

Synthesis and Characterization of Nadorite: PbSbO_2Cl

Yetta Porter and P. Shiv Halasyamani

Department of Chemistry, University of Houston, 4800 Calhoun Blvd., Houston, TX 77204–5003

Reprint requests to Prof. P. Shiv Halasyamani. Fax: (+011) 713-743-2787. E-mail: psh@uh.edu

Z. Naturforsch. **57b**, 360–361 (2002); received November 7, 2001

Oxychloride, Mineral

The first laboratory synthesis and characterization of the mineral Nadorite, PbSbO_2Cl , is reported. The material was synthesized by combining PbCl_2 , PbO and Sb_2O_3 . Powder X-ray diffraction data on the polycrystalline product is consistent with the previously reported crystal structure on the mineral. Infrared and thermogravimetric data are also present.

Sillen phases, denoted $[\text{M}_2\text{O}_2][\text{X}_m]$ where $\text{M} = \text{Pb}^{2+}$, Sb^{3+} or Bi^{3+} and $\text{X} = \text{Cl}^-$ or Br^- , represent a large family of materials [1]. The family consists of fluorite related $[\text{M}_2\text{O}_2]$ layers separated by halide. It has been demonstrated previously that ferroelectric and non-linear optical behavior is possible in some of these phases [2, 3]. One of the first materials discovered by Sillen in 1941 was the naturally occurring mineral Nadorite, PbSbO_2Cl [4]. However, the single crystal structure of Nadorite was not determined until 1973 by Giuseppetti *et al.* [5]. In both instances the naturally occurring mineral was used for structural studies. Surprisingly, no reports of synthetic Nadorite have been published. We report herein the first laboratory synthesis and characterization of Nadorite.

PbSbO_2Cl was synthesized by combining (0.169 g, 0.1 mmol) PbO (99.9%, Aldrich), (0.211 g, 0.1 mmol) PbCl_2 (99.9%, Mallinkrodt), and (0.243 g, 0.11 mmol) Sb_2O_3 (Alfa, 99.6%). The reactants were ground together and placed into a quartz tube that was subsequently evacuated and sealed. The tube was heated at 500 °C for 24 h and then cooled rapidly (2 °C min^{-1}) to room temperature. A polycrystalline yellow-green powder was obtained. Synthesizing pure phase Nadorite proved to be difficult, as many of the reactions resulted in a mixture of phases – Nadorite and PbCl_2 or Sb_2O_3 . We obtained nearly pure phase Nadorite when 10% excess Sb_2O_3 was added to the starting reagents.

X-ray powder diffraction data were collected on a Scintag XDS2000 diffractometer at room temperature ($\text{Cu-K}\alpha$ radiation, θ - θ mode, flat plate geometry) in the 2θ range from 3° – 80° with a step size of 0.02° and step time of 10s. Excellent agreement between our pattern and the calculated one, based on single crystal data [5], is observed (see Fig. 1). We were able to refine a unit cell using the Fullprof program [6] which gave $a = 5.610(3)$, $b = 12.250(7)$, and $c = 5.432(2)$ Å in the orthorhombic space group $Cmcm$ (No. 63). The refined unit cell compares well to the single crystal cell of $a = 5.603(5)$, $b = 12.245(8)$, and $c = 5.448(7)$ Å [5]. Nadorite may be described as a layered structure, consisting of sheets of $[\text{PbO}_{4/4}]^0$ and $[\text{SbO}_{4/4}]^+$ cations that share edges. The cationic sheets are separated by Cl^- anions (see Fig. 2). Both the Pb^{II} and Sb^{III} cations are in asymmetric coordination environments owing to their stereoactive lone pairs.

