^{4+} coordination environment is asymmetric, and this may lead to a noncentrosymmetric crystal structure as a whole. In view of this postulate, selenites have been vigorously studied in recent years (e.g., [3–6]) as new potential piezoelectrics and crystals suitable for second optical harmonics generation.

One more factor favorable for the formation of an acentric crystal structure is the presence of *d* metals inducing structure distortion due to the Jahn–Teller effect.

Based on these views, we carry out systematic analysis of various selenite derivatives of alkaline-earth and *d* metals.

This paper describes the structure of a new nickel selenite $Sr_2Ni(SeO_3)_3$ and the results of the search for similar barium transition-metal phases. To our knowledge, no data on such compounds are available from the literature.

EXPERIMENTAL

Synthesis

New strontium and nickel selenite derivatives were sought by spontaneous crystallization from a $2SrSeO_3 \cdot NiCl_2$ stoichiometric mixture. Strontium selenite was preliminarily prepared by as reported elsewhere [5]. Selenium dioxide was from selenous acid known from [7], the product being purified by sublimation in dried air and nitrogen dioxide streams. Anhydrous nickel chloride was prepared by direct chlorination of nickel metal (carbonylic nickel powder UT-2) in a tubular furnace in a dried chlorine stream at 1023 K. A mixture of the above-indicated composition (weighing ~1 g) was placed in a quartz ampoule, which was evacuated (residual pressure of about 10^{-2} Torr) and sealed off. The sample thus prepared was heated in a muffle furnace in the following schedule: heating to 1023 K in 6 h, maintenance at this temperature for 6 h, and cooling to 663 K over 180 h (2 K/min).

The final product was a powder with a slight amount of small crystals.

The results of single-crystal X-ray diffraction experiment gave composition $Sr_2Ni(SeO_3)_3$, undescribed in the literature.

Table 1. Unit cell parameters of the samples with the composition $Sr_2Ni_{1-x}Cu_x(SeO_3)_3$, space group $P\bar{1}$

x	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å^3
0	7.286(1)	7.581(2)	8.722(2)	103.02(2)	105.58(1)	95.26(1)	446.1(1)
0.1	7.263(2)	7.563(2)	8.682(3)	102.85(3)	105.46(3)	95.49(3)	442.0(2)
0.2	7.269(2)	7.592(2)	8.714(3)	103.02(2)	105.55(2)	95.42(3)	445.1(1)
0.3	7.264(1)	7.615(1)	8.697(1)	102.85(1)	105.48(1)	95.55(1)	445.75(7)

The possibility of replacement of some nickel atoms in the new strontium nickel selenite by other ions was examined by attempted synthesis of mixed compounds $Sr_2Ni_{1-x}Cu_x(SeO_3)_3$. Copper was chosen because the unit cell parameters of $Sr_2Ni(SeO_3)_3$ we found are similar to those known for $Sr_2Cu(SeO_3)_3$ [8].

The initial samples were prepared using selenium dioxide and strontium selenite characterized above. Chemically pure grade nickel oxide and high purity grade copper(II) oxide (OsCh 9-2) were used.

The mixture was prepared according to the equation

$$2SrSeO_3 + (1-x)NiO + xCuO + SeO_2$$
$$= Sr_2Ni_{1-x}Cu_x(SeO_3)_3 \ (x = 0.1, 0.2, 0.3).$$

To this end, stoichiometric amounts of the components were weighed in a dry box, thoroughly mixed, and ground together in an agate mortar. The mixtures thus obtained were annealed in evacuated quartz tubes in a furnace in the following schedule: heating to 300°C over 12 h, maintenance at this temperature for 12 h, heating to 600°C in 6 h, maintenance at this temperature for 120 h, and cooling to room temperature together with the furnace. The samples thus obtained were studied by powder X-ray diffraction (FR 552 Guinier–deWolf camera (Enraf-Nonius), Cu$K_{\alpha1}$ radiation, germanium as the internal standard). The X-ray diffraction patterns of the final products were indexed with the assumption of triclinic system. The unit cell parameters for different x values are summarized in Table 1.

