The Effect of Iridium Oxidation State on the Electronic Properties of Perovskite-type Solid Solutions: $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$

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Abstract

Two novel solid solution series, $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0 - 1.0$) and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0 - 1.0$), were prepared and several changes in structure, moment and charge transport were observed. The $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ series exhibits a transition from a 6M polytype to an orthorhombic perovskite structure with increased La content whereas the $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ series transitioned from a disordered, orthorhombic perovskite to an ordered, cubic perovskite with increased Ca content. Seebeck measurements for both systems showed that Ir(IV)-rich compounds tended to have a n-type conduction mechanism while Ir(V)-rich compounds tended to be p-type. Both systems were found to be semiconducting and the magnitude of the resistivity is dependent on crystal structure and Ir environment. Magnetic measurements show that the μ_{eff} values for both systems are significantly less than predicted for Ir(IV) ($1.73 \mu_B$) and greater than predicted for Ir(V) ($0 \mu_B$). These results are compared to other iridate compound families.

Keywords: Iridium oxides; Spin-orbit coupling; Van Vleck paramagnetism; Perovskites

1. Introduction

Iridium oxides are of interest due to their novel magnetic properties [1–3] and potential as topological insulators [4–6]. A large amount of work has been done on families of compounds with

specific perovskite stoichiometries (e.g. $A_2M\text{IrO}_6$ [7,8] and $A_3M\text{Ir}_2\text{O}_9$ [9–11]) and numerous $A_2\text{Ir}_2\text{O}_7$ pyrochlores [12–15]. Less work has been done aimed at diluting the Ir content or tuning the Ir oxidation state. Such studies are important for determining the structure-property relationships of iridate systems.

The magnetism of iridates especially those containing Ir(IV) or Ir(V) has been the subject of recent debate and interest. One of the most revealing physical properties is the value of the effective moment (μ_{eff}). Interestingly, iridate compounds exhibit large variability in the reported moments. When including the splitting of the t_{2g} orbitals due to spin-orbit coupling (SOC), Ir(IV) should have an μ_{eff} value close to $1.73 \mu_B$ in an octahedral environment while Ir(V) should have no moment at all but should exhibit Van Vleck temperature independent paramagnetism [16]. This is not always the case, however. For example, reported μ_{eff} values for compounds containing Ir(IV) as the only magnetic ion range from close to the spin-only value for a low spin d^5 metal ($1.73 \mu_B$) [7,17–19] to much lower values ($0.1\text{--}0.5 \mu_B$) [10,20–24]. While SOC is an important factor for defining magnetism in iridates, the on-site Coulombic interaction (U) as well as the bandwidth (W) also play a role. This latter interaction will affect the degree of localization for a particular system [25]. In particular, we note that when W , U , and SOC conspire to yield itinerant charges, the value of μ_{eff} will be less than the local moment value of $1.73 \mu_B$. Since W and U can depend on the difference in orbital overlap (which is controlled by the spatial configuration of Ir ions in the lattice), one cannot assume that the local moment in one crystal structure can be compared with that in another. Therefore, the origin for variation of moment, and hence degree of localization, needs to be examined for each structure type.

Tuning the oxidation state of transition metals has long been known to bring about unusual and unexpected properties in oxides. Iridium in oxides is somewhat flexible with respect to oxidation state. The most common state is Ir(IV) though it is not difficult to stabilize Ir(V) and even Ir(VI) under the right

conditions [26–31]. Ir(III) is most common in transition metal complexes but a few examples of extended oxide structures include $\text{BaIrO}_{3-\delta}$, $\text{K}_{1-x}\text{Ir}_4\text{O}_8$ and $\text{Sr}_{2-x}\text{La}_x\text{IrO}_4$ [32–34]. To explore the influence of structure and Ir oxidation state on the magnetic and electrical properties, the other cations in the structure must have a closed shell configuration. In this work, we systemically tune the Ir oxidation state between 4+ and 5+ in perovskite-related structures via A-site and B-site substitutions while monitoring the variation of structure, moment and charge transport.

