Supplemental Material for

Crystal Growth of Novel Osmium-Containing Triple Perovskites

Katharine E. Stitzer,[†] Ahmed El Abed,^{‡,§} Mark D. Smith,[†] Matthew J. Davis,[†] Seung-Joo Kim,[†] Jacques Darriet,[‡] and Hans-Conrad zur Loye^{*,†}

[†]*Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, 29208, USA*

[‡]*Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), 87 Avenue du Dr. Schweitzer, 33608 Pessac Cedex, France*

[§]*Permanent address: Mohamed I Univ., Faculté des Sciences, Oujda, Morocco*

X-ray structure determination of Ba₃LiOs₂O₉

Several single crystals of Ba₃LiOs₂O₉ were tested in which the quality of diffraction was assessed on the basis of the size and sharpness of the diffraction spots. A rapid scan on an Enraf-Nonius Kappa CCD diffractometer using Mo K α radiation (λ = 0.71069 Å) gave a hexagonal cell with parameters a = 5.8025 Å and c = 14.1468 Å. Final data collection was also carried out on the Enraf-Nonius Kappa CCD diffractometer. Data processing and the refinement were performed using the Jana2000 program package.¹ A Gaussian-type absorption correction was applied, in which the shape of the crystal was determined using the video microscope of the KappaCCD instrument.

Systematic absences in the intensity data were consistent with the space group P6₃/mmc. The structure was refined by full-matrix least-squares against F², using the Jana2000 program package.¹ All atoms were refined with anisotropic displacement parameters. No significant deviation from unity occupancy was observed for any atom, based on the refinement of the site occupation factors for all atoms. The largest residual electron density peak and hole remaining in the final difference map are +3.57 and -3.38 e/Å³, near Ba2 and Ba1, respectively.

X-ray structure determination of Ba₃NaOs₂O₉

An irregular black crystal chipped from a larger hexagonal prism was epoxied onto the end of a thin glass fiber. X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer system (Mo K α radiation, λ = 0.71073 Å).²

Crystal quality and initial unit cell parameters were determined based on reflections taken from a set of three scans measured in orthogonal regions of reciprocal space. Subsequently 1640 raw data frames were collected in the omega scan mode (0.3° frame width in ω , 20 s per frame) at five different ω settings. The collection provided 100% coverage of the reciprocal lattice to $2\theta_{\text{max}} = 85.2^\circ$ ($R_{\text{int}} = 0.0395$, average redundancy = 9.04). The raw data frames were integrated with the Bruker SAINT+ program,² which also applied corrections for Lorentz and polarization effects. The final unit cell parameters are based on the least-squares refinement of 4378 reflections with $I > 5\sigma(I)$ from the data set. Analysis of the data showed negligible crystal decay during data

collection. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS.³

Systematic absences in the intensity data were consistent with the space group $P6_3/mmc$. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2 , using the SHELXTL software package.³ All atoms were refined with anisotropic displacement parameters. No significant deviation from unity occupancy was observed for any atom, based on the refinement of the site occupation factors for all atoms. The largest residual electron density peak and hole remaining in the final difference map are +3.30 and −3.78 $e/\text{\AA}^3$, near Ba2 and Ba1, respectively.

References:

1. Petricek, V.; Dusek, M. JANA2000, Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, 2000.
2. SMART Version 5.625, SAINT+ Version 6.02a and SADABS. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1998.
3. Sheldrick, G. M. SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.

Table S1. Comparison of unit cell parameters and interatomic distances for $\text{Ba}_3\text{MRu}_2\text{O}_9$ ($\text{M} = \text{Li}, \text{Na}$)* and $\text{Ba}_3\text{MOs}_2\text{O}_9$ ($\text{M} = \text{Li}, \text{Na}$).

	$\text{Ba}_3\text{LiRu}_2\text{O}_9$	$\text{Ba}_3\text{NaRu}_2\text{O}_9$	$\text{Ba}_3\text{LiOs}_2\text{O}_9$	$\text{Ba}_3\text{NaOs}_2\text{O}_9$
space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
a (Å)	5.7820(2)	5.8729(2)	5.8025(1)	5.8858(1)
c (Å)	14.1490(8)	14.4676(7)	14.1468(4)	14.3451(5)
Li-O (Å)	2.123(3)		2.154(5)	
Na-O (Å)		2.227(3)		2.259(5)
Ru-O (Å)	1.852(3)	1.842(3)		
Ru-O (Å)	2.039(3)	2.046(3)		
Os-O (Å)			1.873(3)	1.852(5)
Os-O (Å)			2.032(4)	2.041(6)
Ru-Ru (Å)	2.768(1)	2.7482(9)		
Os-Os (Å)			2.6053(6)	2.5490(8)

*Stitzer, K.E.; Smith, M.D.; Gemmill, W.R.; zur Loye, H.-C. *J. Am Chem. Soc.* **2002**, *124*, 13877.

Figure S1. ORTEP drawing of $\text{Ba}_3\text{LiOs}_2\text{O}_9$ with 80% thermal ellipsoids. Red: barium cations; yellow: osmium cations; blue: lithium cations; white: oxygen anions.

Figure S2. ORTEP drawing of $\text{Ba}_3\text{NaOs}_2\text{O}_9$ with 80% thermal ellipsoids. Red: barium cations; yellow: osmium cations; blue: sodium cations; white: oxygen anions.