The search for $Ba_2M(SeO_3)_3$ selenites was carried out for M = Co, Ni, and Cu. The synthesis was based on the reaction

$$2BaSeO_3 + MO + SeO_2 = Ba_2M(SeO_3)_3.$$

The starting compounds used were SeO_2, NiO, and CuO characterized above, $BaSeO_3$ prepared by a known procedure [4], and chemically pure grade commercially available CoO. The reaction mixtures were prepared and annealed as described for $Sr_2Ni_{1-x}Cu_x(SeO_3)_3$. This gave powders in which no crystals were detected. The products were examined by powder X-ray diffraction, which showed the absence of phases isostructural to $Sr_2Ni(SeO_3)_3$.

Table 2. Crystal data for $Sr_2Ni(SeO_3)_3$

Composition	$Sr_2Ni(SeO_3)_3$
System	Triclinic
Space group	$P\bar{1}$
Unit cell parameters	
a, Å	7.2860(10)
b, Å	7.581(2)
c, Å	8.722(2)
α, deg	103.02(2)
β, deg	105.58(1)
γ, deg	95.26(1)
V, Å^3	446.1(2)
Z	2
ρ_{calcd}, g/cm^3	4.577
μ, mm^{-1}	26.266
Reflections: collected/independent	2773/2600 [R(int) = 0.019]
GOOF on F^2	1.076
$R1$ ($F_0 > 4\sigma(F_0)$)	0.0365
$wR2$ ($F_0 > 4\sigma(F_0)$)	0.1040
Extinction coefficient	0.0337(17)
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.753/–1.989
ICSD number	419618

Table 3. Atom coordinates (×10^{-4}) and isotropic thermal parameters for $Sr_2Ni(SeO_3)_3$

Atom	*x*	*y*	*z*	U_{eq}, Å^2 × 10^{-3}
Sr(1)	2558(1)	9146(1)	1102(1)	10(1)
Sr(2)	1292(1)	4823(1)	3066(1)	11(1)
Se(1)	4031(1)	12113(1)	5443(1)	8(1)
Se(2)	1393(1)	9168(1)	−2966(1)	9(1)
Se(3)	2654(1)	13626(1)	−883(1)	9(1)
Ni	4062(1)	6639(1)	−2524(1)	9(1)
O(1)	1360(6)	6977(5)	−4025(5)	12(1)
O(2)	−70(5)	8789(6)	−1820(5)	13(1)
O(3)	257(6)	12977(6)	−1460(6)	19(1)
O(4)	3578(5)	9465(6)	−1518(5)	13(1)
O(5)	4323(6)	11899(6)	3557(5)	15(1)
O(6)	3266(6)	13593(6)	1130(5)	14(1)
O(7)	2746(6)	5888(5)	−882(5)	12(1)
O(8)	6660(6)	5805(6)	4235(5)	18(1)
O(9)	3713(6)	7527(6)	3291(5)	16(1)

Table 4. Interatomic distances (*d*) $Sr_2Ni(SeO_3)_3$

Bond	*d*, Å	Bond	*d*, Å
Sr(1)–O(9)	2.499(4)	Sr(2)–O(5)	3.285(5)
Sr(1)–O(5)	2.571(4)	Se(1)–O(9)	1.675(4)
Sr(1)–O(2)	2.611(4)	Se(1)–O(8)	1.687(4)
Sr(1)–O(3)	2.619(4)	Se(1)–O(5)	1.689(4)
Sr(1)–O(4)	2.638(4)	Se(2)–O(2)	1.692(4)
Sr(1)–O(2)	2.685(4)	Se(2)–O(1)	1.703(4)
Sr(1)–O(7)	2.716(4)	Se(2)–O(4)	1.704(4)
Sr(1)–O(4)	2.811(4)	Se(3)–O(3)	1.675(4)
Sr(2)–O(9)	2.514(4)	Se(3)–O(6)	1.698(4)
Sr(2)–O(3)	2.563(4)	Se(3)–O(7)	1.710(4)
Sr(2)–O(6)	2.574(4)	Ni–O(8)	2.022(4)
Sr(2)–O(8)	2.596(4)	Ni–O(6)	2.046(4)
Sr(2)–O(1)	2.676(4)	Ni–O(5)	2.050(4)
Sr(2)–O(2)	2.676(4)	Ni–O(7)	2.074(4)
Sr(2)–O(1)	2.682(4)	Ni–O(1)	2.124(4)
Sr(2)–O(7)	2.968(4)	Ni–O(4)	2.223(4)