2. Experimental

Black polycrystalline samples were prepared by mixing and grinding stoichiometric amounts of BaCO_3 (Cerac, 99.9%), La_2O_3 (Stanford Materials, 99.999%), IrO_2 , CaCO_3 (Mallinckrodt, 99.8%) and In_2O_3 (Stanford Materials, 99.99%) in an agate mortar. The carbonates and La_2O_3 were dried overnight at 120 °C and 850 °C, respectively. IrO_2 was obtained by decomposing IrCl_3 (Alfa Aesar, 99.9%) at 750 °C under air flow for 12 hours. X-ray diffraction characterization was done on a Rigaku Miniflex II diffractometer using Cu K α radiation and a graphite monochromator. Room-temperature time-of-flight (TOF) neutron diffraction data for BaLaInIrO_6 were collected at Oak Ridge National Laboratory using 6 mm vanadium sample cans and center wavelength of 1.33 Å. Low temperature (5-300 K) magnetization measurements were obtained using a Quantum Design MPMS. Seebeck and resistivity measurements were performed at high temperature (300-800 K) on an ULVAC-RIKO ZEM 3 under a static helium atmosphere. Band gaps for all members were calculated using the Arrhenius equation: $\rho = \rho_0 \exp(E_g/2k_B T)$.

3. Results and Discussion

3.1 Substitutions and Structure

3.1.1 La(III) substitution in $\text{Ba}_2\text{InIrO}_6$

$\text{Ba}_2\text{InIrO}_6$ crystallizes in a monoclinically distorted 6H polytype structure [26] similar to $\text{Ba}_3\text{BiIr}_2\text{O}_9$ and $\text{Ba}_3\text{NdIr}_2\text{O}_9$ [35,36]. La(III), despite the significantly smaller ionic radius, has been reported to substitute well for Ba(II) in a handful of BaLaMIrO_6 ($\text{M} = \text{Fe(III)}, \text{Co(II)}, \text{Mg(II)}, \text{Ni(II)}$) perovskites [7]. For the $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ series, substituting La for Ba in the A-site will force Ir to reduce from 5+ to 4+ to compensate for the charge difference. Single phase samples were prepared for $x = 0 - 1.0$.

Figure 1. (a) Powder X-ray diffraction patterns and (b) lattice parameters for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0 - 1$). The a and c parameters of the monoclinic phase (filled points) were divided by $\sqrt{3}$ for a more direct comparison to the orthorhombic parameters (open points). (2-column)

XRD diffraction data (Figure 1a) shows a structural transition from the monoclinic $\text{Ba}_2\text{InIrO}_6$ $C2/c$ structure (Figure 2a) to a disordered orthorhombic $Pbnm$ perovskite structure (Figure 2b) with increasing La content. The transition starts gradually with the characteristic peaks of the 6H polytype slowly decreasing in intensity while a small peak corresponding to the (110) and (002) reflections of orthorhombic perovskite begins to appear at $\sim 21.5^\circ$. After $x = 0.5$, however, the monoclinic phase all but disappears very quickly leaving only the orthorhombic perovskite phase. Additionally, successful substitution of the La(III) for the Ba(II) is supported by the change in the lattice parameters (Figure 1b) which show an overall decrease in the unit cell volume in both crystal structures despite the increase in the a parameter of the monoclinic phase.

Figure 2. Crystal structures of (a) monoclinic 6H polytype $\text{Ba}_2\text{InIrO}_6$ (Ba = green, In = purple, Ir = light brown, O = red) and (b) orthorhombic perovskite BaLaInIrO_6 (Ba/La = green, In/Ir = purple, O = red). (2-column)

Refinements of the TOF neutron diffraction data for BaLaInIrO_6 were performed for both $P2_1/n$ and $Pbnm$ to model order and disorder, respectively, on the B-site. The $P2_1/n$ model refined to show very little B-site ordering (< 5%) and yielded a goodness-of-fit similar to that of the $Pbnm$ model so the latter was chosen due to its higher symmetry.

