New Insulating Antiferromagnetic Quaternary Iridates $\text{MLa}_{10}\text{Ir}_4\text{O}_{24}$ ($M=\text{Sr, Ba}$)

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Recently, oxides of Ir$^{4+}$ have received renewed attention in the condensed matter physics community, as it has been reported that certain iridates have a strongly spin-orbital coupled (SOC) electronic state, $J_{\text{eff}}=\frac{1}{2}$, that defines the electronic and magnetic properties. The canonical example is the Ruddlesden-Popper compound $\text{Sr}_2\text{IrO}_4$, which has been suggested as a potential route to a new class of high temperature superconductor due to the formal analogy between $J_{\text{eff}}=\frac{1}{2}$ and the $S=\frac{1}{2}$ state of the cuprate superconductors. The quest for other iridium oxides that present tests of the underlying SOC physics is underway. In this spirit, here we report the synthesis and physical properties of two new quaternary tetravalent iridates, $\text{MLa}_{10}\text{Ir}_4\text{O}_{24}$ ($M=\text{Sr, Ba}$). The crystal structure of both compounds features isolated IrO$_6$ octahedra in which the electronic configuration of Ir is $d^5$. Both compounds order antiferromagnetically despite the lack of obvious superexchange pathways, and resistivity measurement shows that SrLa$_{10}$Ir$_4$O$_{24}$ is an insulator.

Electrons in 3$d$ transition metal oxides exhibit correlated behavior because the bandwidth, $W$, is relatively narrow, while the electron-electron repulsion, parametrized by a Hubbard $U$, is significant. The result is a set of collective phenomena including high temperature superconductivity$^4$ and colossal magnetoresistance$^2,3$. On the other hand, 5$d$ transition metals are characterized by more extended orbitals, and in general, are expected to be uncorrelated metals, as for example $\text{IrO}_2$ and $\text{Bi}_2\text{Ir}_2\text{O}_7$. Recently, however, Kim et al. found that strong spin-orbital coupling in the layered compound $\text{Sr}_2\text{IrO}_4$ leads to a relatively narrow $J_{\text{eff}}=\frac{1}{2}$ band whose width is of the same scale as electron correlation, yielding a Mott insulating state$^6,7$. With a square IrO$_2$ network, a $U/W \sim 1$, and a magnon dispersion qualitatively the same as cuprates$^4$, $\text{Sr}_2\text{IrO}_4$ has been studied intensely as a potential route to a new class of high temperature superconductor$^8,9$. Some known iridates, including $\text{Ba}_2\text{IrO}_4$,$^{10}$ and $\text{Ca}_2\text{IrO}_6$,$^{12}$, have already shown behavior consistent with a $J_{\text{eff}}=\frac{1}{2}$ description by resonant inelastic X-ray scattering, indicating that the phase space of $J_{\text{eff}}=\frac{1}{2}$ materials extends beyond $\text{Sr}_2\text{IrO}_4$. These discoveries underscore the importance of identifying new iridates with $J_{\text{eff}}=\frac{1}{2}$ states to better understand the phenomenology of these unusual correlated oxides.

The scope of the present work lies firmly in the regime of discovery synthesis of new compounds in a relatively unexplored regime of crystal chemistry as a first step on the way to classifying and understanding the breadth of spin-orbit driven physics in iridates. Toward this end, we have synthesized two new isostructural tetravalent iridates, $\text{MLa}_{10}\text{Ir}_4\text{O}_{24}$ ($M=\text{Sr, Ba}$) and characterized their crystal structures and magnetic, transport, and thermodynamic signatures. Each is comprised of isolated IrO$_6$ octahedra in which the nominal electronic configuration of Ir is $d^5$. They both order antiferromagnetically, and resistivity measurement shows that SrLa$_{10}$Ir$_4$O$_{24}$ exhibits insulating behavior.

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The extensively studied iridates are mostly ternary oxides, which is likely due to the lack of approaches for crystallizing iridates that are compositionally diverse. To expand the horizon in studying iridates as $J_{\text{eff}} = 1/2$ candidates, quaternary and even higher order iridates are desired. Here it is demonstrated that high order iridates can be made with a facile flux crystal growth approach.

