Single crystal growth from separated educts and its application to lithium transition-metal oxides

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Thorough mixing of the starting materials is the first step of a crystal growth procedure. This holds true for almost any standard technique, whereas the intentional separation of educts is considered to be restricted to a very limited number of cases. Here we show that single crystals of $\alpha$-Li$_2$IrO$_3$ can be grown from separated educts in an open crucible in air. Elemental lithium and iridium are oxidized and transported over a distance of typically one centimeter. In contrast to classical vapor transport, the process is essentially isothermal and a temperature gradient of minor importance. Single crystals grow from an exposed condensation point placed in between the educts. The method has also been applied to the growth of Li$_2$RuO$_3$, Li$_2$PtO$_3$, and $\beta$-Li$_2$IrO$_3$. A successful use of this simple and low cost technique for various other materials is anticipated.

The honeycomb iridates $\alpha$-Li$_2$IrO$_3$ and Na$_2$IrO$_3$ attracted a lot of attention after Khaliullin and co-workers proposed that these systems offer a physical realization of the Kitaev interaction in a solid. Motivated by their proposal, several experimental studies on single crystalline Na$_2$IrO$_3$ and polycrystalline $\alpha$-Li$_2$IrO$_3$ have been performed. Direct evidence for the entanglement between spatial and spin directions, which is a consequence of the Kitaev exchange coupling, was recently observed in Na$_2$IrO$_3$ by means of diffuse magnetic X-ray scattering. These experiments were facilitated by the availability of sizable single crystals, however, the microscopic details of the growth are not well understood.

For $\alpha$-Li$_2$IrO$_3$ it has not been possible so far to obtain single crystalline material – not even on a length scale of 10 $\mu$m. Accordingly, there has been no direct access to the anisotropy of the physical properties, and the magnetic structure as well as the contribution of the Kitaev exchange has been still under debate.

The growth procedure presented in this letter allows the growth of single crystals of $\alpha$-Li$_2$IrO$_3$ of one millimeter along a side. A schematic sketch of the synthesis method and the phase formation as function of time and temperature are shown in Fig. 1. A remarkable feature is the isothermal nature of the process that was revealed by careful temperature measurements at different positions of the crucible (see Supplementary Figure 1): instead of a temperature gradient, here $\Delta T < 1 \text{ K/cm}$, it is the formation of $\alpha$-Li$_2$IrO$_3$ itself that drives the transport by maintaining a concentration gradient. The proposed, relevant transport equations are [ref. 8, p. 166, 217]:

\[
\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{LiOH}(g) \tag{1}
\]

\[
\text{IrO}_2(s) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{IrO}_3(g) \tag{2}
\]

Single crystalline $\alpha$-Li$_2$IrO$_3$ forms from gaseous LiOH and IrO$_3$. The X-ray diffraction pattern and the sharpness of the phase transition to the magnetically ordered state revealed a superior sample quality when compared to polycrystalline material (see below). Furthermore, the magnetic structure has been solved by recent single crystal magnetic resonant X-ray diffraction measurements performed on these samples (published separately). The synthesis of $\alpha$-Li$_2$IrO$_3$ was first reported by Kobayashi et al. The polycrystalline material was obtained by heating mixtures of Li$_2$CO$_3$ and IrO$_2$ to temperatures between 650 °C–1050 °C. The presence of a low-spin Ir$^{4+}$ state

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with an effective spin 1/2, as one of the essential ingredients of the Kitaev model, was reported soon after\(^1\). Despite the substantial interest in this material, the basic synthesis root has not changed since: to the best of our knowledge all attempts made are based on using Li\(_2\)CO\(_3\) as starting material. Heating mixtures of Li\(_2\)CO\(_3\) with Ir or IrO\(_2\) to sufficiently high temperatures leads to the formation of \(\alpha\)-Li\(_2\)IrO\(_3\) under release of CO\(_2\). This process, often referred to as ‘calcination’, has been applied to the growth of several other related materials, e.g.: Li\(_2\)RuO\(_3\), Na\(_2\)IrO\(_3\), or Na\(_3\)PtO\(_4\). In this way comparatively large single crystals of Na\(_2\)IrO\(_3\) were obtained\(^2\). The samples show a plate-like habit with typical lateral dimensions of a few square millimeter and a thickness of 100 μm. They grow out of a polycrystalline base (‘poly bed’) and form predominantly at the upper part of the product. For \(\alpha\)-Li\(_2\)IrO\(_3\), however, the similar approach leads to only a fine powder. Different flux methods, especially pre-sintered \(\alpha\)-Li\(_2\)IrO\(_3\) in LiCl flux, failed to increase the crystal size. Nevertheless, a better crystallinity was inferred from X-ray powder diffraction measurements\(^3\). In those attempts, the LiCl does not act as a ‘classical’ flux, it rather promotes a solid state reaction with enhanced diffusion.