Figure 3. Time-of-flight neutron diffraction pattern for BaLaInIrO_6 with calculated intensities (red) and difference curve (blue). The magenta tick marks are the allowed reflections for $Pbnm$. (1.5-column)

Table 1. Unit-Cell, Coordinate and Displacement Parameters for BaLaInIrO₆ (*Pbnm* Space Group)^a

	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> _{iso} (Å ²)
Ba/La	-0.0155(17)	0.5187(11)	0.25	0.5/0.5	0.0026(6)
In/Ir	0	0	0	0.5/0.5	0.0010(4)
O1	-0.0505(17)	-0.003(21)	0.25	1.0	0.0112(12)
O2	0.2321(17)	0.2768(14)	0.0358(8)	1.0	0.0210(11)

^aThe unit-cell parameters are *a* = 5.789(1) Å, *b* = 5.796(1) Å, *c* = 8.174(1) Å, and *V* = 274.28(2) Å³; the reliability parameters are χ^2 = 1.68, *R*_{wp} = 3.88%.

Neither model showed ordering of the A-site. The refinement for *Pbnm* is shown in Figure 3 and the extracted crystallographic data is summarized in Table 1. *Imma* was also considered as a possible space group and fit the neutron data as well as *Pbnm*; however, it was ruled out due to the presence of a peak in the XRD pattern at ~24° which indexes to the (111) reflection under *Pbnm* but is not allowed under *Imma* (Figure 4). The orthorhombic distortion from the ideal perovskite is two-fold: a slight displacement of the Ba/La site along the [110] direction as well as tilting of the octahedral sites. The *Pbnm* space group has a *a⁻a⁻c⁺* Glazer tilt scheme [37] with tilting angles ϑ and φ were calculated using anion coordinates [38] to be 8.158° and 5.208°, respectively; these tilt angles are somewhat lower than expected when compared to values observed for other orthorhombic perovskites [39,40].

Figure 4. Comparison of XRD patterns for BaLaInIrO₆: experimental (top, black), calculated *Pbnm* (middle, red) and *Imma* (bottom, blue). Note that the (111) peak (~24°) is present in both the experimental and *Pbnm* patterns but is absent in the *Imma* pattern. (1-column)

3.1.2 Ca(II) substitution in BaLaInIrO₆

Although BaLaInIrO₆ had not been previously known, the double perovskite Ba₂CaIrO₆ has been reported [28] which suggested BaLaCaIrO₆ would be a viable target in a BaLaIn_{1-y}Ca_yIrO₆ series allowing for tuning of the Ir oxidation state from 4+ to 5+. Single phase samples were successfully prepared for $y = 0 - 1.0$. XRD diffraction data (Figure 5a) shows that as Ca content is increased, the structure transitions from the disordered orthorhombic perovskite ($y = 0 - 0.75$) to an ordered cubic perovskite ($y = 1.0$) with the space group $Fm\bar{3}m$ (Figure 6). The orthorhombic lattice parameters (Figure 5b) gradually come together with increasing Ca content and there is an overall increase in the size of the unit cell, which is expected due to the larger ionic radius of Ca compared to In.

Figure 5. (a) Powder X-ray diffraction patterns and (b) lattice parameters for $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0 - 1.0$). The orthorhombic b and c parameters were multiplied by $\sqrt{2}$ for a more direct comparison to the cubic phase. (2-column)

Figure 6. Crystal structure for ordered cubic perovskite BaLaCaIrO_6 . (Ba/La = green, Ca = blue, Ir = light brown, O = red). (1-column)

The transition is gradual and although the intermediate members can be indexed to the $Pbnm$ space group, the degree of B-site ordering likely increases with Ca content suggesting these members have a partially ordered yet distorted structure with a likely space group of $P2_1/n$. The ordering in BaLaCaIrO_6 is due to the large size and charge separation between Ca(II) and Ir(V) . Ordering aside, it is unexpected to see the transition to higher symmetry (orthorhombic to cubic) given that the tolerance factor decreases from 0.966 for BaLaInIrO_6 to 0.934 for BaLaCaIrO_6 . It is not unknown, however, for low tolerance perovskites to form cubic structures, as there is literature on rhenium double perovskites with similar tolerance factors [41].