Results

Lattice constants and space group ($I\bar{4}1/a$) extracted from single-crystal diffraction measurements were similar to that of the known compound Sr$_9$La$_2$Mo$_4$O$_{24}$$^{13}$, and indeed the crystal structures (see Fig. 1) of the iridates could be solved from this starting model. For SrLa$_{10}$Ir$_4$O$_{24}$, no discernible site mixing between Sr and La was found in the refinement. For BaLa$_{10}$Ir$_4$O$_{24}$, the Ba and La sites were assigned based on the apparent differences in bond lengths of Ba-O and La-O. The structure features isolated IrO$_6$ octahedra with $M$ ($M$ = Sr, Ba) and La atoms located interstitially. There are two independent Ir sites, both occupying special positions, with the Ir atoms in a distorted octahedral environment. The lattice parameters of SrLa$_{10}$Ir$_4$O$_{24}$ are $a = 11.58$ Å, $c = 16.24$ Å, while those of BaLa$_{10}$Ir$_4$O$_{24}$ are $a = 11.66$ Å, $c = 16.17$ Å. Compared to SrLa$_{10}$Ir$_4$O$_{24}$, the Ba analogue has a larger $a$ lattice parameter and a smaller $c$ lattice parameter. In other words, the lattice is “squashed” rather than simply enlarged. The cell volume of BaLa$_{10}$Ir$_4$O$_{24}$ ($2196.9$ Å$^3$) is only slightly larger than that of SrLa$_{10}$Ir$_4$O$_{24}$ ($2183.4$ Å$^3$), a difference of ~0.05%. This weak volume perturbation is not surprising, because although the ionic radius of Ba$^{2+}$ (1.42 Å) is significantly larger than that of Sr$^{2+}$ (1.26 Å), the alkaline earth metal is only a small fraction of the unit cell contents. For SrLa$_{10}$Ir$_4$O$_{24}$, the bond length of Ir1-O ranges from 1.967(15) Å to 2.030(16) Å, while the bond length of Ir2-O ranges from 2.001(16) Å to 2.073(16) Å. For BaLa$_{10}$Ir$_4$O$_{24}$, the bond length of Ir1-O ranges from 1.983(12) Å to 2.046(12) Å, while the bond length of Ir2-O ranges from 2.006(12) Å to 2.086(13) Å. These bond lengths are typical of Ir(IV) in oxides$^{14,15}$.

The temperature-dependent magnetic susceptibility of SrLa$_{10}$Ir$_4$O$_{24}$ shows a cusp characteristic of antiferromagnetic order at $T_N = 12$ K (Fig. 2, top), indicating a non-negligible magnetic exchange among the isolated octahedra. Above this cusp, the magnetic behavior is well approximated as that of a Curie-Weiss paramagnet. A fit of the data to $\chi = C/(T - \theta) + \chi_0$ (where $\chi_0$ phenomenologically accounts for all diamagnetic contributions) from 20 K to 300 K (the results are largely insensitive to the choice of fitting range) gives a Weiss constant of $-8.5$ K, in good agreement with $T_N$. The effective moment ($\mu_{\text{eff}}$) of 1.11 $\mu_B$/Ir is considerably reduced from the 1.73 $\mu_B$/Ir expected for low-spin $d^8$ Ir(IV) in a rigorously $I_{\text{eff}} = 1/2$ configuration (cubic crystal field, $k_B T/\lambda \to 0$)$^{16}$. We note that such reduced effective moments are not uncommonly reported among iridates, including Sr$_3$Ir$_2$O$_7$ (0.69 $\mu_B$/Ir)$^{18}$, $9$ M BaIrO$_3$ (0.13 $\mu_B$/Ir)$^{17}$ and $6$ M BaIrO$_3$ (0.276 $\mu_B$/Ir)$^{19}$. However, other iridates, notably Na$_2$IrO$_3$,$^{20}$ with a reported $\mu_{\text{eff}} = 1.79$ $\mu_B$/Ir, follow more closely the expected behavior. Discrepancies such as these suggest an ‘effective g-factor’ significantly reduced from the free electron value, deriving potentially from non-cubic symmetry, an admixture of configurations other than $t_2g^5$, or the effect of hybridization with the O sublattice network.

