High-Pressure Synthesis of Lu$_2$NiIrO$_6$ with Ferrimagnetism and Large Coercivity

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ABSTRACT: Double-perovskite Lu$_2$NiIrO$_6$ was synthesized at high pressure (6 GPa) and high temperature (1300 °C). Synchrotron powder X-ray diffraction indicates that its structure is a monoclinic double perovskite (space group $P2_1/c$) with a small, 11% Ni/Ir antisite disorder. X-ray absorption near-edge spectroscopy measurements established Ni$^{2+}$ and Ir$^{4+}$ formal oxidation states. Magnetic studies indicate a ferrimagnetic transition at 207 K. The low-temperature magnetization curve of Lu$_2$NiIrO$_6$ features broad hysteresis with a coercive field as high as 48 kOe. These results encourage the search for hard magnets in the class of 3d/5d double-perovskite oxides.

INTRODUCTION

Double-perovskite (DP) oxides have the general formula of $A_2BB'O_6$. DP oxides with 3d and 4d/5d transition-metal (TM) cations at the B and B' sites, respectively, continue to attract attention because of their interesting physical properties including high-temperature ferrimagnetism, half-metallic, ferro- or ferrimagnetic insulation, large magnetoresistance, and exchange bias.1-16 The room-temperature magnetoresistance observed in half-metallic Sr$_2$FeMoO$_6$, which has a Curie temperature ($T_C$) of 415 K, showed prospects for spintronic applications.12 Recently, reports of 3d/5d DP oxides continue to show much progress in the synthesis of 3d/5d DP oxides with respect to high-temperature magnetic ordering and other novel properties.3-16 Relative to 3d, 5d elements generally have larger spin–orbit coupling (SOC) and smaller on-site Coulomb repulsion because of more extended radial orbitals. Consequently, compounds of 5d elements have much different spin, orbital, and the charge degrees of freedom than those of 3d elements.17 For examples, a novel Mott insulating state in Sr$_2$IrO$_4$18 a metal–insulator transition in NaOsO$_3$,19,20 and a transition to a ferroelectric-like metallic state in LiOsO$_3$21 were reported in 5d solid-state oxides.

Many DP oxides containing both 3d and 5d TM ions display interesting properties:5-16 Sr$_2$CrReO$_6$ is half-metallic and high-temperature ferrimagnetic (FiM) with $T_C = 635$ K.7 Transition-metal-only DPs Mn$_2$BrReO$_6$ (B = Fe and Mn) display magnetic and magnetoresistive behavior,10,11 whereas insulating Sr$_2$CrOsO$_6$ and Ca$_2$FeOsO$_6$ feature above-room-temperature FiM transitions.12-14 Typically, DP oxides have
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an ordered rocksalt and three-dimensional arrangement of corner-sharing BO$_6$ and BO$_6$ octahedra and form interpenetrating B and B’ face-centered cubic sublattices. Thus, the magnetic properties are generally determined by exchange interactions between the intra- and inter-sublattices, which are correlated with structural distortions.$^{22,29}$

As an obvious strategy, substitution of smaller cations into the A-site would be expected to introduce significant structural distortions and affect the magnetic properties by magnetostructural coupling. Thus, magnetodielectric effects were reported in Sc$_2$NiMnO$_6$.$^{30}$ In Ln$_2$NiIrO$_6$ (Ln = La, Pr, Nd, and Sm−Gd), the structural distortions enhance the FiM ordering temperature, with the highest $T_C = 170$ K for Gd$_2$NiIrO$_6$.$^{31−33}$

In this work, we aimed to introduce small cations, Lu and Sc, into the A-site of A$_2$NiIrO$_6$ by high-pressure and high-temperature synthesis. Lu$_2$NiIrO$_6$ was successfully synthesized under 6 GPa and 1300 °C, but Sc$_2$NiIrO$_6$ could not be prepared with pressure up to 8 GPa and 1300 °C. Magnetic studies reveal Lu$_2$NiIrO$_6$ with a higher FiM transition (207 K) than that of Gd$_2$NiIrO$_6$ (170 K)$^{31}$ and with a large coercivity of 48 kOe at 5 K. These results motivate the search for hard magnetic materials in 3d/5d DP oxides.

