Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Solid State Sciences 9 (2007) 380–384
Solid State Sciences
www.elsevier.com/locate/ssscie

Synthesis and structural characterization of two new hexagonal osmates: $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$

William R. Gemmill, Mark D. Smith, Hans-Conrad zur Loye*

Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, USA

Received 13 March 2007; accepted 16 March 2007
Available online 31 March 2007

Abstract

Two complex oxides of osmium, $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$, have been prepared as single crystals from molten potassium hydroxide. Both oxides crystallize in the hexagonal space group $P6_3mc$ with $a = 5.7403(1)$ Å and $c = 14.0771(6)$ Å and $a = 5.7745(2)$ Å and $c = 14.0946(7)$ Å for $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$, respectively. The structure of these compounds is related to the 6H–$BaTiO_3$ structure but exhibit mixed occupancy of both metals on the three crystallographically independent metal sites.

Keywords: Osmate; Flux growth; Single crystals

---

1. Introduction

Perovskite oxides are perhaps the most studied family of compounds in solid chemistry due to their inherent ability to accommodate a wide range of elemental compositions and to display a wealth of structural variations. Perovskites have the general formula ABO_3, where A typically represents a large electropositive cation and B represents a smaller transition metal or main group ion. In its ideal form, the cubic ABO_3 perovskite can be described as consisting of corner sharing BO_6 octahedra with the A cation occupying the twelve-fold coordination site in the center of eight such octahedra. The 2H-hexagonal perovskite consists of infinite chains of face-sharing octahedra that are separated by chains of A-site cations [1]. Alternatively, perovskites and related structures may also be described as resulting from the stacking of close packed [AO_3] layers followed by the filling of the generated octahedral sites by the B cations. If the [AO_3] layers are stacked in an (abc) fashion the cubic perovskite results, while (ab) stacking results in the 2H-perovskite structure. Intergrowth structures, such as the 6H–$BaTiO_3$ structure (Fig. 1), contain face sharing and corner sharing octahedra consistent with both (abc) and (ab) stackings. The compounds involved in this study belong to the 6H–$BaTiO_3$ family of perovskite oxides.

Within the realm of perovskite related oxides of the platinum group metals, phases containing osmium are relatively rare and include the simple perovskites, $AOsO_3$ (A = Ca, Sr and Ba) [2,3], and the double perovskites, Sr_2MOsO_6 (M = Li, Na, Mg, Ca, Sr, Fe, Co, Sc, Cr, In and Ga) [4], Ba_2MOsO_6 (M = Pr, Nd, Sm–Lu and Y) [5], Ba_2MOsO_6 (M = Li and Na) [4,6], Ln_2NaOsO_6 (Ln = La, Pr and Nd) [7], and Ln_2LiOsO_6 (Ln = La, Pr, Nd and Sm) [8]. There are few examples of hexagonal perovskites of osmium including $Ba_3MOs_2O_9$ (M = Li and Na) [9] and Ba_2MOsO_6 (M = Co and Ni) [10] which can be alternatively expressed as $Ba_3M_{3/2}Os_{3/2}O_9$ where Os and either Co or Ni order in a 1:1 fashion amongst the octahedral sites.

We have been interested in the single crystal growth of complex osmium oxides from molten hydroxides and have studied several systems including Ba–M–Os–O (M = Li

---

* Corresponding author. Tel.: +1 803 777 6916; fax: +1 803 777 8508.
E-mail address: zurloye@mail.chem.sc.edu (H.-C. zur Loye).

1293-2558/$ - see front matter © 2007 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2007.03.016

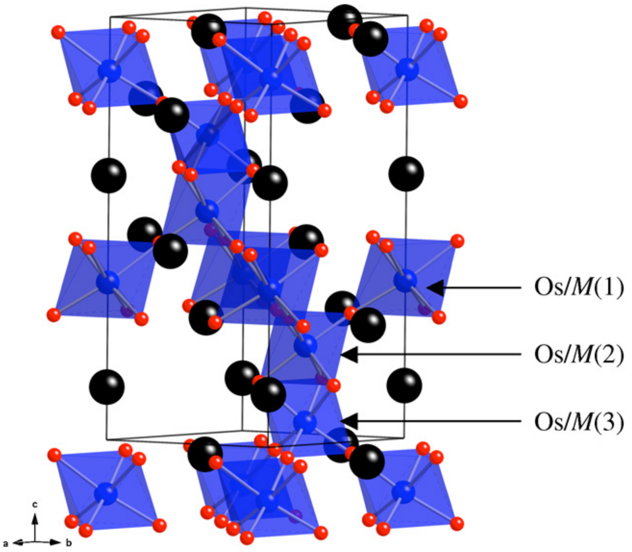

Fig. 1. Representative structural figure of $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$. The three crystallographically independent metal sites associated with space group $P6_3mc$ are labeled.

and Na) [6,9] and Ln–Os–O (Ln = La–Gd) [7,8,11] phase spaces. As an extension of this work, we have begun the study of Ba–M–Os–O (M = 1st row transition metal) quaternary phase space and have prepared two new complex hexagonal perovskites, $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$. These compounds were prepared as single crystals from molten potassium hydroxide and represent examples of 6H related perovskites which exhibit mixing of both metals on the three crystallographically independent metal sites. The crystal growth and structural characterization are reported herein.

