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Synthesis and X-ray Diffraction Characterization of $FeNdSbS_4$, an Analog of Berthierite

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Abstract—A rare-earth-containing analog of the mineral berthierite, with the composition $FeNdSbS_4$, was synthesized for the first time. $FeNdSbS_4$ is isostructural with $FeSb_2S_4$ and crystallizes in orthorhombic symmetry (sp. gr. *Pbam*, $Z = 4$) with lattice parameters $a = 11.395$ Å, $b = 14.136$ Å, and $c = 3.747$ Å.

The crystal-chemical prediction and synthesis of new compounds with a particular structure is of major practical importance. The preparation of analogs of some minerals, in particular berthierite, $FeSb_2S_4$, is of special interest since it allows one to extend the range of known multicomponent compounds [1].

$FeSb_2S_4$ occurs in nature as the mineral berthierite and crystallizes in orthorhombic symmetry [2]. In the structure of berthierite, Sb is in fivefold coordination and sits in two positions 4*c* of the space group *Pbam*. The Sb(1) atom (figure) resides off the base of the hemioctahedron and is slightly displaced toward the center of the adjacent "vertical" trigonal prism. In addition, the vertical trigonal prism shares faces with two empty hemioctahedra. The Sb(2) atom at $z = 3/4$ lies in the base of a hemioctahedron, which shares this face with a "horizontal" trigonal prism. In addition, the horizontal trigonal prism shares one of its rectangular faces with a hemioctahedron occupied by Sb(2) at $z = 1/4$. It is easily seen that a further displacement of Sb(1) toward the center position of the vertical trigonal prism may increase the coordination number (CN) of Sb(1) up to nine. The unit cell of $FeSb_2S_4$ contains four structural units displayed in the figure (not including the hemioctahedron shown by dashed lines).

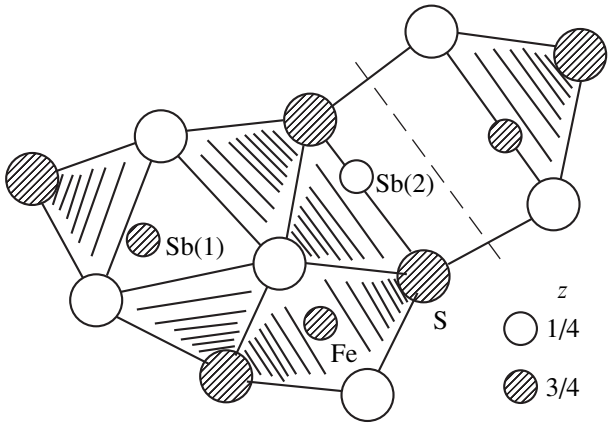
As is known, lanthanides in mixed sulfides may be in octahedral, trigonal prismatic, and mono-, bi-, and tricapped trigonal prismatic coordination (CN = 6 to 9). This suggests that Sb(1) in $FeSb_2S_4$ can be partially substituted by rare-earth elements to give new compounds.

The purpose of this work was to prepare a rare-earth-containing analog of berthierite via partial neodymium substitution for antimony in hemioctahedra.

$FeNdSbS_4$ was synthesized by the sealed-ampule technique from stoichiometric mixtures of NM-O neodymium (99.7+% Ln), carbonyl iron, Su-O antimony (99.999%), and V4 sulfur (99.9999%).

The mixtures (4–5 g) were sealed in silica tubes pumped down to 0.13 Pa and loaded into an electric furnace preheated to 750 K. At this temperature, the reaction, stirred by rotating the tube, took 1 h to reach completion. The furnace was then brought to a vertical position, and the samples were heated to 1250 K and held there for 1 h. Next, the temperature was lowered to 870 K at a rate of 50 K/h, and the samples were homogenized by annealing at this temperature.

The annealing temperature and duration were chosen on the basis of x-ray diffraction (XRD) and microstructural examination results: annealing for 15 days yielded dark gray needle-like crystals of stoichiometric composition.



Structural unit of berthierite, $FeSb_2S_4$.

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XRD data for $FeNdSbS_4$

d_{obs}, Å	*I*, %	*hkl*	d_{calc}, Å	d_{obs}, Å	*I*, %	*hkl*	d_{calc}, Å
6.0177	10	120	6.0064	2.6143	70	231	2.6076
4.3617	25	130	4.3544	2.5397	10	250	2.5326
3.6866	30	310	3.6682	2.5014	20	141	2.5079
3.6129	60	011	3.6219	2.3094	10	160	2.3072
3.5339	40	040	3.5340	2.2220	30	440	2.2179
3.4321	25	111	3.4518	2.1308	10	341	2.1291
3.1888	50	121	3.1791	1.9729	5	161	1.9646
3.0789	30	211	3.0566	1.9294	35	511	1.9289
3.0218	40	240	3.0032	1.8733	30	002	1.8735
2.9631	20	330	2.9572	1.8206	5	460	1.8156
2.8488	100	400	2.8488	1.8072	15	022	1.8110
2.7466	35	150	2.7440	1.7181	20	132	1.7210
2.6442	60	420	2.6422	1.6695	5	640	1.6729

The composition of the material thus prepared was determined by chemical analysis:

Element	Fe	Nd	Sb	S
Assay, wt %	12.41	32.05	27.07	28.50
Calculated for $FeNdSbS_4$, wt %	12.408	32.0478	27.05	28.49

$FeNdSbS_4$ was characterized by XRD (DRON-2 powder diffractometer, Ni-filtered CuK_α radiation), microstructural analysis (MIM-7 optical microscope), and microhardness measurements. The uncertainty in microhardness was ±5%. Lattice parameters were determined with an accuracy of ±0.001 Å. The XRD pattern of $FeNdSbS_4$ was indexed using JCPDS PDF data for $FeSb_2S_4$, Sb_2S_3, and Nd_2S_3 [4].

According to XRD results, $FeNdSbS_4$ is isostructural with $FeSb_2S_4$ (table) and crystallizes in the orthorhombic system (sp. gr. *Pbam*, $Z = 4$) with lattice parameters $a = 11.395$ Å, $b = 14.136$ Å, and $c = 3.747$ Å ($V = 603.566$ Å^3).

This compound is stable in air and does not react with water, alkalies, or organic solvents. Concentrated nitric acid dissolves $FeNdSbS_4$; the reaction is accompanied by H_2S release. The microhardness of $FeNdSbS_4$ is 1.75 GPa.

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