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Layered Compounds

# The Lone-Pair Cation $I^{5+}$ in a Hexagonal Tungsten Oxide-Like Framework: Synthesis, Structure, and Second-Harmonic Generating Properties of $Cs_2I_4O_{11}$**

*Kang Min Ok and P. Shiv Halasyamani**

Noncentrosymmetric (NCS) oxides exhibit a variety of technologically important properties including ferroelectricity, piezoelectricity, pyroelectricity, and second-order nonlinear optical behavior.[1–3] The rational design of new NCS materials, however, remains a challenge, although a number of strategies have been suggested.[4–9] We have focused on synthesizing materials containing cations with lone pairs (e.g., $Sb^{3+}$, $Se^{4+}$, $Te^{4+}$, etc.) in order to increase the incidence of NCS in any new compound.[10,11] A structural topology that is often observed in NCS is the hexagonal tungsten oxide (HTO) framework. This structure has been reported for a variety of cations, including $V^{5+}$, $Mo^{6+}$, $W^{6+}$, and $Sb^{5+}$.[12–18] The framework consists of corner-sharing $MO_{6/2}$ octahedra that are linked to form an array of three- and six-membered rings. To date, structures have been observed in which other cations, for example, $Se^{4+}$, $Te^{4+}$, $P^{5+}$, and $Sb^{3+}$, bridge, cap one side, or cap both sides of the HTO layer. In instances of one-sided capping, an NCS polar material is observed, often with highly efficient second-harmonic generating (SHG) properties, that is, $SHG > 400 \times SiO_2$.[13,17] In the reported materials, the HTO framework has been restricted to octahedrally coordinated $d^0$ transition metals and the $d^{10}$ $Sb^{5+}$ cation. We describe herein $Cs_2I_4O_{11}$, the first material with a layered HTO-like framework that contains a lone-pair cation, $I^{5+}$. The material also has $I^{5+}$ cations capping the layer on one side, which renders the structure NCS. Hence, SHG measurements are also presented.

Crystals of $Cs_2I_4O_{11}$ were grown hydrothermally by combining $Cs_2CO_3$, $Nb_2O_5$, $HIO_3$, and $H_2O$ in a Teflon-lined autoclave at 220 °C for 4 d. The product consisted of large (maximum dimension 3 mm), colorless, faceted, hexagonal crystals.

$Cs_2I_4O_{11}$ exhibits a layered HTO-like framework consisting of asymmetric $IO_5$ and $IO_3$ polyhedra.[19] Both the five- and three-coordinate $I^{5+}$ cations are in asymmetric coordination environments attributable to their lone pair. The five-coordinate $I^{5+}$ cation exhibits one short I–O bond of 1.783(9) Å, three intermediate I–O bonds of 2.027(15), 2.128(2), and 2.150(2) Å, one long I–O bond of 2.441(16) Å, and angles of 71.0(6)–171.2(2)°. The three-coordinate $I^{5+}$ cation has a unique intermediate I–O bond of 1.943(18) Å and angles of 93.0(7)–134.8(8)°. These bond lengths and angles are consistent with those of previously reported iodates.[20–24] The $IO_5$ and $IO_3$ polyhedra share corners to form the layered structure. In connectivity terms, the layer can be described as a $[3(IO_{2/3}O_{2/1}O_{1/2})^{4/3-}(IO_{3/2})^{2+}]^{2-}$ anion, with charge balance attained by two $Cs^+$ cations.

