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Sm$_2$NaIrO$_6$, a monoclinically distorted double perovskite

Samuel J. Mugavero III, Irina V. Puzdrjakova, Mark D. Smith and Hans-Conrad zur Loye
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Single crystals of the lanthanide-containing iridate, disamarium sodium iridium hexaoxide, Sm$_2$NaIrO$_6$, 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 NaO$_6$ and IrO$_6$ distorted octahedra. Samarium occupies the eightfold coordination site generated by the connectivity of the octahedra.

Comment

Recently the crystal growth and characterization of the double perovskites Ln$_2$LiIrO$_6$ (Ln = La, Pr, Nd, Sm and Eu) and Ln$_2$NaMO$_6$ (Ln = La, Pr and Nd, and M = 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. Sm$_2$NaIrO$_6$, a distorted double perovskite, was grown from a molten NaOH/CsOH flux at 923 K.

In its ideal form, the cubic perovskite $ABO_3$ consists of corner-sharing $BO_6$ 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 $A_2BB'O_6$ 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 $BO_6$ and $B'O_6$ octahedra to accommodate the small size of the A cation (Woodward, 1997a,b). The Glazer tilt system assigned to the $P2_1/n$ space group is $#10$, $a^-a^-b^+$ (Glazer, 1972). Sm$_2$NaIrO$_6$ is a monoclinically distorted structure of an ideal double perovskite where the Na$^+$ and Ir$^{5+}$ cations occupy the two crystallographically independent octahedral sites (site symmetry 1, Wyckoff symbol 2a; site symmetry 1, Wyckoff symbol 2b), while the Sm$^{3+}$ cations occupy the A site in an eightfold coordination environment (site symmetry 1, Wyckoff symbol 4e).

Experimental

Single crystals of Sm$_2$NaIrO$_6$ were grown from an ‘acidic’ high-temperature hydroxide melt. Sm$_2$O$_3$ (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 Sm₂NaIrO₆ with the [010] direction shown going into the page and displacement ellipsoids drawn at the 50% probability level. Sm⁺⁺ shown in blue, Ir⁵⁺ in black, Na⁺ in yellow and O²⁻ 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
Sm₂NaIrO₆
Mr = 611.89
Monoclinic, P2₁/n
a = 5.4656 (2) Å
b = 5.8880 (2) Å
c = 7.8714 (3) Å
β = 91.097 (1)°
V = 253.27 (2) Å³
Z = 2

Data collection
Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan, (SADABS; Bruker, 2001)
Tmin = 0.075, Tmax = 0.140
4588 measured reflections

Refinement
Refinement on F²
R[F² > 2σ(F²)] = 0.026
wR(F²) = 0.052
S = 1.13
1112 reflections

1112 independent reflections
1049 reflections with I > 2σ(I)

Dab = 8.024 Mg m⁻³
Mo Kα radiation
Cell parameters from 3184 reflections
θ = 2.6–35.0°
µ = 49.13 mm⁻¹
T = 294 (1) K
Prism, black
0.06 × 0.04 × 0.04 mm

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Distance (Å)</th>
<th>Atoms</th>
<th>Distance (Å)</th>
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<td>2.623 (4)</td>
<td>Na1-O1</td>
<td>2.254 (4)</td>
</tr>
<tr>
<td>Sm1-O2</td>
<td>2.340 (4)</td>
<td>Na1-O1si</td>
<td>2.255 (4)</td>
</tr>
<tr>
<td>Sm1-O3</td>
<td>2.348 (4)</td>
<td>Na1-O1sii</td>
<td>2.313 (4)</td>
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<tr>
<td>Sm1-O3si</td>
<td>2.552 (5)</td>
<td>Ir1-O2</td>
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<tr>
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<td>Ir1-O2</td>
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<tr>
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<tr>
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<td>Ir1-O2-Na1si</td>
<td>137.7 (2)</td>
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</tbody>
</table>

Symmetry codes: (i) -x+1, y-1/2, z-1/2; (ii) -x+1, y-1/2, z+1/2; (iii) x, y-1, z; (iv) x+1, y, z; (v) -x+1, y-1, z; (vi) x, y+1, z; (vii) x-1, y, z; (viii) x, -y+1, z; (ix) x+1, y+1/2, z+1/2; (x) x, y+1, z.

The highest residual electron density and the deepest hole are located approximately 1 Å 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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References