Similarly, the temperature dependent magnetic measurement of BaLa$_{10}$Ir$_4$O$_{24}$ shows antiferromagnetic ordering at a somewhat lower temperature, $T_N = 6$ K (Fig. 2, bottom), and also follows Curie-Weiss

Figure 1. The crystal structure of MLa$_{10}$Ir$_4$O$_{24}$ ($M$ = Sr, Ba). The purple color denotes IrO$_6$ octahedra, and the green and blue spheres denote La and M atoms ($M$ = Sr, Ba), respectively (a) viewed from approximately (001) direction (b) viewed approximately from (010) direction.
behavior above this temperature, with $\mu_{\text{eff}} = 1.35 \mu_B$, slightly larger than that of SrLa$_{10}$Ir$_4$O$_{24}$. The Weiss constant obtained is $-5.1$ K, close to the measured $T_N$. For both SrLa$_{10}$Ir$_4$O$_{24}$ and BaLa$_{10}$Ir$_4$O$_{24}$, at temperatures below the $T_N$, the susceptibility has a small upturn, which may arise from a small amount of paramagnetic impurity spins.

Heat capacity measurements were carried out on both compounds. Above the magnetic transition, the data can be described by the expression $C = C_{\text{electron}} + C_{\text{phonon}} = \gamma T + \beta T^3$ (Fig. 3a). The values of $\gamma$ and $\beta$ extracted from the fits for SrLa$_{10}$Ir$_4$O$_{24}$ are $0.405$ Jmol$^{-1}$K$^{-2}$ and $0.00205$ Jmol$^{-1}$K$^{-4}$, and for BaLa$_{10}$Ir$_4$O$_{24}$, $\gamma$ and $\beta$ value are $0.47$ Jmol$^{-1}$K$^{-2}$ and $0.00224$ Jmol$^{-1}$K$^{-4}$. Corresponding Debye temperatures were calculated to be $333$ K for SrLa$_{10}$Ir$_4$O$_{24}$, and $324$ K for BaLa$_{10}$Ir$_4$O$_{24}$. The magnetic entropy in the low-T regime can then be calculated as $S_{\text{mag}}(T) = \int_0^T C_{\text{mag}}/T \, dT$ (Fig. 3b), where $C_{\text{mag}} = C_{\text{mol}} - C_{\text{electron}} - C_{\text{phonon}}$, yielding $S_{\text{mag}} = 6.31$ J mol$^{-1}$ K$^{-1}$ for SrLa$_{10}$Ir$_4$O$_{24}$ and $6.17$ J mol$^{-1}$ K$^{-1}$ for BaLa$_{10}$Ir$_4$O$_{24}$ (Fig. 3b). The expected entropy of the magnetic transition ($S_{\text{mag}}$) equals to $R \ln(2J+1)$, where $R$ is the gas constant, and $J$ is the total angular momentum. For $J_{\text{eff}} = \frac{1}{2}$, the expected value is $5.76$ J mol$^{-1}$ K$^{-1}$, in fair agreement with that measured here.

Resistivity measurement shows that SrLa$_{10}$Ir$_4$O$_{24}$ exhibits insulating behavior (Fig. 4), which is expected given that the crystal structure features isolated IrO$_6$ octahedra. With the caveat that the behavior is evaluated in a narrow temperature range of 260 K to 350 K, it was found that the resistivity is best modeled by simple thermally activated hopping, with $\text{Ea} \sim 0.26$ eV, while three-dimensional and two-dimensional variable range hopping and small polaron models yield poorer agreement with the measured data. Unfortunately, BaLa$_{10}$Ir$_4$O$_{24}$ crystal specimens are too small for a conductivity measurement at this time. Due to the similar crystal structure, one may expect similar electronic transport behavior to that of the Sr analogue.

