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Structure, properties, and disorder in the new distorted-Hollandite $PbIr_4Se_8$

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ABSTRACT

The synthesis and physical properties of the new distorted-Hollandite $PbIr_4Se_8$ are reported. Powder X-ray diffraction and transmission electron microscopy show that the structure consists of edge- and corner-sharing $IrSe_6$ octahedra, with one-dimensional channels occupied by Pb. The structure contains Se-Se anion-anion bonding, leading to an electron count of $Pb^{2+}(Ir^{3+})_4(Se_2)^{2-}(Se^{2-})_6$, confirmed by bond-valence sums and diamagnetic behavior. Structural and heat capacity measurements demonstrate disorder on the Pb site, due to the combination of lone-pair effects and the large size of the one-dimensional channels. Comparisons are made to known Hollandite and pseudo-Hollandite structures, which demonstrates that the anion-anion bonding in $PbIr_4Se_8$ distorts its structure, to accommodate the Ir^{3+} state. An electronic structure calculation indicates semiconductor character with a band gap of 0.76 (11) eV.

1. Introduction

The Hollandite structure, prototypically α-MnO_2, is a well studied family of materials for battery, [1–3] thermoelectric, [4,5] and even magnetic applications. [6,7] The formula can be better written as $M_xT_4O_8$, where M=early lanthanides, alkali metals, or alkali earth metals, x=0–1, and T=Mn, Mo, Ru, or Ir.[8–11] A similar compound, the pseudo-Hollandites, have an even more expansive series, $M_xT'T_4Ch_8$ where M=Tl, In, Cd, Sn, Pb, alkali metals, or alkaline earth metals, x=0–1, T,T' = Ti, V, or Cr, and Ch = S, Se, or Te. [12,13] The structure of both series consists of double chains of edge-sharing T-O octahedra which corner-share with other double octahedral chains to form a framework structure containing large one-dimensional (1-D), with a cation M, occupying the site in the channels.

Despite the wealth of cations and transition metals which take this structure, only KIr_4O_8 and $Rb_{0.68}Ir_4O_8$ contain a 5d transition metal, [9,14] which have recently attracted significant interest due to strong spin-orbit coupling which could lead to nontrivial behavior [15]. These relativistic effects having comparable energy scales with crystal field stabilization or electron correlations is expected to lead to exotic quantum or magnetic behavior [16–18]. Iridium in particular, especially iridium chalcogenides, has been heavily studied for these reasons.

Though some non-oxide iridium chalcogenides have been studied, they are primarily derivatives of the binary compounds IrS_2, $IrSe_2$, and $IrTe_2$ [19–22]. Some recent work has been done on stoichiometric ternary Ir-Sn-Se compounds, [23,24] though none have yet looked at other stoichiometric ternary Ir-Se-X compounds.

Here we report the synthesis, structure, and some physical properties of the new compound $PbIr_4Se_8$. This structure is analogous, but structurally distinct, to Hollandite, which contains similar 1-D channels. As far as the authors are aware, this is the first non-oxide 5d Hollandite. Due to the large size of the 1-D channels, and Pb lone-pair effects, considerable disorder is seen on the Pb site, evidenced by power X-ray diffraction (PXRD), selected area electron diffraction (SAED), X-ray pair distribution analysis (PDF), and heat capacity. $PbIr_4Se_8$ is diamagnetic, indicative of low-spin 5d^6 Ir^{3+}, and has semiconducting character, evidenced by heat capacity and band structure calculations.

2. Experimental

2.1. Preparation

Polycrystalline $PbIr_4Se_8$ was grown by placing Ir (Alfa Aesar 99.95%), Pb (Alfa Aesar 99.999%), and Se (Alfa Aesar 99.999%) in

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the stoichiometric ratio of $(PbSe)_{1.1}(IrSe_2)_2$, in a fused silica tube, for a total of 300 mg. Tubes were backfilled with 1/3 atm of Ar to minimize vaporization of Se. The tube was heated quickly to 500 °C, followed by a 50 °C/h ramp to an annealing temperature of 950 °C, and held for four days before quenching in water. The resulting boule was pulverized, and the heat sequence and quench were repeated a second time. This resulted in shiny, silver PbSe micro-rings as well as loose, gray powder. After PbSe was mechanically removed, the resulting phase pure powder was used for all physical property and characterization methods. Attempts to target a myriad of alternate stoichiometries at several lower temperatures all led to the same $PbIr_4Se_8$ material with varied amounts of PbSe/$IrSe_2$ impurities. Specifically, attempts with less Pb and Se always included non-phase separating $IrSe_2$ impurities.

2.2. Characterization

Laboratory powder X-ray diffraction (PXRD) patterns were collected using a Cu K_α ($\lambda_{avg}=1.5418$ Å) on a Bruker D8 Focus diffractometer with a LynxEye detector. Peak searching and LeBail refinements were used for phase identification and initial lattice parameter estimates in TOPAS (Bruker AXS). Simulated annealing was then used to estimate atomic positions. Finally, Rietveld refinements determined precise atomic positions and lattice parameters, using TOPAS and GSAS-II [25] respectively. To verify the choice of lattice parameters and spacegroup, transmission electron microscopy (TEM) was used with a Phillips CM300 atomic resolution transmission electron microscope equipped with a field emission gun with an accelerating voltage of 300 kV. A CCD camera (bottom mounted Orius camera) was used to collect a tilt series of selected area electron diffraction (SAED) images, tilting from the [001] direction to the $[\bar{2}\,\bar{1}3]$ direction. Structures were visualized using VESTA [26].