At temperatures above 1000 °C the formation of \(\alpha\)-Li\(_2\)IrO\(_3\) competes with the high-temperature polytype \(\beta\)-Li\(_2\)IrO\(_3\)\(^4\)\(^5\). After repetitive heating of \(\alpha\)-Li\(_2\)IrO\(_3\) at 1100 °C small single crystals up to several 10 μm of \(\beta\)-Li\(_2\)IrO\(_3\) form\(^6\). Annealing \(\beta\)-Li\(_2\)IrO\(_3\) at temperatures below 1000 °C did not lead to the formation of \(\alpha\)-Li\(_2\)IrO\(_3\), indicating that the transition is irreversible. Small single crystals of a third modification, the ‘harmonic’ honeycomb \(\gamma\)-Li\(_2\)IrO\(_3\), were obtained by the calcination of Li\(_2\)CO\(_3\) and IrO\(_2\) followed by annealing in molten LiOH at 700 °C to 800 °C\(^7\). An advantage of the calcination process is the ability to start from carbonates which are comparatively easy to handle and store. In contrast, elemental lithium is air sensitive and has been avoided as an educt in previous approaches. Furthermore, lithium reacts with many standard crucible materials and develops a moderately high vapor pressure (17 mbar at 900 °C\(^8\)). On the other hand, elemental lithium has several advantages for the use as a flux. Its low melting point of 180 °C in comparison with a high boiling temperature of 1342 °C fulfill two key characteristics of a good flux\(^9\). Furthermore, lithium has a good solubility for iridium\(^10\). However, all our attempts to grow single crystals of \(\alpha\)-Li\(_2\)IrO\(_3\) from a lithium-rich flux and mixtures of lithium with LiCl, LiOH, LiBO\(_2\) and/or Li\(_2\)CO\(_3\) failed. A comprehensive overview of those attempts is given in the Supplementary Table 1.

Comparatively large single crystals of several millimeter along a side, as observed for Na\(_2\)IrO\(_3\)\(^4,7\) are not expected to grow in a solid state reaction due to the limited diffusion length. Given that the calcination process is completed at these temperatures (at 1050 °C) and the compound does not melt congruently it indicates the relevance of a vapor transport process within the crucible. In order to investigate the possible formation and transport of Li-O, Ir-O, and/or Li-Ir-O gas species during the syntheses of \(\alpha\)-Li\(_2\)IrO\(_3\), we started a growth attempt from elemental lithium and iridium in air. Lithium granules were placed on iridium powder in an Al\(_2\)O\(_3\) crucible. The mixture was heated to 900 °C over 4 h, held for 72 h and quenched to room temperature. To our surprise, already the first attempt revealed \(\alpha\)-Li\(_2\)IrO\(_3\) single crystals of up to 50 μm along a side. The whole product appeared homogeneous and X-ray powder diffraction pattern showed only small amounts of IrO\(_2\) and Ir. This is even more surprising since only three small lithium granules (roughly 4 mm in length with a diameter of 1.5 mm) were used but \(\alpha\)-Li\(_2\)IrO\(_3\) formed over the whole bottom of the crucible (inner diameter of 16 mm). This observation strongly supports the idea of vapor transport playing a decisive role for the growth of this material. However, a classical vapor transport along a temperature gradient does not seem to take place: various growth attempts in a horizontal tube furnace indicated that once \(\alpha\)-Li\(_2\)IrO\(_3\) has formed it does not transport anymore. This observation is corroborated by an estimate of the free enthalpy of formation for \(\alpha\)-Li\(_2\)IrO\(_3\): 

\[
\Delta H_\text{f,298}^0 = -880 \text{ kJ mol}^{-1} \text{ mol}^{-1} \text{ K}^{-1}
\]

and

\[
S_\text{f,298}^0 = 89 \frac{\text{J mol}^{-1} \text{ K}^{-1}}{\text{ mol}^{-1} \text{ K}^{-1}}
\]

