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Samuel J. Mugavero III
University of South Carolina - Columbia

Irina V. Puzdrjakova
University of South Carolina - Columbia

Mark D. Smith
University of South Carolina - Columbia, mdsmith3@mailbox.sc.edu

Hans-Conrad zur Loye
University of South Carolina - Columbia, zurloye@mailbox.sc.edu

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Sm₂NaIrO₆, a monoclinically distorted double perovskite

Samuel J. Mugavero III, Irina V. Puzdrjakova, Mark D. Smith and Hans-Conrad zur Loye*

Department of Chemistry and Biochemistry,
University of South Carolina, Columbia,
South Carolina 29208, USA

Correspondence e-mail: zurloye@sc.edu

Key indicators

Single-crystal X-ray study
 $T = 294\text{ K}$
Mean $\sigma(\text{m-O}) = 0.004\text{ \AA}$
 R factor = 0.026
 wR factor = 0.052
Data-to-parameter ratio = 22.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Single crystals of the lanthanide-containing iridate, disamarium sodium iridium hexaoxide, Sm₂NaIrO₆, were prepared *via* high-temperature flux growth and structurally characterized by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/n$ and is a double perovskite, consisting of a 1:1 ordered rock-salt-type lattice of corner-shared NaO₆ and IrO₆ distorted octahedra. Samarium occupies the eightfold coordination site generated by the connectivity of the octahedra.

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Comment

Recently the crystal growth and characterization of the double perovskites Ln₂LiIrO₆ (Ln = La, Pr, Nd, Sm and Eu) and Ln₂NaMO₆ (Ln = La, Pr and Nd, and $M = \text{Ru}$ and Ir) from molten hydroxide fluxes was reported (Gemmill *et al.*, 2004; Davis *et al.*, 2004; Mugavero *et al.*, 2005). High-temperature flux growth from molten hydroxides has proven to be an effective medium for oxide crystal growth. Sm₂NaIrO₆, a distorted double perovskite, was grown from a molten NaOH/CsOH flux at 923 K.

In its ideal form, the cubic perovskite ABO₃ consists of corner-sharing BO₆ octahedra with the A cation occupying the 12-fold coordination site formed in the middle of a cube of eight such octahedra (Mitchell, 2002). The ideal double perovskite structure of the general formula A₂BB'O₆ is obtained when the B cation is substituted by a B' cation in an ordered 1:1 fashion, doubling the unit cell. The $P2_1/n$ space group allows for a 1:1 ordered arrangement of the B and B' cations in a rock-salt-type lattice and the tilting of the BO₆ and B'O₆ octahedra to accommodate the small size of the A cation (Woodward, 1997*a,b*). The Glazer tilt system assigned to the $P2_1/n$ space group is #10, $a^-a^-b^+$ (Glazer, 1972). Sm₂NaIrO₆ is a monoclinically distorted structure of an ideal double perovskite where the Na⁺ and Ir⁵⁺ cations occupy the two crystallographically independent octahedral sites (site symmetry $\bar{1}$, Wyckoff symbol 2*a*; site symmetry $\bar{1}$, Wyckoff symbol 2*b*), while the Sm³⁺ cations occupy the A site in an eightfold coordination environment (site symmetry 1, Wyckoff symbol 4*e*).

Experimental

Single crystals of Sm₂NaIrO₆ were grown from an 'acidic' high-temperature hydroxide melt. Sm₂O₃ (Alfa Aesar 99.9%, 0.75 mmol), Ir (Engelhard, 99.9%, 0.5 mmol), NaOH (Fisher, ACS reagent, 3.0 g) and CsOH (Alfa Aesar, 98%, 2.0 g) were loaded into a silver tube that had been previously flame-sealed at one end. The top of the tube was crimped and folded three times before being placed upright into a programmable box furnace. The tube was heated to 923 K over a

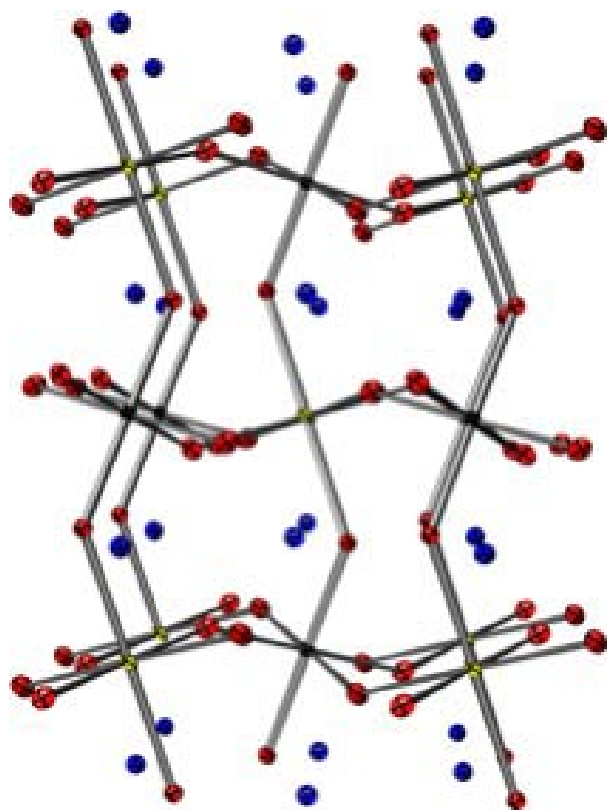


Figure 1

Octahedral tilting in $\text{Sm}_2\text{NaIrO}_6$, with the [010] direction shown going into the page and displacement ellipsoids drawn at the 50% probability level. Sm^{3+} shown in blue, Ir^{5+} in black, Na^+ in yellow and O^{2-} in red.

period of 1 h, held at that temperature for 24 h and then cooled to room temperature by shutting off the furnace. The black dodecahedral-shaped crystals were removed from the flux matrix by dissolving the flux in water and isolating the crystals by vacuum filtration.