One of the most novel aspects of the structure is the two-dimensional $IO_5$ layer (Figure 1). The HTO-like layer consists of six-membered rings containing corner-sharing $IO_5$ polyhedra in alternating orientation as one proceeds around the ring. $Cs_2I_4O_{11}$ is the first example of a lone-pair cation in a HTO-like topology. In the rings themselves, three lone pairs point inward and three outward. Thus, the lone pairs and oxide anions alternate around the ring. The lone pairs have two important structural consequences. First, the local dipole moment on each $IO_5$ polyhedron is in the direction of the lone pair. If we sum all of the dipole moments with respect to the $IO_5$ group, the resultant moment is zero. In other words, there is complete cancellation of the dipole moments with respect to the $IO_5$ polyhedra, that is, the $IO_5$ layer is pseudocentrosymmetric. This type of pseudocentrosymmetric layer was observed previously in $Rb_2TeW_3O_{12}$ and $Cs_2TeW_3O_{12}$.[17] The cancellation is relevant to the SHG efficiency. Second, the $Cs^+$ cations are not coplanar with the $IO_5$ ring, attributable to the lone pairs. As shown in Figure 2, the $Cs^+$ cations sit above and below the rings. The environments of the $Cs^+$ cations influence any possible ion-exchange capabilities of the material.[25] The $IO_5$ layer is capped on one side by an asymmetric three-coordinate $I^{5+}$ cation, that is, an $IO_3$ group (see Figure 3). Alignment of the $IO_3$ polyhedra in the [001] direction results in an NCS and polar structure. The lone pairs associated with the $IO_3$ polyhedra also point along the [001]

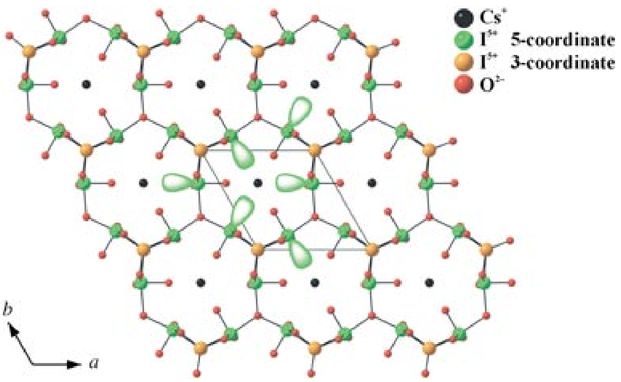

***Figure 1.*** Ball-and-stick representation of the $IO_5$ six-membered rings in $Cs_2I_4O_{11}$ with the lone-pairs shown schematically. Note how the lone pairs on the $IO_5$ polyhedra cancel, rendering the layer pseudocentrosymmetric.

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[*] Dr. K. M. Ok, Prof. P. S. Halasyamani
Department of Chemistry
University of Houston
136 Fleming Building, Houston, TX 77204-5003 (USA)
Fax: (+1) 713-743-2787
E-mail: psh@uh.edu

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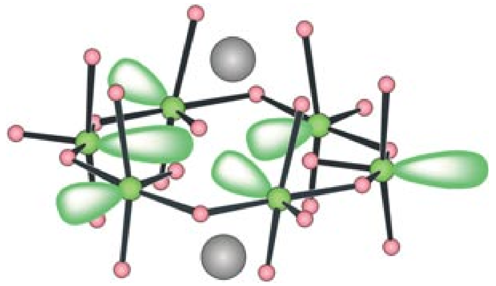

*Figure 2.* Ball-and-stick representation of one six-membered $IO_5$ ring with the lone pairs shown schematically. The $Cs^+$ cations (gray spheres) reside above and below the rings because of the lone pairs.