**Discussion**

Flux crystal growth is an important approach to grow single crystals of new materials$^{21-26}$. For exploratory crystal growth of new iridates, KOH and K$_2$CO$_3$ fluxes have typically been used$^{27,28}$. Remarkably, for the synthesis of SrLa$_{10}$Ir$_4$O$_{24}$, Ir metal was used as the source of Ir and wasoxidized to Ir(IV) in the SrCl$_2$ flux. It is known that some fluxes like KOH can dissolve O$_2$ from the atmosphere to provide an
oxidizing environment; mostly Ir(V) compounds have been synthesized from KOH flux, but some Ir(VI)
and Ir(V) oxides are also reported 29,30. Evidently SrCl₂ also dissolves sufficient O₂ from the atmosphere
to oxidize Ir metal to Ir(IV). However, under the conditions of our synthesis, SrCl₂ apparently provides
a less oxidizing environment compared to KOH, as we found no higher oxidation state products. EDS
shows no evidence of chlorine incorporation in the crystals.

\[ \text{M}_{\text{La10I}_{\text{r4O24}}} (\text{M} = \text{Sr, Ba}) \] compounds have similar lattice parameters as the Mo(VI) oxide,
\[ \text{Sr}_{\text{9La}_{2}}\text{Mo}_{\text{4O24}} \] 13. Although the atomic coordinates of \[ \text{Sr}_{\text{9La}_{2}}\text{Mo}_{\text{4O24}} \] were not reported 13, the stoichiometry and similar lattice parameters leads one to expect that the structures of \[ \text{M}_{\text{La10I}_{\text{r4O24}}} (\text{M} = \text{Sr, Ba}) \] and \[ \text{Sr}_{\text{9La}_{2}}\text{Mo}_{\text{4O24}} \] are closely related. Apparently this structure type can adjust its \( M:La \) ratio to accommodate either the tetravalent Ir or the hexavalent Mo. When only alkaline earth metal is involved and rare earth metal is excluded, the structure type can host transition metal with mixed oxidation states, which has been shown by the synthesis of \[ \text{Ca}_{\text{11Re}_{4}}\text{O}_{\text{24}} \] 31 \[ \text{Sr}_{\text{11Re}_{4}}\text{O}_{\text{24}} \] 32 and \[ \text{Ba}_{\text{11Os}_{4}}\text{O}_{\text{24}} \] 33.

Magnetization data show that the effective moment of \[ \text{M}_{\text{La10I}_{\text{r4O24}}} (\text{M} = \text{Sr, Ba}) \] is significantly
reduced vis-à-vis that expected for a \( J = \frac{1}{2} \) Kramer’s ion. In the case of \( 6\text{M-BaIrO}_3 \) it has been suggested

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**Figure 3.** Heat capacity of \( \text{SrLa}_{\text{10I}_{\text{r4O24}}} \) and \( \text{BaLa}_{\text{10I}_{\text{r4O24}}} \). Red points are for \( \text{SrLa}_{\text{10I}_{\text{r4O24}}} \) and blue points are for \( \text{BaLa}_{\text{10I}_{\text{r4O24}}} \). Fits are shown in black (see text). (a) Total heat capacity (b) magnetic contribution to the heat capacity. Inset to (b) shows the entropy of the magnetic transition.

**Figure 4.** Resistivity vs. temperature for \( \text{SrLa}_{\text{10I}_{\text{r4O24}}} \).
that such a reduced effective moment may arise from the d electron hybridization with oxygen p states. Putting any such argument on a stronger, more quantitative footing calls for a broader materials search and theoretical input beyond the scope of this report.

As mentioned earlier, the eff state has been implicated as foundational to the understanding of iridate physics, although this description rigorously applies only in the case of an isolated and ideal octahedral crystal field. The former criterion eliminates band structure effects and super-exchange, while the latter guarantees the symmetry of the eff wavefunction (assuming that the eg states lie at sufficiently high energy that the contribution from excited configurations such as t2g eg1 are negligible. This latter assumption has been questioned recently by Katakuri et al. from quantum chemical calculations. By isolating the octahedra and thus eliminating bandwidth and super-exchange as a competing influence on the electronic structure, compounds such as MLa10Ir4O24 offer a platform for testing the intrinsic nature of the eff description.

Conclusion

In summary, we report the discovery and characterization of two new quaternary iridates, SrLa10Ir4O24 and BaLa10Ir4O24, with the crystal structure similar to Ca12Re4O24, Sr12Re4O24 and Ba12Os4O24. By isolating the octahedra and thus eliminating bandwidth and super-exchange as a competing influence on the electronic structure, compounds such as these can provide a platform for testing the detailed nature and range of applicability of the eff description using, for example, resonant inelastic x-ray scattering. More generally, the synthetic approaches reported here provide valuable insights that can stimulate the efforts in crystal growth of new iridates, particularly quaternary iridates, that will be essential to achieving a broader understanding of correlated electron physics in the presence of strong spin-orbit coupling.