It is also interesting to observe that the presence of In(III) in the B-site seems to induce disorder especially considering the size difference between Ir(IV) and In(III). One might suggest that the charge separation is too small. However, no ordering is observed in the $\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}$ family [26] where the charge difference is 2 or greater. Additionally, ordering is known to occur based solely on difference in ionic radii of the B cations in several $\text{A}_2\text{B}^{4+}\text{B}'^{4+}\text{O}_6$ ($\text{A}^{2+} = \text{Ba, Sr}$; $\text{B}^{4+} = \text{Ce, Tb, Pr}$; $\text{B}'^{4+} = \text{Ir, Pt}$) double perovskites [42–44]. The B-site ionic radii differences based on Shannon radii [45] in these compounds range from 0.245 Å to 0.14 Å which bookend the value 0.175 Å for Ir(IV) and In(III) very well. Both In and Ir are also known to order with other similarly sized ions such as in $\text{Ba}_2\text{InOsO}_6$ and $\text{Ba}_2\text{ScIrO}_6$ [46,47]. Based on these examples, it is reasonable to expect In and Ir to order in a perovskite structure; the fact that they do not suggests there may be a unique characteristic about the In/Ir pair.

3.2 Electronic Transport

High temperature electrical resistivity and Seebeck data for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0 - 1.0$) and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0 - 0.75$) are shown in Figure 7 with calculated band gaps for both systems in Table 2. Semiconductor behavior is observed for all members of both systems based on the trends seen in the $\rho(T)$ data. For $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$, there is no obvious trend or large changes in the resistivity behavior as the La content is varied. However, analysis of the band gaps shows a slight increase in their value from $x = 0$ to 0.2, followed by a sudden drop at $x = 0.5$ and a subsequent increase as La content is increased beyond 0.5.

Figure 7. High temperature resistivity (ρ) and Seebeck coefficient plots for (a,b) $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0 - 1.0$) and (c,d) $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0 - 0.75$). (2-column)

Table 2. Estimated band gaps for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$

$\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$		$\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$	
x	E_g (eV)	y	E_g (eV)
0	0.450(11)	0	0.356(3)
0.2	0.496(7)	0.25	0.456(4)
0.5	0.335(3)	0.5	0.517(5)
0.8	0.336(3)	0.75	0.563(6)
1.0	0.356(3)		

The general increasing trend on either side of $x = 0.5$ could be attributed to the increase in orbital overlap as the crystal structure contracts. The sudden drop is likely due to the structure

transition from the 6H structure, where the Ir environment is more localized, to the disordered perovskite structure where there is increased long range connectivity between IrO_6 octahedra.

The data for $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$, show a much clearer trend where the resistivity and band gaps increase with increasing Ca content. However, this increase is unexpected when considering the unit cell expansion observed as Ca is substituted into the structure and the expected decrease in metal-oxygen orbital overlap. Since the B-site ordering increases with increasing y , however, the trend is likely due to the loss of connectivity between the IrO_6 octahedra caused by their growing isolation from one another.

The Seebeck behavior (Figure 7) for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ is similar to that seen in the $\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}$, in which a negative to positive sign change occurs, suggesting that both hole and electron charge carriers are present and whose dominance is temperature dependent. As the La content increases and the Ir is reduced from 5+ to 4+, this transition is suppressed and the system eventually becomes p-type throughout the temperature range. Unlike the resistivity data, there is no dramatic change around $x = 0.5$, suggesting the crystal structure has limited influence on the behavior. The data for $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ shows p-type character initially, but transitions to n-type when $y > 0.25$, indicating that the electrons take over as the dominant charge carrier. Increasing the Ca content further caused the Seebeck behavior to grow more negative and more temperature dependent.

