



# BaSn<sub>6</sub>Co<sub>6</sub>O<sub>19</sub>—A novel frustrated antiferromagnet with the magnetoplumbite type structure

L. Shlyk, R. Niewa\*

Institut für Anorganische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany

## ARTICLE INFO

### Article history:

Received 2 July 2011

Received in revised form

11 September 2011

Accepted 22 September 2011

Available online 4 October 2011

### Keywords:

Magnetoplumbite

Frustrated antiferromagnetism

Kagome lattice

## ABSTRACT

Single crystals of the novel compound BaSn<sub>6</sub>Co<sub>6</sub>O<sub>19</sub> with maximum width 1 mm and thickness around 0.05 mm were grown from a barium chloride flux. The composition was determined from refinements of single crystal X-ray diffraction data and microprobe analysis. BaSn<sub>6</sub>Co<sub>6</sub>O<sub>19</sub> crystallizes in the magnetoplumbite type structure (hexagonal, space group *P6<sub>3</sub>/mmc*, *a* = 6.0940(1) Å, *c* = 23.9633(5) Å, *V* = 770.69 Å<sup>3</sup>, *Z* = 2). A significant disorder is generated by random occupation of two octahedrally coordinated crystallographic sites with Co<sup>2+</sup> and Sn<sup>4+</sup> ions, while further sites are exclusively occupied by either Co<sup>2+</sup> (tetrahedrally coordinated) or Sn<sup>4+</sup> (octahedrally coordinated). One site with mixed occupation realizes the topology of a kagome net. The temperature dependence of the magnetic susceptibility for a single crystal BaSn<sub>6</sub>Co<sub>6</sub>O<sub>19</sub> reveals a low temperature antiferromagnetic order at *T<sub>N</sub>* = 14 K. A relatively large value of frustration factor  $f_{||} = |\Theta_{W||}|/T_N \approx 26$  and  $f_{\perp} = |\Theta_{W\perp}|/T_N \approx 12$  implies a frustrated antiferromagnetism.

© 2011 Elsevier Inc. All rights reserved.

## 1. Introduction

Transition metal oxides continue to attract great attention in solid state physics and chemistry. In particular, cobalt oxide based materials has been actively investigated, primarily because they exhibit a wide variety of unusual magnetic and electronic properties. Recently, a number of cobalt oxide materials have been synthesized which display a fascinating diversity of behavior including various forms of charge, spin and orbital ordering. Obvious examples are perovskites La<sub>1-x</sub>A<sub>x</sub>CoO<sub>3</sub> (*A* = Ca, Sr, Ba) [1], LnBaCo<sub>2</sub>O<sub>5+x</sub> (*Ln* = Eu, Gd) [2,3], LnCoO<sub>3</sub> (*Ln* = La, Dy) [4] possessing giant magnetoresistivity and anomalously high thermoelectric effect, and the recently discovered superconductor Na<sub>x</sub>CoO<sub>2</sub>·yH<sub>2</sub>O (*T<sub>c</sub>* = 5 K) [5]. In an attempt to explore the formation of new oxobalates we have investigated the synthesis and crystal growth of Co bearing members of the magnetoplumbite structure. This large family is composed of magnetoplumbite-related members, i.e. AFe<sub>12</sub>O<sub>19</sub>, where *A* = Pb, Ca, Sr, Ba, which is a very important class of magnetic oxides. Some representatives of this family such as Sr- and Ba-bearing ferrites possess extraordinary magnetic properties, which make them excellent materials for use as permanent magnets, recording media, and as components in microwave devices. Within this structural family the A<sup>2+</sup> ion can also be replaced by trivalent ions of about the same size, e.g., by Ln<sup>3+</sup> (from La<sup>3+</sup> to Eu<sup>3+</sup>) or by Al<sup>3+</sup>(Ga<sup>3+</sup>) ions, which leads to a new family of magnetoplumbite type oxides exhibiting interesting optical properties [6,7]. The transition metal atoms may also be substituted