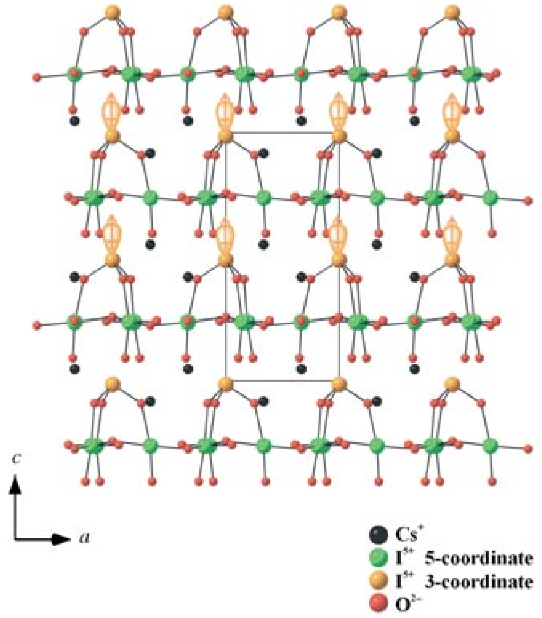

*Figure 3.* Ball-and-stick representation of $Cs_2I_4O_{11}$ in the *ac* plane. The lone pairs on two rows of $I^{5+}$ cations are shown schematically, along with the direction of the dipole moment. Note how all the $I^{5+}$ lone pairs point in the same direction and render $Cs_2I_4O_{11}$ noncentrosymmetric.

direction and produce a dipole moment in that direction (Figure 3).

Since $Cs_2I_4O_{11}$ is NCS, we performed powder SHG measurements on the compound.[26] A detailed description of the measurement was reported earlier.[27] $Cs_2I_4O_{11}$ has an SHG efficiency of approximately 300 × $SiO_2$. This efficiency is comparable to other NCS iodates, including $HIO_3$ (300 × $SiO_2$),[26] $LiIO_3$ (300 × $SiO_2$),[26] $NdMoO_2(IO_3)_4(OH)$ (350 × $SiO_2$),[28] and $AMoO_3(IO_3)$ (A = Rb or Cs, 400 × $SiO_2$).[29] By sieving the polycrystalline powder into various particle sizes (20–150 μm) and measuring the SHG as a function of particle size, we were able to determine that $Cs_2I_4O_{11}$ is non-phase-matchable (Type 1). This information along with the SHG efficiency allows us to estimate $\langle d_{\mathrm{eff}}\rangle_{\mathrm{exptl}}$, which for $Cs_2I_4O_{11}$ is 9.6 pm V⁻¹. We have previously published a structural model that allows us to calculate $\langle d_{\mathrm{eff}}\rangle_{\mathrm{calcd}}$ on the basis of metal–oxygen bond hyperpolarizabilities $\beta$(M–O).[27] With $Cs_2I_4O_{11}$, we only have $\beta$(I–O) which is $140 \times 10^{-40}\,\mathrm{m^4\,V^{-1}}$, and since the $IO_5$ layer is pseudocentrosymmetric the only $\beta$(I–O) that contribute to the SHG are those of the $IO_3$ group. Using this model, which also approximates the contribution attributable to the lone pair to be 20 % of $\beta$(I–O), we calculate a $\langle d_{\mathrm{eff}}\rangle_{\mathrm{calcd}}$ of 13.0 pm $V^{-1}$. This value is in reasonable agreement with $\langle d_{\mathrm{eff}}\rangle_{\mathrm{exptl}}$ of 9.6 pm $V^{-1}$.

In conclusion, we have reported the first example of a lone-pair cation, $I^{5+}$, in a HTO-like framework topology. The material is NCS and exhibits a SHG efficiency of 300 × $SiO_2$. We are in the process of examining other NCS properties of $Cs_2I_4O_{11}$, including ferroelectric, pyroelectric, and piezoelectric behavior.