Refinement of $Sr_2Ni(SeO_3)_3$ Structure

For single-crystal X-ray diffraction, a crystal taken from the reaction mixture was mounted on the goniometric head of a Nonius CAD-4 diffractometer (graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha) = 0.71073$ Å, room temperature, $\omega/2\theta$ scan mode). The triclinic unit cell parameters were refined over 24 reflections in the angle range $16.0° < \theta < 17.9°$. Absorption corrections were applied by azimulthal scanning of 10 reflections with χ values close to 90°. The structure was solved by a direct method (SHELXS-97 [9]) in assuming centrosymmetrical space group $P\bar{1}$. During the solution, the positions of strontium, nickel, selenium, and some of oxygen atoms were located. The rest of the oxygen positions were found by alternation of least-squares refinement and difference Fourier syntheses (SHELXL-97 [9]). The final anisotropic refinement gave $R_1 = 0.036$. The key data collection and crystal structure refinement data are presented in Table 2, the positional and thermal parameters of atoms are in Table 3, and selected interatomic distances are in Table 4. X-Ray experiment details are available from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldsgafen, Germany (Fax (+49)7247-808-666; e-mail: crisdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) for CSD 419618.

RESULTS AND DISCUSSION

It follows from the X-ray diffraction experiment that the single crystals obtained correspond to the new strontium nickel selenite $Sr_2Ni(SeO_3)_3$ isostructural to cobalt and copper analogs [8, 10]. The crystal structure of $Sr_2Ni(SeO_3)_3$ (Fig. 1) contains two crystallographically independent strontium atoms each having a coordination environment of eight oxygen atoms (Table 4), which form irregular eight-vertex polyhedra SrO_8 (Fig. 2). These polyhedra share faces or vertices thus being connected into layers parallel to the *bc* plane. The nickel atom has a distorted octahedral coordination (Table 4). The NiO_6 octahedra share edges and vertices with the strontium polyhedra of different layers to form a three-dimensional framework with end-to-end channels (Fig. 3). These channels accommodate the selenium atoms (Fig. 3) each bonded to three oxygen atoms at typical Se–O distances of 1.67–1.71 Å. Thus, the selenium atoms occupy pyramid apices, the triangular bases of the pyramids being each formed by three oxygen atoms. The corners of these bases also belong to strontium and nickel polyhedra. Presumably, selenium lone pairs reside in framework voids.

Our experiments showed that the nickel atoms in the structure can be replaced by copper up to at least 30%. Figure 4 shows the variation of the triclinic unit cell