by a variety of different metal species, for example, in SrFe<sub>12</sub>O<sub>19</sub>, Fe<sup>3+</sup> can be partially replaced by Cr<sup>3+</sup>, leading to solid solutions SrFe<sub>12-x</sub>Cr<sub>x</sub>O<sub>19</sub> (0 < *x* < 8) (Ref. [7] and references therein). The magnetic ground state of these solutions varies from long-range magnetic order to spin-glass freezing with increasing *x*. Furthermore, magnetic Fe<sup>3+</sup> can be replaced by nonmagnetic Ga<sup>3+</sup>, therefore, yielding SrGa<sub>12-x</sub>Cr<sub>x</sub>O<sub>19</sub> (0 ≤ *x* < 1) (SCGO), which is a quasi-2D insulator with an extreme degree of magnetic frustration ( $|\Theta_{W||}|/T_f > 117$ ) [8]. This compound attracted a considerable theoretical and experimental interest in attempts to clarify the properties of geometrically frustrated systems. Apart from the Fe-bearing ferrimagnets mentioned above, frustrated antiferromagnets seem to have no practical use, but they are of interest from the point of view of fundamental science since they demonstrate various intriguing low-temperature phenomena such as spin-liquid, spin-glass and spin-ice state [9–11]. Note here, that the magnetoplumbite type crystal structure may be considered to consist of alternating spinel (*S* = M<sub>6</sub>O<sub>8</sub><sup>2+</sup>) and hexagonal stacked (*R* = AM<sub>6</sub>O<sub>11</sub><sup>2-</sup>) layers, where *M* is a transition metal in +3 oxidation state. The structural AM<sub>6</sub>O<sub>11</sub><sup>2-</sup> units contain a kagome lattice of the transition metal ions within the **ab**-plane, suggesting the possibility of geometrical frustration at low temperatures when spins of *M* are coupled antiferromagnetically. It is believed that frustration in SCGO is associated with two-dimensional kagome layers of antiferromagnetically coupled Cr<sup>3+</sup> (*S* = 3/2) ions. In spite of the very high Curie–Weiss temperature of SCGO,  $\theta_{CW} \approx -500$  K, the temperature of the actual spin glass freezing was found to be very low *T<sub>g</sub>* = 3.3 K. Furthermore, it is shown that the low-temperature specific heat of SCGO is proportional to *T*<sup>2</sup>, instead of usual linear *T* dependence of spin glasses [12]. These anomalous properties imply that a new type of spin excitations exist on the kagome planes of SCGO [13].

\* Corresponding author. Fax: +49 711/685 64241.

E-mail address: [rainer.niewa@iac.uni-stuttgart.de](mailto:rainer.niewa@iac.uni-stuttgart.de) (R. Niewa).

Up to our knowledge the formation of the magnetoplumbites  $\text{ACo}_{12}\text{O}_{19}$  was not reported up to date. It occurred to us that they might be stabilized by the combination of  $\text{Co}^{2+}$  and  $\text{Sn}^{4+}$  in an equimolar amount. Therefore, we successfully synthesized the novel magnetoplumbite  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$ . The crystal structure contains kagome layers of antiferromagnetically coupled  $\text{Co}^{2+}$  ions, separated by further  $\text{Co}^{2+}$  containing layers. Disorder in this compound stems from the dilution of the magnetic  $\text{Co}^{2+}$  sub-lattice by nonmagnetic  $\text{Sn}^{4+}$ . These structural features are similar to those of SCGO. As a consequence  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$  reveals a behavior characteristic of frustrated antiferromagnets.

We have recently developed a technique for single crystal growth of Ba containing R-type ferrites from a  $\text{BaCl}_2$  flux [14–16]. We have adapted this method to grow single crystals of  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$  up to 1 mm in size sufficient for structure determination and detailed studies of magnetic properties. Herein we report crystallographic data of this new phase, together with magnetic measurement data, which have been unavailable in literature.