During the proofing process of this manuscript, we became aware of a paper reporting the synthesis and magnetic properties of SrLa11-xIr4O24 (B.F. Phelan et al. Phys. Rev. B 91, 155117 (2015)). The crystallographic data presented by Phelan et al. for single crystal Sr4.25La6.75Ir4O24 are qualitatively consistent with those of SrLa10Ir4O24. More generally, the synthetic approaches reported here are expected to facilitate the preparation of similar compounds with potentially significant magnetic properties.

Table 1. Crystal data and structure refinement for MLa10Ir4O24 (M = Sr, Ba) at 293(2) K.

| Property | SrLa10Ir4O24 | BaLa10Ir4O24 |
|----------|--------------|--------------|
| Formula weight | 2629.52 | 2679.24 |
| Temperature | 293(2) K | 293(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Tetragonal | Tetragonal |
| Space group | I4/a | I4/a |
| Unit cell dimensions | a = 11.5899(16) Å, \(\alpha = 90.00^\circ\), \(b = 11.5899(16) Å, \beta = 90.00^\circ\), \(c = 16.255(3) Å, \gamma = 90.00^\circ\) | a = 11.6569(6) Å, \(\alpha = 90.00^\circ\), \(b = 11.6569(6) Å, \beta = 90.00^\circ\), \(c = 16.1673(9) Å, \gamma = 90.00^\circ\) |
| Volume | 2183.4(6) Å³ | 2196.9(2) Å³ |
| Z | 4 | 4 |
| Density (calculated) | 7.999 g/cm³ | 8.101 g/cm³ |
| Absorption coefficient | 45.869 mm⁻¹ | 44.942 mm⁻¹ |
| F(000) | 4432 | 4504 |
| Crystal size | 0.134 × 0.105 × 0.092 mm³ | 0.0237 × 0.0170 × 0.0084 mm³ |
| θ range for data collection | 5.32 to 24.98° | 5.32 to 29.25° |
| Index ranges | −13<=h<=13, −13<=k<=12, −19<=l<=19 | −15<=h<=15, −15<=k<=6, −22<=l<=22 |
| Reflections collected | 6661 | 5180 |
| Independent reflections | 968 \(|R_{int} = 0.1041|\) | 1424 \(|R_{int} = 0.0754|\) |
| Completeness to \(θ = 29.25^\circ\) | 99.9% | 95.6% |
| Refined method | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 968 / 0 / 94 | 1424 / 0 / 93 |
| Goodness-of-fit | 1.088 | 1.076 |
| Final R indices \([>2σ(1)]\) | \(R_{int} = 0.0480, \text{w}R_{int} = 0.1353\) | \(R_{int} = 0.0532, \text{w}R_{int} = 0.1219\) |
| R indices \([all data]\) | \(R_{int} = 0.0563, \text{w}R_{int} = 0.1613\) | \(R_{int} = 0.0603, \text{w}R_{int} = 0.1268\) |
| Largest diff. peak and hole | 4.662 and −2.694 e Å⁻³ | 2.537 and −2.193 e Å⁻³ |
the same as ours with a slightly smaller average Ir-O bond length that can be attributed to a slightly more Ir(V) concentration in the specimen of Phelan et al. Magnetic properties of the x = 1 member of this series (polycrystalline specimens in the Phelan et al. report) are comparable to those here, showing Curie-Weiss behavior at a cusp at ~12 K. Curiously, the effective moment for SrLa10Ir4O24 reported by Phelan et al differs considerably from that we find and is closer to that expected by an isolated Ir(IV). We do not have an explanation for this discrepancy, but note that the synthetic processes are different.