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**Synthesis and Synchrotron Powder X-ray Diffraction.** Polycrystalline samples of Lu$_2$NiIrO$_6$ were synthesized by solid-state reactions from Lu$_2$O$_3$ (99.9%, Alfa), NiO (99%, Alfa), and IrO$_2$ (99.99%, Alfa). A molar ratio 1:1:1 of Lu$_2$O$_3$, NiO, and IrO$_2$ was well ground and sealed in a Pt capsule inside a MgO crucible. The precursors were then statically compressed at a pressure of 6 GPa in a Walker-type multianvil press$^{34}$ and were heated at 1300 °C for 1 h, with the pressure maintained at 6 GPa. The sample was then quenched to ambient temperature by stopping heating before the pressure was slowly released.

Small pieces of Lu$_2$NiIrO$_6$ were ground to a fine powder, which was then characterized by synchrotron powder X-ray diffraction (SPXD, $\lambda = 0.41270$ Å) at ambient temperature at the beamline 11-BM of the Advanced Photon Source (APS) of Argonne National Laboratory. Rietveld refinements of the SPXD data were done with the JANA2006 software,$^{35}$ and the crystal structures were drawn with the VESTA software.$^{36}$

**X-ray Absorption Near-Edge Spectroscopy.** The X-ray absorption near-edge spectroscopy (XANES) experiments on Lu$_2$NiIrO$_6$ and standards were performed at the national synchrotron light source (NSLS), NSLS-I and NSLS-II at Brookhaven National Labs. The prior work, on the standards, was performed at NSLS-I on beamlines X19A (X18B) with a Si-111 double-crystal (channel cut) monochromator. The measurement on Lu$_2$NiIrO$_6$ has been carried out at the next-generation NSLS-II facility on the 6-BM, BMM beamline with a Si-311 double-crystal monochromator. The NSLS-II high flux insertion device 8-ID ISS beamline was also used in these measurements. Both transmission mode and fluorescent measurements were made on all samples, and simultaneous standards were used in all measurements for precision energy calibration. Standard linear background and post-edge normalization to unity were used in the analysis.$^{37−51}$

**Transport and Magnetism.** Using a polycrystalline pellet, the electrical resistivity ($\rho$) was measured with direct current (0.1 mA) in a four-point in-line arrangement of a Physical Property Measurement System (PPMS, Quantum Design). Au wires and silver paste were used to make electrical contacts. The temperature dependence of the magnetic susceptibility was measured in the same PPMS. The measurements were conducted under zero-field cooling (ZFC) and field cooling (FC) in the temperature range 2−400 K in an applied magnetic field of 1 kOe. Isothermal magnetization curves were initially recorded for fields up to ±60 kOe at temperatures of 5, 200, and 300 K with the same PPMS. As the magnetization curves showed a broad hysteresis and were unsaturated at 5 K, further magnetization curves at 5 K were measured with fields up to ±140 kOe using another PPMS (PPMS-14T, Quantum Design).

**RESULTS AND DISCUSSION**

Crystal Structure. The room-temperature SPXD data of Lu$_2$NiIrO$_6$ were successfully refined in a monoclinic DP structure with space group $P2_1/n$ (no. 14); this crystal structure was also adopted by other Ln$_2$NiIrO$_6$ phases.$^{01−33}$ The Rietveld refinements of the SPXD data of Lu$_2$NiIrO$_6$ are shown in Figure 1. In this space group, the Lu and the three O atoms (O1, O2, and O3) fully occupy the Wyckoff positions 4e ($x,y,z$). The Ni and Ir atoms occupy Wyckoff positions 2b (1/2,0,0) and 2c (1/2,0,1/2), respectively; however, the refinements revealed a ~11% Ni/Ir antisite disorder. Detailed atomic positions and atomic displacement factors of Lu$_2$NiIrO$_6$ obtained from the SPXD refinements are summarized in Table 1.