Crystal data

$\text{Sm}_2\text{NaIrO}_6$	$D_x = 8.024 \text{ Mg m}^{-3}$
$M_r = 611.89$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3184 reflections
$a = 5.4656(2) \text{ \AA}$	$\theta = 2.6\text{--}35.0^\circ$
$b = 5.8880(2) \text{ \AA}$	$\mu = 49.13 \text{ mm}^{-1}$
$c = 7.8714(3) \text{ \AA}$	$T = 294(1) \text{ K}$
$\beta = 91.097(1)^\circ$	Prism, black
$V = 253.27(2) \text{ \AA}^3$	$0.06 \times 0.04 \times 0.04 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART APEX CCD diffractometer	1112 independent reflections
ω scans	1049 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan, (SADABS; Bruker, 2001)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.075$, $T_{\text{max}} = 0.140$	$\theta_{\text{max}} = 35.1^\circ$
4588 measured reflections	$h = -8 \rightarrow 8$
	$k = -9 \rightarrow 8$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 3.1589P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.13$	$\Delta\rho_{\text{max}} = 2.08 \text{ e \AA}^{-3}$
1112 reflections	$\Delta\rho_{\text{min}} = -1.74 \text{ e \AA}^{-3}$
50 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.0085 (4)

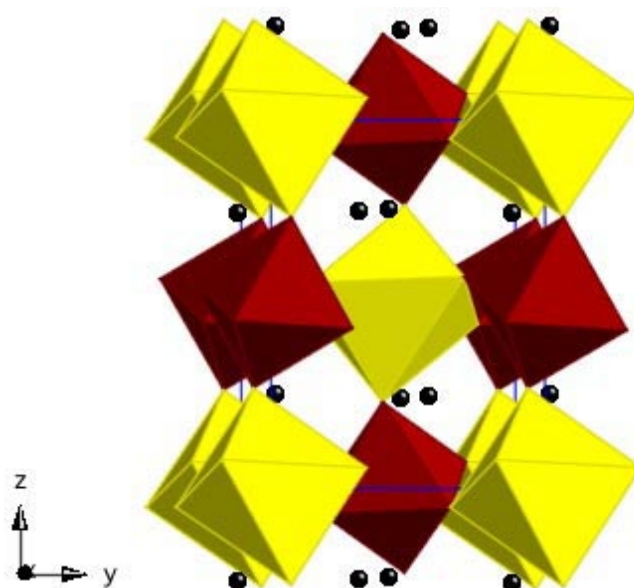


Figure 2

Polyhedral view of $\text{Sm}_2\text{NaIrO}_6$, approximately along [100]. IrO_6 octahedra are shown in red, NaO_6 octahedra in yellow and Sm atoms in black.

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Sm1}-\text{O2}^{\text{i}}$	2.293 (4)	$\text{Na1}-\text{O1}$	2.254 (4)
$\text{Sm1}-\text{O1}^{\text{ii}}$	2.339 (4)	$\text{Na1}-\text{O1}^{\text{vii}}$	2.255 (4)
$\text{Sm1}-\text{O2}$	2.340 (4)	$\text{Na1}-\text{O3}^{\text{iii}}$	2.313 (4)
$\text{Sm1}-\text{O3}^{\text{iii}}$	2.348 (4)	$\text{Na1}-\text{O3}^{\text{iii}}$	2.313 (4)
$\text{Sm1}-\text{O3}^{\text{ii}}$	2.552 (5)	$\text{Ir1}-\text{O2}^{\text{v}}$	1.965 (4)
$\text{Sm1}-\text{O1}$	2.623 (4)	$\text{Ir1}-\text{O2}$	1.965 (4)
$\text{Sm1}-\text{O1}^{\text{iv}}$	2.705 (4)	$\text{Ir1}-\text{O1}$	1.968 (4)
$\text{Sm1}-\text{O3}^{\text{v}}$	2.896 (4)	$\text{Ir1}-\text{O1}^{\text{v}}$	1.968 (4)
$\text{Na1}-\text{O2}^{\text{vi}}$	2.254 (4)	$\text{Ir1}-\text{O3}^{\text{v}}$	1.970 (4)
$\text{Na1}-\text{O2}^{\text{ii}}$	2.254 (4)	$\text{Ir1}-\text{O3}$	1.970 (4)
$\text{Ir1}-\text{O1}-\text{Na1}$	144.0 (2)	$\text{Ir1}-\text{O3}-\text{Na1}^{\text{x}}$	139.2 (2)
$\text{Ir1}-\text{O2}-\text{Na1}^{\text{ix}}$	137.7 (2)		

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (vii) $-x, -y, -z$; (viii) $-x, -y + 1, -z$; (ix) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (x) $x, y + 1, z$.

The highest residual electron density and the deepest hole are located approximately 1 \AA from Sm1.

Data collection: *SMART NT* (Bruker, 2001); cell refinement: *SAINT-Plus NT* (Bruker, 2001); data reduction: *SAINT-Plus NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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