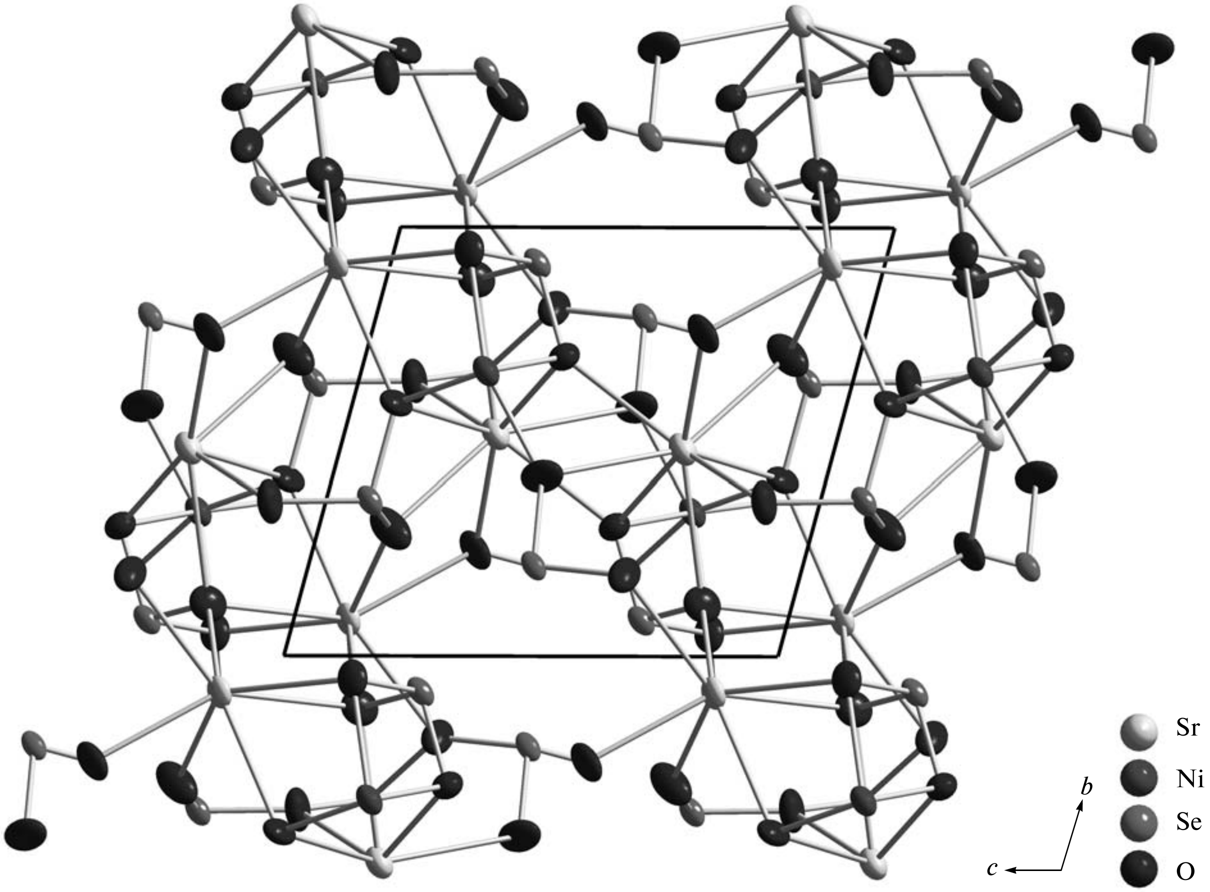

Fig. 1. Structure of $Sr_2Ni(SeO_3)_3$ projected onto the *bc* plane.

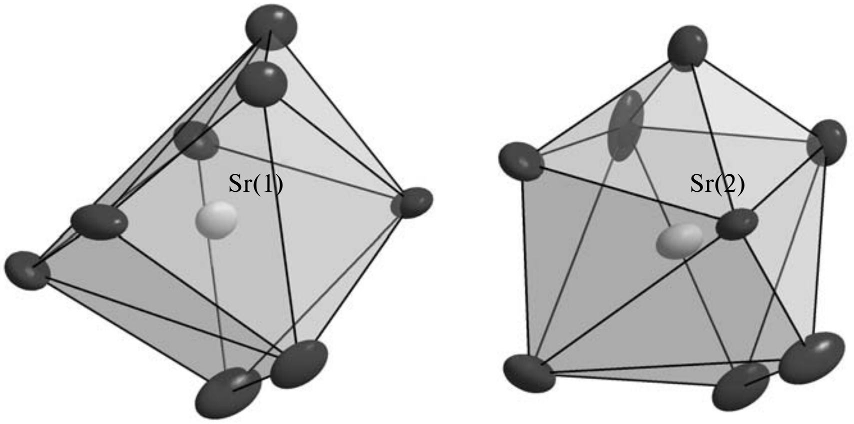

Fig. 2. Sr(1) and Sr(2) polyhedra in the $Sr_2Ni(SeO_3)_3$ structure.