## 2. Experimental

For single crystal growth of  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$  initial amounts of 2.7 mmol  $\text{SnO}_2$ , 2 mmol  $\text{Co}_3\text{O}_4$  and 3.2 mmol  $\text{BaCl}_2$  were mixed and then pressed into a pellet. The final pellet was heated to 1320 °C and kept at this temperature for several days. Then the furnace was slowly cooled to room temperature. Black hexagonal platelets with maximal sizes of 1 mm and thickness of about 0.05–0.07 mm were obtained. For X-ray diffraction intensity data collection a small black crystal with the shape of hexagonal platelet was selected. The data were collected at ambient temperature using a four circle diffractometer (NONIUS- $\kappa$ -CCD, Bruker AXS GmbH) with monochromatic  $\text{MoK}\alpha$  radiation. An absorption correction based on symmetry-equivalent reflections was applied (program X-SHAPE). The structure was solved using direct methods, and refined in space group  $P6_3/mmc$  (no. 194; centrosymmetric, programs SHELXS-97-2, SHELXL-97-2 [17]) leading to a composition of  $\text{BaSn}_{5.8(2)}\text{Co}_{6.2}\text{O}_{19}$ . Information concerning the data collection and results of the structural refinements for the crystals studied in this work are collected in Tables 1 and 2. Table 3 gathers selected interatomic distances. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax +49(0)7247/808-666; e-mail: [crysddata@fiz-karlsruhe.de](mailto:crysddata@fiz-karlsruhe.de)) or quoting the depository number CSD-423256.

**Table 1**  
Crystal structure data for  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$ .

|  |  |
|--|--|
| Formula  | $\text{BaSn}_{5.8(2)}\text{Co}_{6.2}\text{O}_{19}$ |
| Crystal system   | Hexagonal  |
| Space group  | $P6_3/mmc$   |
| <i>a</i> (Å)   | 6.0940(1)  |
| <i>c</i> (Å)   | 23.9633(5)   |
| <i>V</i> (Å <sup>3</sup> )   | 770.69   |
| <i>Z</i>   | 2  |
| <i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )                              | 6.443  |
| $\mu$ ( $\text{MoK}\alpha$ ) (mm <sup>-1</sup> )                             | 18.31  |
| <i>F</i> (000), e  | 1330.8   |
| <i>hkl</i> range   | ± 8, −7–8, −30–31                                  |
| <i>2</i> $\theta$ <sub>max</sub> (deg.)                                      | 55.74  |
| Refl. measured   | 11,026   |
| Refl. unique   | 401  |
| <i>R</i> <sub>int</sub>  | 0.095  |
| Param. refined   | 44   |
| <i>R</i> ( <i>F</i> )/ <i>wR</i> ( <i>F</i> <sup>2</sup> ) (all reflections) | 0.031/0.065  |
| GoF ( <i>F</i> <sup>2</sup> )  | 1.273  |
| $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )                               | 2.00   |

**Table 2**

Positional parameters for  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$ . *U*-values given in Å<sup>2</sup>.

| Atom                      | Site        | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>eq</sub> |
|---------------------------|-------------|------------|------------|------------|------------------------|
| Ba                        | 2 <i>d</i>  | 2/3        | 1/3        | 1/4        | 0.0111(3)              |
| <i>M</i> (1) <sup>a</sup> | 2 <i>a</i>  | 0          | 0          | 0          | 0.0067(6)              |
| Co(2)                     | 2 <i>b</i>  | 0          | 0          | 1/4        | 0.0176(6)              |
| Co(3)                     | 4 <i>f</i>  | 1/3        | 2/3        | 0.02618(6) | 0.0080(4)              |
| Sn(4)                     | 4 <i>f</i>  | 1/3        | 2/3        | 0.18942(3) | 0.0052(3)              |
| <i>M</i> (5) <sup>a</sup> | 12 <i>k</i> | 0.16588(4) | 2 <i>x</i> | 0.89507(2) | 0.0070(3)              |
| O(1)                      | 4 <i>e</i>  | 0          | 0          | 0.1513(3)  | 0.007(1)               |
| O(2)                      | 4 <i>f</i>  | 1/3        | 2/3        | 0.9416(3)  | 0.005(1)               |
| O(3)                      | 6 <i>h</i>  | 0.1874(6)  | 2 <i>x</i> | ¼          | 0.009(1)               |
| O(4)                      | 12 <i>k</i> | 0.1532(4)  | 2 <i>x</i> | 0.0536(2)  | 0.010(1)               |
| O(5)                      | 12 <i>k</i> | 0.5048(4)  | 2 <i>x</i> | 0.1508(2)  | 0.007(1)               |

<sup>a</sup> Occupation of *M*(1)=0.296(5) Sn, 0.704 Co; *M*(5)=0.584(3) Sn, 0.416 Co.