The crystal structure of Lu$_2$NiIrO$_6$ based on the SPXD refinement is shown in Figure 2. The corner-sharing Ni- and Ir-dominant octahedra form a rock-salt-like lattice. The inter-octahedral Ni−O−Ir bond angles are 135.4(2)°, 142.5(3)°, and 140.8(3)°, which deviate strongly from 180° and indicate strong octahedral tilting. The bond distances for the local coordination of Ni and Ir ions are summarized in Table 2. These values are comparable to those in other Ni$^{2+}$ and Ir$^{4+}$ DPs.$^{31−33}$ Bond valence sum (BVS), calculated from the bond distances, is 2.33 and 3.77 for the Ni- and Ir-dominant octahedral sites, respectively. The parameters $B = 0.37$, $R_0$(Ni$^{2+}$) = 1.675, and $R_0$(Ir$^{4+}$) = 1.87 were used for the calculation.$^{53}$ The somewhat larger BVS for Ni$^{2+}$-dominant sites and smaller BVS for Ir$^{4+}$-dominant sites may reflect the effect of antisite disorder between Ni and Ir sites.

X-ray Absorption Near-Edge Spectroscopy. To further examine the valence states of Ni and Ir in Lu$_2$NiIrO$_6$, the Ni-K edges and Ir-L$_3$ edges of XANES were measured. XANES is...
used for locally probing the valence states of ions in solids. The near-edge characteristics at the K edges of 3d transition-metal, TM(3d), compounds are due to transitions from the 1s to 4p states of the TM, combined with a step feature for the continuum onset.37

Multiple 4p states associated with different local ligand coordinations, polyhedra edge/corner sharing, mixed 3d configurations (3d−4p), and different orbital orientations complicate near-edge structure.38−40,42 Nevertheless, the systematic TM(3d)-K main-edge energy shift to higher energy with increasing oxidation state can serve as a signature of charge transfer in such compounds.37−51

The Ni-K main edge of Lu₂NiIrO₆ is compared to various standard oxide compound spectra (with octahedral TM−O coordination) in Figure 3. Here, the multiple edge-sharing octahedra in NiO standard and the single perovskite layer in the La₂NiO₄ standard lead to additional splittings in the main-edge p-feature peak.41,42 The steep rising edge onset of the ∼Ni²⁺ standard spectra coincides well with the ∼Ni²⁺, LaNiO₃. Note the pre-edge region, discussed in the Supporting Information, is identified.

Supporting Information, the Ni-K pre-edge feature results (see Figure S1) also support the ∼Ni²⁺ configuration in this material. The L₃ edges of 5d TMs are dominated by very intense “white line” (WL) features because of dipole transitions into final d states (see Figures 4 and S2).39,43−51 One signature of increasing TM-valence states (decreasing d-count) is the chemical shift of the centrum of the WL-feature to higher energy with increasing oxidation state can serve as a signature of charge transfer in such compounds.37−51

Figure 3. Ni-K edge of Lu₂NiIrO₆ compared to those of standard compounds: Ni⁰, elemental Ni; ∼Ni²⁺, NiO, La₂NiVO₆, La₂NiO₄; and ∼Ni³⁺, LaNiO₃. Note the pre-edge region, discussed in the Supporting Information, is identified.

Figure 4. Systematic TM-L₃ edge WL-feature variation with 5d-electron (hole) count from d⁰ to d⁵ (10−5), note the bimodal A/B structure corresponding to transitions into t₂g/eg final states.
energy. The WL-feature and its chemical shift are illustrated by the prominent shift between Lu$_2$NiIrO$_6$ and Sr$_2$CaIrO$_6$ spectra in Figure S2. The chemical shifts of Ir compounds will be returned to later after the WL-feature structure is discussed, as discussed in the Supporting Information; the energy of the “continuum resonance” (CR) feature (see Figure S2) is indicative of the Ir–O first-shell bond length and therefore of the Ir-valence. The CR-feature results in the Supporting Information section suggest an Ir$^{4+}$ configuration.

Perhaps, the strongest signature of increasing 5d-TM-valence states (decreasing d-count) lies in the dramatic, systematic evolution of the prominent bimodal A/B structure of the WL-feature for octahedrally coordinated TM–O compounds, as illustrated in Figure 4. This bimodal A (t$_{2g}$ related)/B (e$_g$ related) structure arises from the octahedral O–ligand coordination ligand field (LF), splitting of the d-states, into lower energy, 6X degenerate, t$_{2g}$ and higher energy, 4X degenerate, e$_g$ multiplets. This LF splitting is most clearly illustrated in the d$^3$ compound spectra shown in Figure 4. The systematic filling of the t$_{2g}$ orbitals with increasing 5d-orbital count (decreasing final state hole-count) clearly leads to a systematic decrease of the A-feature (t$_{2g}$-hole coupled) intensity as is illustrated in Figure 4 for a series of compounds spanning d$^0$–d$^3$. Here, the spectra of the various compounds have been displaced to nominally align the A/B features.