Table 5. Results of indexing for a $BaNi(SeO_3)_2$ sample

$2\theta_{exp}$, deg	d_{exp}, Å	Q^{*}_{exp}	I/I_0^{**}	h	k	l	Q_{calcd}	ΔQ
17.119	5.1754	373.35	10	2	0	1	373.04	0.31
20.262	4.3792	521.45	50	2	1	0	516.10	5.34
20.518	4.3252	534.55	10	0	1	1	533.05	1.50
21.718	4.0888	598.15	50	3	0	1	595.59	2.56
23.755	3.7426	713.93	10	2	1	1	711.10	2.83
				4	0	0	712.17	1.75
24.906	3.5722	783.66	10	0	0	2	779.97	3.69
25.588	3.4785	826.45	50	1	0	2	824.48	1.97
26.796	3.3244	904.84	10	4	0	1	907.17	−2.32
27.595	3.2299	958.57	10	2	0	2	958.01	0.55
30.469	2.9315	1163.64	70	1	1	2	1162.54	1.10
30.699	2.9100	1180.90	10	3	0	2	1180.57	0.33
31.570	2.8317	1247.11	100	4	1	1	1245.23	1.89
32.230	2.7752	1298.41	50	2	1	2	1296.08	2.33
32.362	2.7642	1308.76	50	5	0	1	1307.76	1.00
32.964	2.7150	1356.63	70	0	2	0	1352.24	4.39
34.644	2.5872	1493.96	10	4	0	2	1492.14	1.82
36.422	2.4648	1646.03	50	5	1	1	1645.82	0.20
37.358	2.4052	1728.61	10	2	2	1	1725.28	3.33
38.123	2.3586	1797.59	50	6	0	1	1797.38	0.21
				1	0	3	1799.45	−1.85
38.402	2.3422	1822.85	10	4	1	2	1830.21	−7.35
39.556	2.2765	1929.59	50	2	0	3	1932.98	−3.39
39.762	2.2652	1948.89	50	3	2	1	1947.83	1.06
40.977	2.2007	2064.80	10	4	2	0	2064.41	0.39
38.181	2.3552	1802.79	50	6	0	1	1797.38	5.40
42.112	2.1440	2175.46	10	1	2	2	2176.72	−1.27
				7	0	0	2181.03	−5.57
43.486	2.0794	2312.72	10	2	2	2	2310.26	2.47
44.119	2.0510	2377.22	10	7	0	1	2376.02	1.19
				6	0	2	2382.36	−5.15
45.585	1.9884	2529.25	10	3	2	2	2532.81	−3.56
46.792	1.9399	2657.30	50	5	2	1	2660.00	−2.70
47.277	1.9211	2709.57	10	7	1	1	2714.08	−4.52
48.102	1.8901	2799.18	50	4	1	3	2805.17	−5.99
48.505	1.8753	2843.53	50	4	2	2	2844.39	−0.85
				8	0	0	2848.69	−5.16
49.514	1.8394	2955.61	10	6	2	0	2954.63	0.98
				7	0	2	2961.00	−5.39
50.328	1.8116	3047.02	10	0	3	0	3042.54	4.48
				8	0	1	3043.69	3.34
51.189	1.7831	3145.20	10	6	2	1	3149.62	−4.42
				1	2	3	3151.69	−6.49
52.353	1.7462	3279.53	10	1	3	1	3282.05	−2.51
				2	2	3	3285.22	−5.69
55.319	1.6594	3631.60	10	8	0	2	3628.66	2.93
				2	1	4	3635.99	−4.39
				3	3	1	3638.13	−6.53
56.083	1.6386	3724.38	10	7	2	1	3728.26	−3.88
57.182	1.6096	3859.79	10	3	1	4	3858.54	1.25
				1	3	2	3867.03	−7.23
57.841	1.5929	3941.15	10	7	0	3	3935.97	5.18
				9	1	0	3943.44	−2.29

Notes: * $Q = \frac{1}{d^2} \times 10^4$.