## Experimental Section

$Cs_2I_4O_{11}$ was obtained by hydrothermal reaction. $Cs_2CO_3$ (1.0 mmol, 99+ %, Aldrich), $HIO_3$ (28.5 mmol, 99.99 %, Aldrich), $Nb_2O_5$ (1.9 mmol, 99.99 %, Aldrich), and 5.0 mL of water were loaded into a 23 mL Teflon-lined autoclave and subsequently sealed. The autoclave was gradually heated to 220 °C, held for 4 d, and cooled slowly to room temperature at a rate of 6 °C $h^{-1}$. The mother liquor was decanted from the products, which were then washed with water and ethanol. The product was obtained as a mixture of large colorless hexagonal crystals in 85 % yield based on cesium and white powder. The white powder was confirmed to be $Nb_2O_5$ by powder X-ray diffraction. The $Cs_2I_4O_{11}$ crystals were extracted manually from the bulk. Despite repeated attempts at different temperature, molar ratios, and filling volumes, we were unable to grow single crystals of $Cs_2I_4O_{11}$ in the absence of $Nb_2O_5$. The role of $Nb_2O_5$ in the crystal growth is unclear. IR (KBr, $cm^{-1}$): 829 ($\nu_{\mathrm{I-O}}$, m), 816 ($\nu_{\mathrm{I-O}}$, m), 798 ($\nu_{\mathrm{I-O}}$, m), 778 ($\nu_{\mathrm{I-O}}$, m), 764 ($\nu_{\mathrm{I-O}}$, s), 747 ($\nu_{\mathrm{I-O}}$, m), 670 ($\nu_{\mathrm{I-O}}$, m), 538 ($\delta_{\mathrm{I-O}}$, s), 458 ($\delta_{\mathrm{I-O}}$, m), 435 ($\delta_{\mathrm{I-O}}$, m), 422 ($\delta_{\mathrm{I-O}}$, m), 409 ($\delta_{\mathrm{I-O}}$, s). Thermogravimetric measurements indicate that $Cs_2I_4O_{11}$ is stable up to 420 °C. Two rapid weight-loss events that occur above this temperature result in total volatilization around 800 °C.

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[19] Crystal data for $Cs_2I_4O_{11}$: colorless hexagonal prismatic crystal ($0.02 \times 0.04 \times 0.10$ mm), $M_r = 949.42$, hexagonal $P6_3$ (no. 173), $a = b = 7.348(3)$, $c = 13.871(6)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 648.5(5)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 4.862$ g cm$^{-3}$, $\mu = 151.85$ cm$^{-1}$. Data collection: Siemens SMART CCD area detector, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 293$ K. A total of 3858 unique reflections were measured, of which 997 with $I > 2.0\sigma(I)$ were used for the structure solution. Corrections were made for Lorentzian and polarization effects, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Psi scans were used for the absorption correction on the hemisphere of data. The data were solved and refined by using SHELXS-97 and SHELXL-97, respectively. Final $R/R_w$ on $|F^2|$ were 0.0453/0.1017, GOF = 1.090 for 36 parameters. The final Fourier difference map revealed minimum and maximum peaks of $-1.650$ and $+1.736$ e Å$^{-3}$. All calculations were performed by using the WinGX-98 crystallographic software package. Even though large crystals (up to 3 mm) were sometimes obtained, a small crystal as described above was used for the crystal structure determination to minimize absorption. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-413942. G. M. Sheldrick, SHELXS-97—A program for automatic solution and crystal structures, University of Göttingen, Göttingen, Germany, **1997**; G. M. Sheldrick, SHELXL-97—A program for crystal structure refinement, University of Göttingen, Göttingen, Germany, **1997**; L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

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[25] Attempts to exchange the $Cs^+$ ions were unsuccessful. Since $Cs_2I_4O_{11}$ is water soluble, about 100 mg of the material was stirred in 5 mL of a 0.5 M solution of $MNO_3$ ($M = Na^+, K^+, Rb^+$) in ethanol/water (4/1). Experiments at 60 °C for 3 d resulted in incomplete reactions; therefore, the reactions were performed at 90 °C for 4 d in sealed fused-silica tubes to prevent evaporation of ethanol. Under these conditions $Cs_2I_4O_{11}$ reacted with the alkali metal nitrates to produce $NaIO_3$ ($Pbnm$),[23] $KIO_3$ ($P1$),[22] and $RbIO_3$ ($R3m$)[20] in phase-pure form. The phase purity of these materials was confirmed by powder X-ray diffraction analysis, and the refined unit cell for each material matched the literature values (see Supporting Information).

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