Figure 5 shows a detailed comparison of the Ir-L$_3$ WL features of Lu$_2$NiIrO$_6$ along with the standard spectra for ~Ir$^{4+}$-d$^3$, Sr$_2$CaIrO$_6$, ~Ir$^{4+}$-d$^3$, Sr$_2$SrIrO$_6$, and Sr$_2$YIrO$_3$ and ~Ir$^{5+}$-d$^2$, IrO$_2$, and La$_2$CuIrO$_6$. Inset: An expanded superimposed comparison of the Lu$_2$NiIrO$_6$ and ~Ir$^{4+}$-d$^3$ standard spectra illustrating the decreased A-feature intensity in the former. Note that the Lu$_2$NiIrO$_6$ spectrum is narrower because of higher energy resolution and that the superimposed spectra involve an energy shift and amplitude rescaling.

The second point to note is the systematic decrease of the A-feature intensity (relative to the B-feature) in the same ~Ir$^{4+}$-d$^3$ to ~Ir$^{5+}$-d$^3$ to ~Ir$^{4+}$-d$^2$ sequence of spectra. The Lu$_2$NiIrO$_6$ spectrum clearly falls in an energy range consistent with an ~Ir$^{4+}$-d$^3$ configuration.

The experimental obtained $\mu_{\text{eff}}$ of 3.47 $\mu_B$/f.u. is consistent with the calculated spin-only $\mu_{\text{eff}} = 3.32 \mu_B$/f.u. and comparable to $\mu_{\text{eff}}$ of 3.28 $\mu_B$ reported for the isoelectronic La$_2$NiIrO$_6$. However, the real nature of the magnetic state of Ir$^{4+}$ remains unknown.
At 300 K, the linear behavior of the temperatures above and below the ordering temperature indicates a paramagnetic state. The saturated magnetization is about 0.52 μB/f.u. that the hysteresis loop is not closed. The magnetization is not understood with this scenario.18

To further understand the magnetic transition, isothermal magnetization curves, M(H), of Lu2NiIrO6 were measured at temperatures above and below the ordering temperature (Figure 8). At 300 K, the linear behavior of the M(H) data indicates a paramagnetic state. The M(H) plot recorded at 200 K is supportive of an FM or FiM state. The M(H) data at 5 K between −140 and +140 kOe, as shown in Figure 8b, show that the hysteresis loop is not closed. The magnetization is not saturated and is about 0.52 μB/f.u. The observed magnetization (0.52 μB/f.u.) is much lower than the theoretically calculated spin-only moment of 3.0 μB/f.u., assuming that Ni2+ has t2g S = 1 and Ir4+ has t2g S = 1/2 electronic configuration and that they are ferromagnetically coupled. Nevertheless, it is close to the difference of Ni2+ and Ir4+ spin-only moment (1.0 μB/f.u.). The data, therefore, indicate a FiM order. The specific heat in Figure 9 shows a lambda-type feature at 207 K, which confirms the long-range magnetic order in Lu2NiIrO6. In Figure 8, the M(H) data of Lu2NiIrO6 at 5 K display a remarkably high coercive field Hc = 48 kOe, which is much larger than the Hc ≈ 14 kOe observed in Eu3NiIrO6.31