** The intensity was estimated visually against a 100-point scale.

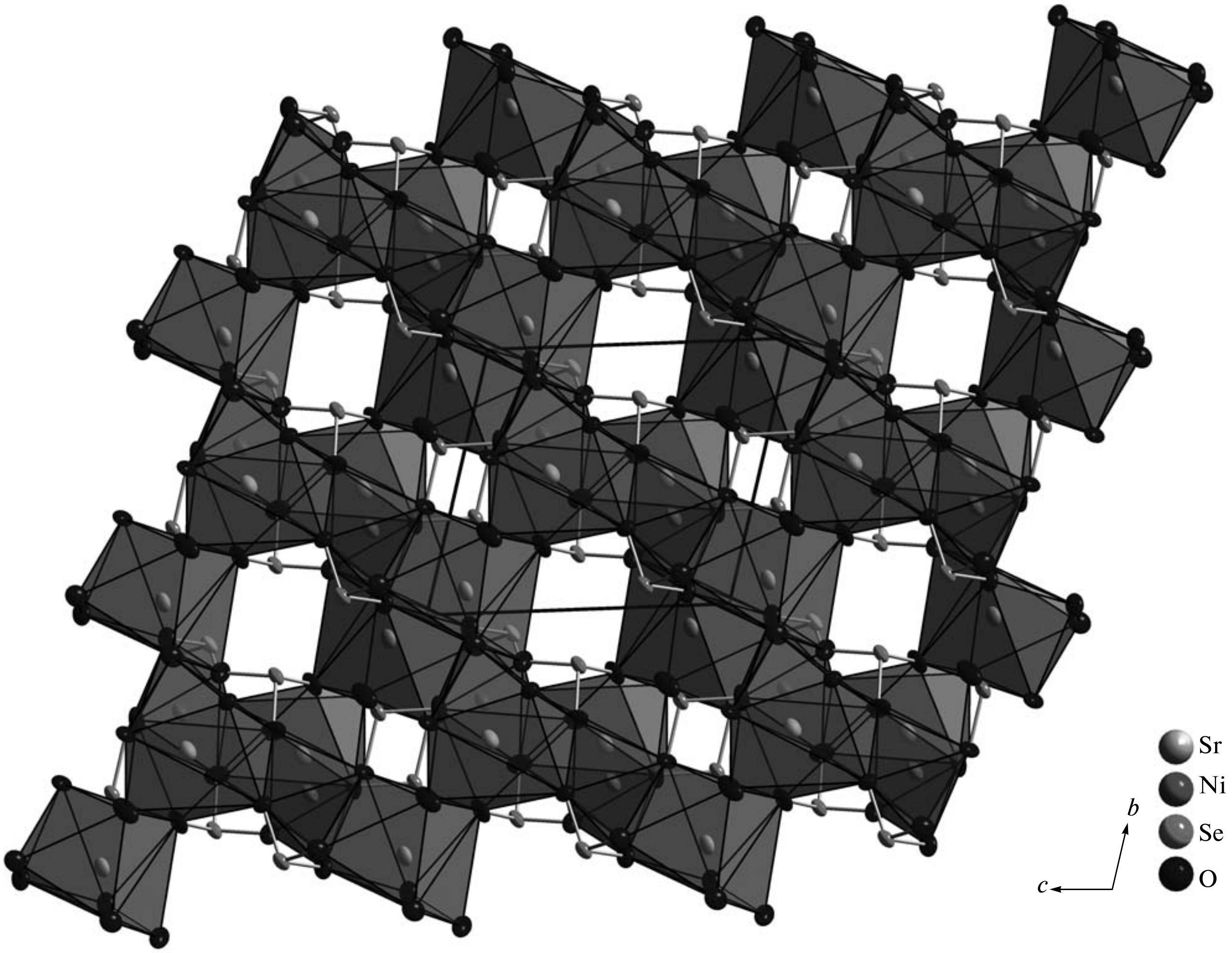

Fig. 3. Framework of the strontium and nickel polyhedra in the $Sr_2Ni(SeO_3)_3$ structure.