Synchrotron X-ray diffraction for pair distribution analysis (PDF) was collected at the beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory with an X-ray wavelength of 0.2112 Å. A CeO_2 standard was used to estimate the

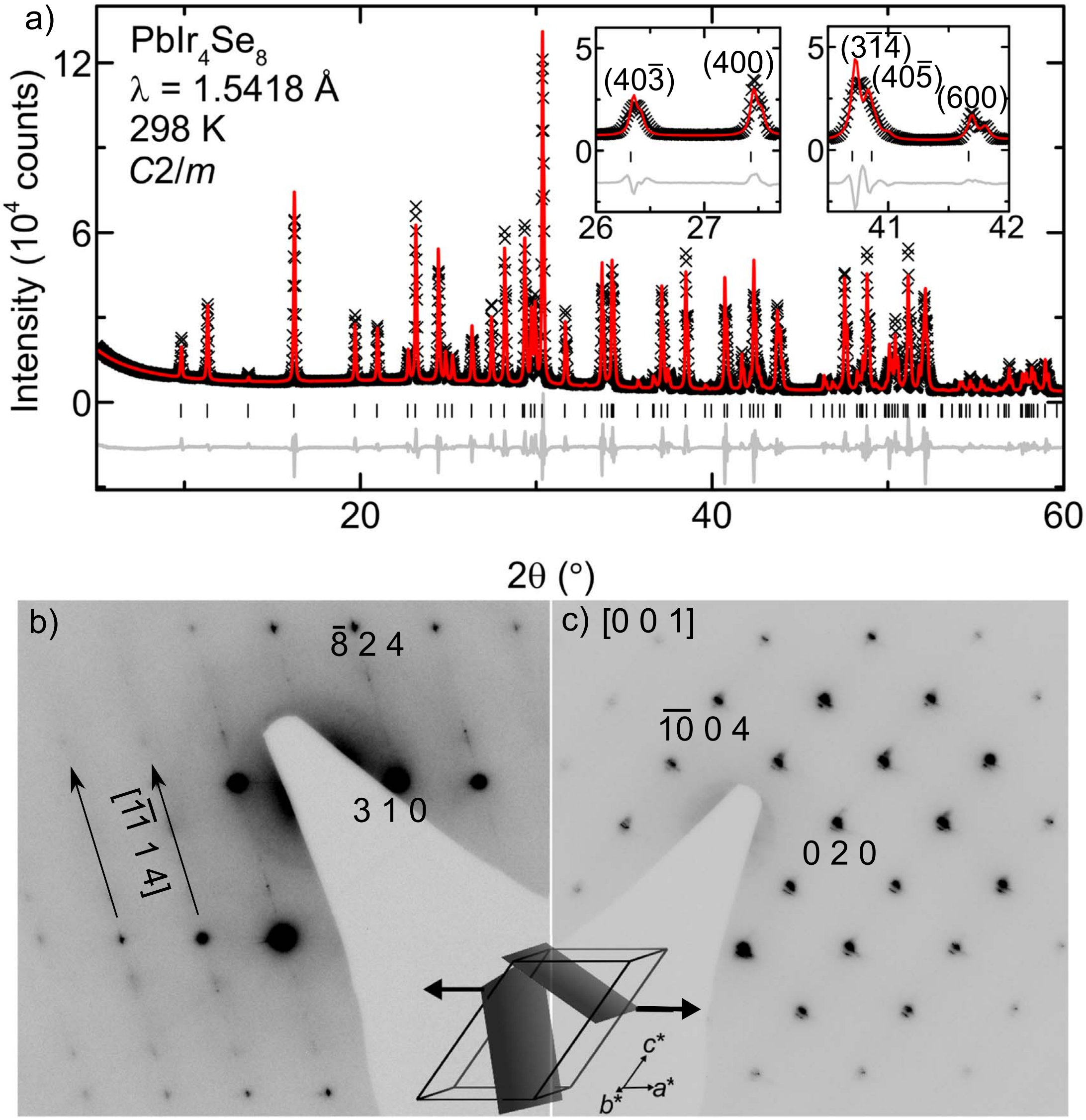

Fig. 1. a) Laboratory powder X-ray diffraction for $PbIr_4Se_8$ shown as black X's, fit in red, and difference in gray. Insets demonstrate some peaks are appreciably broadened. b) Transmission electron diffraction close to the $[\bar{1}\bar{2}\ \bar{5}\ 39]$ direction and c) along the [001] direction for $PbIr_4Se_8$. The inset displays the corresponding planes. Diffuse scattering (streaking) is seen in the $[\bar{1}\bar{1}1\ 4]$ direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)