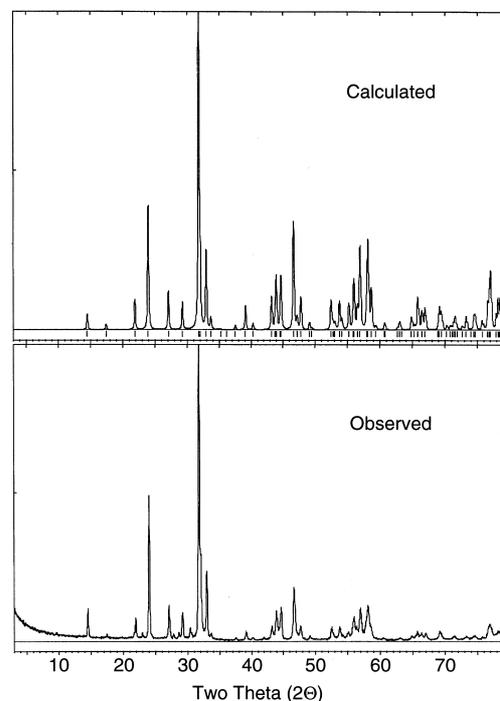


Fig. 1. Calculated and experimental powder X-ray diffraction data for PbSbO_2Cl .

Infrared data were recorded on a Matheson FTIR5000 spectrometer on a film sample of PbSbO_2Cl with KBr: $\nu = 742$ (Sb-O), 589 cm^{-1} (Pb-O). These values are in good agreement with those reported earlier [7, 8]. Thermogravimetric

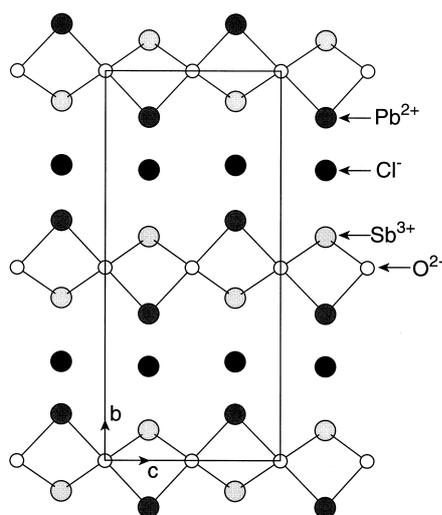
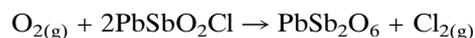


Fig. 2. Ball-and-stick diagram for Nadorite in the bc -plane.

measurements were performed on a Seiko 320 TG/DTA on polycrystalline PbSbO_2Cl . The material was heated, in static air, from r.t. to $900\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C min}^{-1}$. PbSbO_2Cl undergoes one large weight loss event, of 31.0%, between 550 and $710\text{ }^\circ\text{C}$. The resultant material was shown to be PbSb_2O_6 [9] by powder X-ray diffraction. Thus the TGA is consistent with the following reaction:



Acknowledgements

We thank the Robert A. Welch Foundation for support. This work used the MRSEC / TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award No. DMR-9632667 and the Texas Center for Superconductivity at the University of Houston. This work was also supported by the NSF-Career Program through DMR-0092054 and an acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

- [1] L. G. Sillen, *Z. Anorg. Allg. Chem.* **246**, 1941 (1941).
 [2] V. A. Dolgikh, L. N. Kholodkovskaya, *Russ. J. Inorg. Chem.* **37**, 488 (1992).
 [3] A. M. Kusainova, S. Y. Stefanovich, V. A. Dolgikh, A. V. Mosunov, C. H. Hervoches, P. Lightfoot, *J. Mater. Chem.* **11**, 1141 (2001).
 [4] L. G. Sillen, L. Melander, *Z. Kristallogr.* **103**, 420 (1941).

- [5] G. Giuseppetti, C. Tadini, *Periodico di Mineralogia* **42**, 335 (1973).
 [6] J. C. Rodriguez, ILL Grenoble (1990).
 [7] P. C. Christidis, P. J. Rentzeperis, *J. Appl. Crystallogr.* **10**, 486 (1977).
 [8] R. K. Khanna, Y. J. Park, *Spectr. Acta.* **42A**, 603 (1986).
 [9] R. J. Hill, *J. Solid State Chem.* **71**, 12 (1987).