| Label     | x    | y    | z    | Occupancy | Ueq \(*^\) |
|-----------|------|------|------|-----------|------------|
| SrLa10Ir4O24 |      |      |      |           |            |
| Ir(1)     | 0.5000 | 0.5000 | 0    | 1         | 35(1)      |
| Ir(2)     | 0    | 0.5000 | 0    | 1         | 35(1)      |
| La(1)     | 0.7715 (2) | 0.4530 (2) | 0.1159 (1) | 1         | 38(1)      |
| La(2)     | 0.7059 (2) | 0.7264 (2) | 0.348 (1) | 1         | 39(1)      |
| La(3)     | 0.5000 | 0.7500 | -0.1400 (2) | 1         | 52(1)      |
| Sr(1)     | 0    | 0.7500 | -0.1250 | 1         | 90(3)      |
| O(1)      | 1.0087 (12) | 0.5358 (15) | -0.1220 (11) | 1         | 44(4)      |
| O(2)      | 0.8684 (15) | 0.6115 (15) | 0.0047 (10) | 1         | 46(4)      |
| O(3)      | 0.3927 (13) | 0.4232 (13) | 0.0761 (10) | 1         | 44(3)      |
| O(4)      | 0.5865 (12) | 0.5801 (14) | 0.0924 (10) | 1         | 42(3)      |
| O(5)      | 0.6099 (13) | 0.3656 (12) | 0.0295 (10) | 1         | 40(3)      |
| O(6)      | 1.1266 (14) | 0.6231 (15) | 0.0203 (10) | 1         | 42(3)      |
| BaLa10Ir4O24 |      |      |      |           |            |
| Ir(1)     | 0.5000 | 0.5000 | 0    | 1         | 16(1)      |
| Ir(2)     | 0    | 0.5000 | 0    | 1         | 16(1)      |
| La(1)     | 0.2307 (1) | 0.4543 (1) | 0.1156 (1) | 1         | 17(1)      |
| La(2)     | 0.2942 (1) | 0.7263 (1) | 0.0341 (1) | 1         | 19(1)      |
| La(3)     | 0.5000 | 0.7500 | -0.1416 (1) | 1         | 21(1)      |
| Ba(1)     | 0    | 0.2500 | 0.1250 | 1         | 22(1)      |
| O(1)      | -0.0090 (11) | 0.5176 (11) | -0.1233 (7) | 1         | 20(2)      |
| O(2)      | 0.6096 (11) | 0.4306 (12) | 0.0793 (7) | 1         | 22(3)      |
| O(3)      | 0.4080 (12) | 0.5748 (11) | 0.0933 (8) | 1         | 23(3)      |
| O(4)      | 0.1339 (12) | 0.6108 (12) | 0.0011 (7) | 1         | 20(2)      |
| O(5)      | 0.3963 (12) | 0.3661 (12) | 0.0272 (9) | 1         | 26(3)      |
| O(6)      | -0.1304 (13) | 0.6204 (12) | 0.0165 (8) | 1         | 24(3)      |

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å×10^3) for MLa10Ir4O24 (M = Sr, Ba) at 293(2) K with estimated standard deviations in parentheses. *Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

| Label     | x    | y    | z    | Occupancy | Ueq \(*^\) |
|-----------|------|------|------|-----------|------------|
| SrLa10Ir4O24 |      |      |      |           |            |
| Ir(1)-O(3) | 1.967 (15) × 2 | 1.983 (12) × 2 |
| Ir(1)-O(5) | 2.006 (14) × 2 | 2.023 (13) × 2 |
| Ir(1)-O(4) | 2.030 (16) × 2 | 2.046 (12) × 2 |
| Ir(2)-O(2) | 2.001 (16) × 2 | 2.006 (12) × 2 |
| Ir(2)-O(1) | 2.028 (17) × 2 | 2.026 (13) × 2 |
| Ir(2)-O(6) | 2.073 (16) × 2 | 2.086 (13) × 2 |
| BaLa10Ir4O24 |      |      |      |           |            |
| Ir(1)-O(3) | 1.967 (15) × 2 | 1.983 (12) × 2 |
| Ir(1)-O(5) | 2.006 (14) × 2 | 2.023 (13) × 2 |
| Ir(1)-O(4) | 2.030 (16) × 2 | 2.046 (12) × 2 |
| Ir(2)-O(2) | 2.001 (16) × 2 | 2.006 (12) × 2 |
| Ir(2)-O(1) | 2.028 (17) × 2 | 2.026 (13) × 2 |
| Ir(2)-O(6) | 2.073 (16) × 2 | 2.086 (13) × 2 |