2. Experimental

2.1. Crystal growth

For $Ba_2Fe_{0.92}Os_{1.08}O_6$, 1 mmol Os (J&J Materials, 99.98%), 0.5 mmol Fe_2O_3 (Johnson Matthey, 99.999%), 3.5 mmol $Ba(OH)_2 \cdot 8H_2O$ (Alfa, ACS reagent), and 4.0 g KOH (Fisher, reagent grade) were added to a silver tube 0.5″ in diameter that had been flame sealed at one end and securely crimped shut on the other end. Similarly for $Ba_2Co_{0.77}Os_{1.23}O_6$, 1 mmol Os (J&J Materials, 99.98%), 0.35 mmol Co_3O_4 (Alfa, 99.7%), 3.5 mmol $Ba(OH)_2 \cdot 8H_2O$ (Alfa, ACS reagent), and 4.0 g KOH (Fisher, reagent grade) were added to a silver tube. For both $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$ the reaction mixtures were heated at a rate of 10 °C/min to 600 °C, held at temperature for 24 h, cooled to 400 °C at a rate of −1 °C/min, and then allowed to cool to room temperature by turning off the furnace. The crystals were removed from the flux by washing with water, aided by the use of sonication.

2.2. Single crystal X-ray diffraction

X-ray intensity data from a black crystal fragment and a black hexagonal bipyramid were measured at 294 K for $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$, respectively, on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) [16]. For $Ba_2Fe_{0.92}Os_{1.08}O_6$, the data collection covered reciprocal space to $2\theta_{max} = 65.0°$, with an average redundancy of 20.7 and $R_{int} = 0.068$ for $Ba_2Co_{0.77}Os_{1.23}O_6$, the data collection covered reciprocal space to $2\theta_{max} = 70.2°$, with an average redundancy of 13.7 and $R_{int} = 0.050$. Raw area detector data frame integration was performed with SAINT+ [12]. Final unit cell parameters were determined by least-squares refinement of 1328 ($Ba_2Fe_{0.92}Os_{1.08}O_6$) and 1722 ($Ba_2Co_{0.77}Os_{1.23}O_6$) reflections from the data sets with $I > 5\sigma I$. Analysis of the data showed negligible crystal decay during data collection. The data were corrected for absorption effects with SADABS [12]. Full-matrix least-squares refinement against F^2 were performed with SHELXTL [13].

For both $Ba_2Fe_{0.92}Os_{1.08}O_6$ and $Ba_2Co_{0.77}Os_{1.23}O_6$, systematic absences in the intensity data indicated the presence of a 6_3 screw axis operation and a *c*-glide operation perpendicular to $[1\bar{1}0]$. Based on the similarity of the unit cell symmetry and lattice constants to a hexagonal perovskite structure type, an initial refinement of the structure was carried out in the space group $P6_3/mmc$. $P6_3/mmc$ implies two independent transition metal sites, two barium atom sites and two oxygen atom sites. The two transition metal sites generate an MO_6 octahedron and a centrosymmetric M_2O_9 bioctahedron.

In $Ba_2Fe_{0.92}Os_{1.08}O_6$, M is a disordered mixture of iron and osmium, based on refinement of the occupancies. Refinement in $P6_3/mmc$ was unsatisfactory, converging to $R1 = 0.0662/wR2 = 0.1170$, with large difference map extrema of $+7.8/-6.2$ e$^-$/Å^3, regardless of the various metal atom site occupation models. A reasonable refinement was obtained in the space group $P6_3mc$. $P6_3mc$ allows three transition metal sites, with the two metal sites of the M_2O_9 bioctahedron now being inequivalent. There are also three barium sites and three oxygen atoms sites. Refinement of the occupancies of each of the three transition metal sites indicated Fe/Os site substitution on each site. Therefore, each site was refined as a mixed Fe/Os site constrained to sum to full occupancy. Atomic coordinates and displacement parameters were constrained to remain equal during the cycles. The final refined occupancies are Fe(1)/Os(1) = 0.650(8)/0.350(8), Fe(2)/Os(2) = 0.12(1)/0.88(1) and Fe(3)/Os(3) = 0.60(1)/0.40(1). No indication of less than full occupancy was observed for the barium atoms. All metal atoms were refined with anisotropic displacement parameters. The three oxygen atoms were refined isotropically to prevent the occurrence of physically unrealistic (“non-positive definite”) ellipsoids. This is most likely caused by the pseudosymmetry (emulation of $P6_3/mmc$) discussed below. The largest peak and hole in the final difference map are $+2.30$ e$^-$/Å^3 and -2.92 e$^-$/Å^3, located 1.34 Å from the Os(2)/Fe(2) site and 1.60 Å from Ba(2). The absolute structure (Flack) parameter is 0.07(3), indicating the correct orientation of the polar axis and the absence of racemic twinning. Examination of the atomic positions derived in $P6_3mc$ shows that they are in fact consistent with the space group $P6_3/mmc$ [14]. The correct