3.3 Magnetism

The magnetization as a function of temperature, $M(T)$, was measured for all samples of both systems in a field, H , of 0.1 Tesla. No non-linearity in $M(H)$ was observed, allowing the susceptibility, $\chi(T)$, to be simply expressed as M/H . After subtraction of the core diamagnetic component, a positive constant representing the Van Vleck susceptibility was subtracted from $\chi(T)$ to obtain a linear $1/\chi(T)$, from which an effective moment, μ_{eff} , was obtained using a least-squares fit in the region 100-300 K. These data are plotted in Figure 9 as $\mu(T)_{\text{eff}} = \chi(T)T \cdot 3k_B/N_A\mu_B^2$, and the near constant values above

100 K demonstrate the validity of the effective moment approximation. The data below 60K for $x = 0.8$ and 1.0 are consistent with the onset of ferromagnetic correlations, while below 20K, antiferromagnetic correlations dominate. The ferromagnetic correlations are suppressed by oxidizing Ir(IV) to Ir(V) while the antiferromagnetic correlations are persistent even at the lowest La concentrations. Thus, the low-temperature behavior is suggestive of antiferromagnetic nearest neighbor interactions, and ferromagnetic next nearest neighbor interactions, the latter of which only appear with high concentrations of Ir(IV). In $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$, these cooperative correlations are suppressed much faster with Ir oxidation possibly due to the increasing isolation of the IrO_6 octahedra.

Figure 9. $\mu(T)_{\text{eff}}$ plots for (a) $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ and (b) $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$. The temperature independence of the data above 100 K suggests Curie-Weiss behavior. (1-column)

In Figure 9a are shown $\mu(T)_{\text{eff}}$ data for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$, with $0 \leq x \leq 1.0$ and we see that μ_{eff} ranges from $0.38 \mu_B$ for $x = 0$ (nominal Ir(V) valence) to $0.81 \mu_B$ for $x = 1.0$ (nominal Ir(IV) valence). In Figure 9b are shown $\mu(T)_{\text{eff}}$ data for $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ for $0 \leq y \leq 1.0$ and we see similar values of $\mu(T)_{\text{eff}}$ for $T > 100$ K. In Figure 10 is shown the fit value of μ_{eff} vs. the nominal Ir valence state for both compound series. We see that, even for nominal valence near 4.0, both compound series exhibit μ_{eff} values significantly less than the value $1.73 \mu_B$ expected for an $s = 1/2$ free spin. With increasing valence, the moment decreases even further.

Figure 10. A plot of μ_{eff} as a function of Ir valence for $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ (triangles) and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ (squares). The dashed line is the trend the expected μ_{eff} values should follow when considering SOC effects. (1-column)

As mentioned earlier, values of μ_{eff} much less than the nominal values are not uncommon in iridates and have been observed in SrIrO_3 ($0.117 \mu_B$) [48], 5M BaIrO_3 ($0.215 \mu_B$) [49], 6M BaIrO_3 ($0.276 \mu_B$) [24], 9M BaIrO_3 ($0.13 \mu_B$) [2], Sr_2IrO_4 ($0.33 - 0.50 \mu_B$) [22,50], Ba_2IrO_4 ($0.18 \mu_B$) [51], $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ ($0.26 \mu_B$) [10], $\text{Ba}_3\text{TiIr}_2\text{O}_9$ ($0.28 \mu_B$) [10], $\text{Ba}_3\text{CeIr}_2\text{O}_9$ ($0.31 \mu_B$) [52], $\text{Y}_2\text{Ir}_2\text{O}_7$ ($0.54 \mu_B$) [53], $\text{Sr}_3\text{Ir}_2\text{O}_7$ ($0.69 \mu_B$)