Table 3. Selected bond lengths [Å] for MLa10Ir4O24 (M = Sr, Ba) at 293(2) K with estimated standard deviations in parentheses.
Methods
Syntheses. Crystals of the MLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24} (M = Sr, Ba) were grown by a flux method. For the synthesis of SrLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24}, La\textsubscript{2}O\textsubscript{3} (Alfa Aesar, 99.9%, 0.51 mmol), Ir metal (0.5 mmol), and anhydrous SrCl\textsubscript{2} (12.6 mmol) were loaded into a platinum crucible. The crucible was placed into a box furnace, heated to 1200 °C at 300 °C/hour, held at that temperature for 12 h, cooled to 900 °C at 12 °C/hour, and finally cooled to room temperature by turning off the furnace. For the synthesis of BaLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24}, La\textsubscript{2}O\textsubscript{3} (Alfa Aesar, 99.9%, 0.82 mmol) IrO\textsubscript{2} (0.82 mmol), anhydrous BaCl\textsubscript{2} (30 mmol) were loaded into a platinum crucible. The crucible was placed into a box furnace, heated to 900 °C at 300 °C/hour, then heated to 1200 °C at 12 °C/hour, held at 1200 °C for 12 h, cooled to 950 °C at 10 °C/hour, and finally cooled to room temperature by turning off the furnace. For both compounds, the crystals were separated from the flux by dissolving the flux in water aided by sonication, and then isolated with vacuum filtration and rinsing with acetone. The crystals are stable in air and water. They are black in color with an irregular polyhedral shape, and the crystal sizes are about 100 microns from one face to the face across.

Single Crystal X-ray Diffraction and EDS. Single crystals with irregular polyhedral shape were selected and mounted on tips of glass fibers for X-ray diffraction. Intensity data were collected at room temperature on a STOE imaging plate diffractometer system (IPDS-II) using graphite-monochromatized Mo–Kα radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA with a 34 cm diameter imaging plate. For SrLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24}, individual frames were collected with a 15 min exposure time and a 1° ω rotation at a φ angle of 98°, while for BaLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24} individual frames were collected with a 5 min exposure time and a 1° ω rotation at a φ angle of 78°. Data reduction and integration absorption correction were performed using X-Area software provided by STOE, and the crystal structures were solved with SHELXL 97 software package\textsuperscript{6}. The parameters for data collection and the details of the structure refinement are given in Table 1. Atomic coordinates, isotropic thermal displacement parameters (Ueq) and occupancies of all atoms are given in Table 2, and selected bond lengths are given in Tables 3 for both compounds. Anisotropic displacement parameters are given in the supplemental material. The isotropic thermal parameter for Sr1 in SrLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24} is relatively large, and the anisotropic thermal parameters for Sr1 have an elongated ellipsoid shape. This may be a sign of disordering for this site. The Ba in BaLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24} on the other hand, is well behaved. Electron dispersive X-ray spectroscopy data were collected on Oxford INCA Model 6498 and no discernible chlorine peaks were detected.

Magnetism. The DC magnetic susceptibilities of the ground samples were measured using a Quantum Design PPMS XL SQUID magnetometer. Samples were measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions in an applied field of 5000 G. For SrLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24}, the magnetization was measured upon warming the samples from 1.8 to 300 K. For BaLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24}, the magnetization was measured upon warming the samples from 2 to 300 K. The very small diamagnetic contribution of the gelatin capsule had a negligible contribution to the overall magnetization and was not subtracted.

Electrical Conductivity and Heat Capacity. Electrical conductivity of a single crystal of SrLa\textsubscript{10}Ir\textsubscript{4}O\textsubscript{24} was measured on a Quantum Design PPMS with a four-probe method. It was found that below 260 K the resistance is too large to be measured, thus data between 260 K and 350 K were measured. Heat capacity was measured on a Quantum Design PPMS with a four-probe method. It was found that below 260 K the resistance is too large to be measured, thus data between 260 K and 350 K were measured. Heat capacity for both compounds was measured on the PPMS from 2 K to 30 K.

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