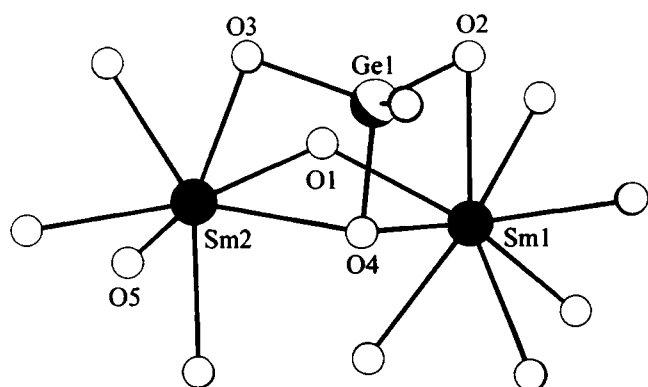


Redetermination of the crystal structure of sodium trisamarium digermanate dihydroxide, $\text{NaSm}_3(\text{GeO}_4)_2(\text{OH})_2$

M. Emirdag-Eanes*

Izmir Institute of Technology, Department of Chemistry, Izmir, 35437, Turkey

Received October 30, 2000, accepted January 25, 2002; CSD-No. 409594



Abstract

$\text{Ge}_2\text{H}_2\text{NaO}_{10}\text{Sm}_3$, monoclinic, $C12/c1$ (No. 15), $a = 18.323(3)$ Å, $b = 5.2369(8)$ Å, $c = 12.108(2)$ Å, $\beta = 131.230(2)^\circ$, $V = 873.8$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.037$, $wR_{\text{ref}}(F^2) = 0.010$, $T = 153$ K.

Source of material

Yellow crystals of $\text{NaSm}_3(\text{GeO}_4)_2(\text{OH})_2$ were obtained from a hydrothermal reaction of 0.035 g (0.10 mmol) Sm_2O_3 and 0.020 g (0.20 mmol) GeO_2 in 0.4 mL of NaOH (10.5 M) solution sealed in a silver tube that was heated at 797 K for 3 days.

Discussion

Hydrothermal methods have been used successfully to synthesize many compounds [1,2]. The title compound was first synthesized in [3,4], and the structure was described in the noncentrosymmetric space group Cc . However, we believed that the space group determination was not right based on the position of the atoms. In addition, a review article by Demianets gives the space group as $I2/a$ for the same compound, but they did not give any explanation or new characterization [5].

Our X-ray single crystal structure determination of the compound was done with a final reliability factor $R = 0.037$ and space group was determined as $C2/c$. The hydrogen atoms were not localized. This structure has an olivine type chain parallel to a -axis [6]. The cation polyhedral chain is made up with alternation Na and Sm polyhedra. There are two crystallographically independent Sm atoms. The Sm1 is coordinated by eight oxygen atoms and Sm2 is coordinated by seven oxygen atoms in an irregular polyhedron. The Sm1—O distances range from 2.359(5) Å to 2.644(5) Å. The Sm2—O distances range from 2.353(5) Å to 2.507(5) Å. The Ge atom has four coordinating oxygen atoms forming a distorted tetrahedron. The Ge—O distances range from 1.741(5) Å to 1.786(5) Å.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.058 × 0.118 × 0.150 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	267.36 cm ⁻¹
Diffractometer, scan mode:	Bruker SMARTCCD, $\Delta\omega = 0.3^\circ$
$2\theta_{\text{max}}$:	57.62°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3997, 1023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 970
$N(\text{param})_{\text{refined}}$:	78
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
Na(1)	8f	0.23	0.247(3)	0.246(7)	0.509(4)	0.006(4)
Na(2)	8f	0.27	0.264(1)	0.295(3)	0.480(2)	0.006

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	4e	0	0.29016(9)	1/4	0.0066(3)	0.0027(3)	0.0031(3)	0	0.0039(3)	0
Sm(2)	8f	0.11829(2)	0.29557(7)	0.08559(4)	0.0070(3)	0.0047(3)	0.0029(3)	0.0013(1)	0.0035(2)	0.0000(1)
Ge(1)	8f	0.14042(5)	0.7395(1)	0.29168(8)	0.0077(4)	0.0028(4)	0.0045(4)	-0.0004(2)	0.0048(4)	-0.0005(2)
O(1)	8f	0.1258(3)	0.0696(9)	0.2718(5)	0.008(2)	0.001(2)	0.004(2)	-0.001(2)	0.003(2)	-0.000(2)
O(2)	8f	0.1503(3)	0.5952(9)	0.4316(5)	0.011(2)	0.006(2)	0.006(2)	-0.002(2)	0.007(2)	-0.002(2)
O(3)	8f	0.2233(3)	0.615(1)	0.2779(5)	0.008(2)	0.006(2)	0.013(2)	0.001(2)	0.008(2)	0.001(2)
O(4)	8f	0.0339(4)	0.5799(9)	0.1375(5)	0.009(2)	0.005(2)	0.003(2)	-0.001(2)	0.004(2)	-0.001(2)
O(5)	8f	0.0876(4)	-0.118(1)	-0.0127(5)	0.015(2)	0.006(2)	0.006(2)	-0.002(2)	0.007(2)	-0.002(2)

* (e-mail: emirdag@likya.iyte.edu.tr)

Acknowledgments. We gratefully acknowledge help from Clemson University and Dr. Joseph Kolis.

References

1. Emirdag, M.; Schimek, G. L.; Pennington, W. T.; Kolis, J. W.: Synthesis of Two New Metallic Alkali Metal Silver Selenides, K₂Ag₁₂Se_{7.11} and RbAg₅Se₃, from Supercritical Ethylenediamine. *J. Solid State Chem.* **144** (1999) 287-296.
2. Emirdag, M.; Schimek, G. L.; Kolis, J. W.: Synthesis and characterization of K₃Cu₁₁Te₁₆ from supercritical ethylenediamine. *J. Chem. Soc., Dalton Trans.* (1999) 1531-1532.
3. Emelchenko, G. A.: Crystal Structure of Basic Samarium Germanate, NaSm₃(GeO₄)₂(OH)₂. *Sov. Phys. Dokl. Akad. SSSR.* **222** (1975) 343-345.
4. Emelchenko, G. A.; Demianets, L. N.; Lobachev, A. N.: The investigation of the Hydrothermal Crystallization in Nd₂O₃-GeO₂-NaOH-H₂O Systems. *Mat. Res. Bull.* **9** (1974) 1151-1156.
5. Demianets, L. N.; Lobachev, A. N.; Emelchenko, G. A.: Organic crystals germinates, semiconductors. Springer-Verlag, Berlin: New York. 1980.
6. Paques-Ledent, M. Th.: Vibrational studies of olivine-type compounds-III. Orthosilicates and germanates A^{II}B^{III}X^{IV}O₄. *Spectrochim. Acta* **32A** (1976) 383-395.
7. Sheldrick, G. M.: SHELXS-97. Program for the solution of crystal structures. University of Göttingen, Göttingen, Germany 1997.
8. Sheldrick, G. M.: SHELXL-97. Program for the refinement of crystal structures. University of Göttingen, Göttingen, Germany 1997.