[23], and $\text{Sr}_2\text{TiIrO}_6$ ($0.699 \mu_B$) [20]. Among these compounds, resistivity has been measured for SrIrO_3 , all above mentioned polymorphs of BaIrO_3 , Sr_2IrO_4 , Ba_2IrO_4 , $\text{Y}_2\text{Ir}_2\text{O}_7$ and $\text{Sr}_3\text{Ir}_2\text{O}_7$ and each shows either metallic (SrIrO_3 , 5M and 6M BaIrO_3), small gap semiconducting (9M BaIrO_3 , Sr_2IrO_4 , Ba_2IrO_4) or variable range hopping behavior ($\text{Y}_2\text{Ir}_2\text{O}_7$). Indeed, for the systems studied here, we observe small gap semiconducting behavior for temperatures above 300 K, where the moments are well-developed. It is also worth noting that the Seebeck effect data in the same temperature region, do not resemble that expected for medium size gap semiconductor (0.5 – 1.0 eV). These results indicate that in the present systems, like several of the small- μ_{eff} compounds listed above, delocalization of the Ir valence electrons is responsible for moment reduction. Since the effective moment is a parameterization of the ground state multiplet, which for Ir(IV) is a Kramer's doublet, octahedral distortions will not play a role in the affecting the moment's value.

It should also be noted that sizeable effective moments of 0.38 and $0.59 \mu_B$ are observed for BaInIrO_6 and BaLaCaIrO_6 , respectively, both of which should have a formal valence corresponding to Ir(V). Other examples of non-zero μ_{eff} values for Ir(V) have been reported in literature [1,20,54–56] and were attributed to the weakening of SOC interactions through structural distortion or the presence of Ir(IV) due to oxygen vacancies which are common in perovskites. It is also a possibility that BaInIrO_6 and BaLaCaIrO_6 possess a small amount of Ir(VI) due to the presence of electropositive ions (i.e. Ba^{2+} and Ca^{2+}) which are known to stabilize higher Ir oxidation states [20,26,57].

4. Conclusions

The $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ ($x = 0 - 1.0$) solid solution was observed to transition from the 6M polytype structure to a disordered, distorted perovskite structure with the $Pbnm$ space group. Based on our neutron diffraction refinements, BaLaInIrO_6 showed little tendency toward B-site ordering and the octahedra tilted along all three axes with a $a^-a^-c^+$ Glazer tilt scheme. $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ ($y = 0 - 1$) retained

a perovskite structure throughout the entire series, transitioning gradually from a disordered, orthorhombically distorted form to an ordered, cubic form. Both systems were found to be semiconducting with transitions in the dominant charge carrier. The resistivity of the $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ series was observed to increase with increasing La content and was also affected heavily by the structure transition, characterized by a large drop in the band gap at $x = 0.5$. There was no similar abrupt change observed in the Seebeck behavior, however, which has a temperature dependent n-type to p-type transition that was gradually suppressed with increased Ir(IV) concentration. For the $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ series, increasing the Ca content, and therefore the Ir(V) concentration, was found to both increase the resistivity as well as cause the electrons to become the dominant charge carriers. The increasing resistivity is likely caused by the greater separation of the Ir ions due to ordering on the B-site. The magnetic susceptibility data show that both $\text{Ba}_{2-x}\text{La}_x\text{InIrO}_6$ and $\text{BaLaIn}_{1-y}\text{Ca}_y\text{IrO}_6$ display Curie-Weiss behavior above 100 K. The trends in their μ_{eff} values going from Ir(IV) to Ir(V), however, did not correlate well with the predicted nominal values. In both series, the μ_{eff} values for compounds with Ir valence closer to 4 tended to be too low, whereas those with valence close to 5 tended to be too high. Other iridates similar to our compounds, where Ir(IV) is the only magnetic ion and μ_{eff} is much lower than predicted, were also found to be quite conductive suggesting the lower values are caused by electron delocalization.

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BaLaInIrO₆

BaLaCaIrO₆

The Ir moments for the novel perovskite solid solutions $\text{Ba}_{2-x}\text{La}_x\text{IrIrO}_6$ and $\text{BaLaIr}_{1-y}\text{Ca}_y\text{IrO}_6$ were found to deviate from the trend predicted by tuning Ir oxidation state from Ir(IV) to Ir(V).