**Table 3**

Selected distances (Å) for  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$ , with estimated standard deviations in parentheses.

|                   |           |     |
|-------------------|-----------|-----|
| Ba–O(5)           | 2.927(4)  | 6 × |
| Ba–O(3)           | 3.0548(4) | 6 × |
| <i>M</i> (1)–O(4) | 2.065(5)  | 6 × |
| Co(2)–O(3)        | 1.978(6)  | 3 × |
| Co(2)–O(1)        | 2.366(7)  | 2 × |
| Co(3)–O(4)        | 2.013(4)  | 3 × |
| Co(3)–O(2)        | 2.026(8)  | 1 × |
| Sn(4)–O(5)        | 2.032(4)  | 3 × |
| Sn(4)–O(3)        | 2.117(5)  | 3 × |
| Sn(4)–Sn(4)       | 2.904(1)  | 1 × |
| <i>M</i> (5)–O(5) | 2.058(3)  | 2 × |
| <i>M</i> (5)–O(1) | 2.074(4)  | 1 × |
| <i>M</i> (5)–O(4) | 2.088(3)  | 2 × |
| <i>M</i> (5)–O(2) | 2.090(4)  | 1 × |

Chemical  $\mu$ -probe analyses result in very consistent compositions observed for all crystals investigated, and the inferred atomic density ratios  $n(\text{Ba})/n(\text{Sn})/n(\text{Co})=1.02 \pm 4 : 6.04 \pm 7 : 5.96 \pm 7$  (the oxygen content could not be quantified with this technique), is in excellent agreement with the composition  $\text{BaSn}_{5.8(2)}\text{Co}_{6.2}\text{O}_{19}$  inferred from the X-ray diffraction data. No additional elements were detected. The X-ray diffraction and microprobe results indicate the single crystals examined were single phase and of excellent quality. The magnetization data for oriented single crystals were acquired over a temperature range  $2 \text{ K} \leq T \leq 300 \text{ K}$  in applied magnetic fields  $0 \leq \mu_0 H \leq 5 \text{ T}$  using a Quantum Design MPMS7 Magnetometer. The ac magnetic susceptibility was measured with an amplitude of 5 Oe and at frequencies 20, 215, 900 Hz.

## 3. Results and discussion

### 3.1. Crystal structure and composition

$\text{BaSn}_6\text{Co}_6\text{O}_{19}$  crystallizes in the hexagonal space group  $P6_3/mmc$  in the well known structure of magnetoplumbite  $\text{PbFe}_{12}\text{O}_{19}$  [18,19] (Fig. 1). As usual for ferrites the crystal structure of  $\text{BaSn}_6\text{Co}_6\text{O}_{19}$  can be traced down to a closed packed motif with cubic and hexagonal stacking in the sequence **BAB'ABCAC'AC** along the [001] direction. In this sense, the layers **A**, **B**, and **C** constitute exclusively from oxide ions, while the layers **B'** and **C'** have the composition  $\text{BaO}_3$ . Sn and Co occupy voids exclusively formed by oxide ions. The structure can be partitioned into two alternating sections: spinel-like blocks (so-called S-blocks) with cubic stacking sequence of close packed layers and blocks with hexagonal stacking sequence (so-called R-blocks). In the spinel-like blocks three layers of edge-sharing octahedral voids are filled with mixed

Download English Version:

<https://daneshyari.com/en/article/1330519>

Download Persian Version:

<https://daneshyari.com/article/1330519>

[Daneshyari.com](https://daneshyari.com)