parameters of the $Sr_2Ni_{1-x}Cu_x(SeO_3)_3$ phases, which can be fitted by linear dependences. This is indicative of the formation of solid solutions in the indicated concentration range of the $Sr_2Ni(SeO_3)_3$–$Sr_2Cu(SeO_3)_3$ system (strontium copper selenite also corresponds to space group $P\bar{1}$; $a = 7.229$ Å, $b = 7.710$ Å, $c = 8.656$ Å, $\alpha = 102.68°$, $\beta = 105.31°$, $\gamma = 96.12°$ [8]).

No barium compounds with the desired stoichiometry are formed under our experimental conditions. Analysis of the X-ray diffraction patterns of the final barium samples showed that after annealing, the reaction mixtures of the as-batch composition $Ba_2M(SeO_3)_3$ with M = Co, Cu are mixtures of known selenites $BaM(SeO_3)_2$ (M = Co or Cu) and barium selenite $BaSeO_3$. The X-ray diffraction pattern of the final nickel-containing product is similar to the powder X-ray diffraction patterns of the cobalt and copper products [11, 12]; thus, we assumed the existence of previously unknown selenite $BaNi(SeO_3)_2$. To verify this assumption, we carried out additional annealing of a stoichiometric mixture of $BaSeO_3$, NiO, and SeO_2 under above-described conditions according to the reaction

$$BaSeO_3 + NiO + SeO_2 = BaNi(SeO_3)_2.$$

The X-ray diffraction pattern of the sample was completely indexed by the homology method with the assumption of orthorhombic system (space group *Pnma*) (Table 5) with the parameters $a = 14.989(5)$ Å, $b = 5.439(2)$ Å, $c = 7.161(3)$ Å ($F(30) = 17.3$, $M(20) = 12.7$, $Z = 4$), indicating the single-phase composition of the sample.

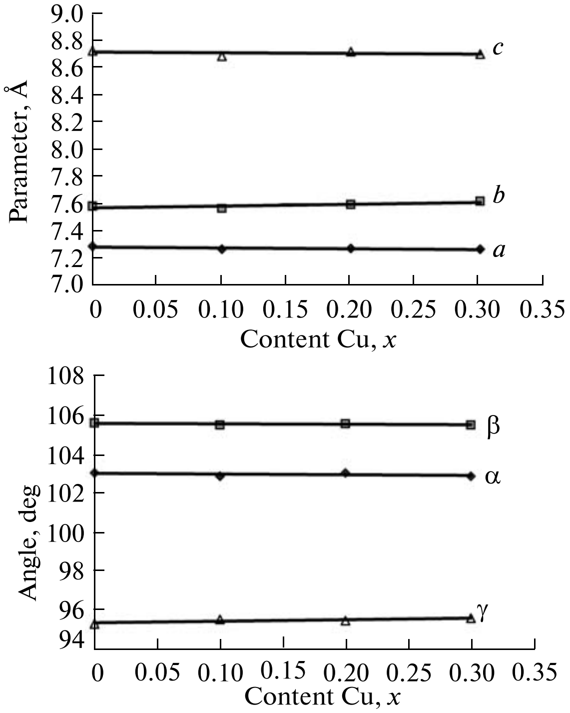

Fig. 4. Triclinic unit cell parameters of the $Sr_2Ni_{1-x}Cu_x(SeO_3)_3$ phase vs. copper content.

Thus, in the family of alkaline-earth and *d*-metal selenites, the following trend is observed: compounds with the compositions of $SrM(SeO_3)_2$ (M= Mn [13], Cu [12], Zn [14]) and $Sr_2M(SeO_3)_3$ (M = Co [10], Ni (this work), Cu [15]) are both possible for strontium, whereas for barium, the compound $BaM(SeO_3)_2$ is preferred. In all probability, this is due to the pronounced difference between the Sr^{2+} and Ba^{2+} ion radii (1.26 and 1.42 Å, respectively [16]).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 06-03-32134 and 08-03-0058.

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