The disagreement between the experimental (0.52 μB/f.u.) and theoretical FiM spin-only moment (1.0 μB/f.u.) magnetization is attributed to the unsaturated M(H) curve and antisite disorder of Ni/Ir atoms of Lu2NiIrO6. The antisite disorder is known to decrease the magnetic moment by M = Mexp × (1 − 2AS). Mexp is the theoretical spin-only moment, and AS is the degree of antisite disorder.55−58 In Lu2NiIrO6 Mexp is 1 μB/f.u. and AS is 0.11 (11% disorder). When the effect of antisite disorder was considered, the theoretical spin-only moment for Lu2NiIrO6 was 0.78 μB/f.u. which is approaching the observed moment of 0.52 μB/f.u. It should be noted that the spin-only scenario is unlikely to be valid because of the strong SOC of Ir ions.18 Theoretical studies of ferrimagnetic La2CoIrO6 and La2NiIrO6 indicate that the orbital contribution (mO = 0.43 μB/Ir for La2CoIrO6 and 0.32 μB/Ir for La2NiIrO6) of Ir4+ is comparable with the spin contribution (mS = 0.44 μB/Ir for La2CoIrO6 and 0.32 μB/Ir for La2NiIrO6).59−60 However, an X-ray magnetic circular dichroism (XMCD) study of La2CoIrO6 derived an mS = 0.205 μB/Ir and an mO = 0.177 μB/Ir.61 A future XMCD study on Lu2NiIrO6 could further clarify this issue.

Lu2NiIrO6 compared with Ln2NiIrO6 (Ln = La, Pr, Nd, and Sm−Gd)31−37 shows the smallest Ni−O−Ir bond angle (see Figure 10), or the largest structural distortions, and the highest ordering temperature. The structure−property relationship for Ni−Ir-based DPs is clearly revealed in Figure 10: the greater the structural distortions, the higher the magnetic ordering temperature. A similar correlation was also observed in the 3d/5d DPs Ca3−SrFeOsO6.22,27 The ferrimagnetic nature of Lu2NiIrO6 indicates that Ni2+ and Ir4+ ions are AFM coupled, indicating that the AFM Ni2+−O−Ir4+ interactions are dominant. Because the t2g orbitals of Ni2+ are completely filled, the AFM exchange coupling between Ni2+ and Ir4+ can only be mediated via virtual hopping between half-filled Ni-e_g and partially filled Ir-t2g orbitals. However, in the cubic DP structure, where the Ni2+−O−Ir4+ pathway is linear, the Ni-e_g...
and Ir-$t_{2g}$ orbitals are orthogonal. Nevertheless, hopping between Ni-$e_g$ and Ir-$t_{2g}$ orbitals becomes possible in the distorted DP where the Ni$^{3+}$-O-Ir$^{4+}$ bond angles strongly deviate from 180°.\(^6\) With increasing structural distortion (relative to other larger Ln A-cations), the AFM exchange coupling between half-filled Ni-$e_g$ and partially-filled Ir-$t_{2g}$ orbitals is expected to enhance in Lu$_2$NiIrO$_6$; thus, the magnetic ordering temperatures increase (Figure 10).

## CONCLUSIONS

Targeting the preparation of A$_2$NiIrO$_6$ DPs with small A-site ions, Lu$_2$NiIrO$_6$ was synthesized at high pressure and temperature. Structural studies with SPXD show that Lu$_2$NiIrO$_6$ adopts a monoclinic DP structure (space group $P2_1/n$) with near Ni/Ir rocksalt-like order. The magnetic data indicate a ferrimagnetic transition below 207 K, which is the highest ordering temperature in Ir-based DP oxides so far. A remarkable feature of the polycrystalline sample of Lu$_2$NiIrO$_6$ is a high coercive field of 48 kOe. These 3d/5d DPs are of interest for hard magnets. High coercivities of 41, 90, and 120 kOe were reported for TM oxides of ferrimagnetic La$_2$Ni$_{1.19}$Os$_{0.81}$O$_6$, LuFe$_2$O$_4$, and weakly FM Sr$_5$Ru$_5$O$_{15}$, respectively.\(^6\) However, the origin of the observed huge coercivity is not fully understood. Large magnetocrystalline anisotropy, as well as frustration and/or defects (disorder), was found to favor large coercivities.\(^6\) Because Lu$_2$NiIrO$_6$ has a low-symmetry crystal structure and heavy Ir atoms, a large magnetocrystalline anisotropy is expected.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02557.

### Notes

Discussions about Ni-K pre-edge and CR features of Ir-L3 edge

### Accession Codes

CCDC 1866087 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Figure 10.** Magnetic ordering temperatures and Ni−O−Ir bond angles of the Ln$_2$NiIrO$_6$ (Ln = La, Pr, Nd, Sm, Eu, Gd, and Lu).


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