[M. Schmidt, MPI-CPfS, private communication]. It corresponds to a large, exothermic value of the free reaction enthalpy of −332 kJ mol\(^{-1}\).
Figure 2. Crystal growth equipment (crucible diameter 16 mm). Arrangement of the materials before and after the growth process is depicted in (a,b), respectively. The rings with spikes are oriented like a spiral staircase in order to allow for nucleation at different positions with less intergrowth of the crystals. Formation of the largest α-Li2IrO3 single crystals is observed on spikes placed roughly 4 mm above the Ir starting material. (c) individual setup parts made from Al2O3 and (d) typical appearance of one of the lower spikes covered with α-Li2IrO3 crystals at the bottom side, scale bar 1 mm.

Figure 3. Sample quality and magnetic anisotropy of α-Li2IrO3. (a) comparatively large single crystal (1.2 mm × 0.4 mm × 0.5 mm and m = 1.7 mg) grown from separated educts (scale bar 0.3 mm). The corresponding Laue-back-reflection pattern, depicted in (b), shows the (nearly) three-fold rotation symmetry perpendicular to the honeycomb layers. (c) temperature dependent specific heat of the single crystal shown in (a) in comparison with a typical polycrystalline sample. (d) an easy-plane anisotropy is apparent from the temperature dependent magnetic susceptibility ($\mu_0H = 1$ T, $\chi_{ab}: H \perp c^*$, $\chi_{c}: H \parallel c^*$).
Therefore, we started to investigate the growth from spatially separated educts. For this purpose a specially designed setup has been constructed as depicted in Fig. 2a–c. It consists of a standard crucible, rings (washers), rings with spikes and a disc with a center hole (aperture). All parts are made from Al2O3. The rings act as spacers, hold the aperture in place and allow to vary the distance between starting materials and spikes. The spikes provide an exposed condensation point in between the educts. They are stacked as a ‘spiral staircase’ in order to identify the ideal position for the growth. The aperture is placed above the spikes and acts as a platform for one of the starting materials. The other educt is placed on the bottom of the crucible in the center of two spacers. This avoids a direct contact between the material and the spikes which sit on top of the spacers. For the growth of $\alpha$-Li$_2$IrO$_3$, iridium metal powder and lithium granules are used as starting materials. Iridium is placed on the bottom of the crucible, lithium on top of the aperture. The distance between the elements is roughly 11 mm.

\[ \text{IrO}_3(g) + 2\text{LiOH}(g) \rightarrow \text{Li}_2\text{IrO}_3(s) + \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2 \]  

Therefore, we started to investigate the growth from spatially separated educts. For this purpose a specially designed setup has been constructed as depicted in Fig. 2a–c. It consists of a standard crucible, rings (washers), rings with spikes and a disc with a center hole (aperture). All parts are made from Al$_2$O$_3$. The rings act as spacers, hold the aperture in place and allow to vary the distance between starting materials and spikes. The spikes provide an exposed condensation point in between the educts. They are stacked as a ‘spiral staircase’ in order to identify the ideal position for the growth. The aperture is placed above the spikes and acts as a platform for one of the starting materials. The other educt is placed on the bottom of the crucible in the center of two spacers. This avoids a direct contact between the material and the spikes which sit on top of the spacers. For the growth of $\alpha$-Li$_2$IrO$_3$, iridium metal powder and lithium granules are used as starting materials. Iridium is placed on the bottom of the crucible, lithium on top of the aperture. The distance between the elements is roughly 11 mm.
with five spikes placed in-between. The masses were chosen in their stoichiometric ratio. The whole setup is placed in a box furnace at 200 °C, heated to 1020 °C with a rate of 180 °C per hour, held for three days and finally quenched to room temperature. While heating, lithium transforms to a Li2O/LiOH mixture at moderate temperatures. At 900 °C all lithium is burned to Li2O. See a detailed analysis of this process in the Supplementary Figure 2. Only small amounts of Li2O are found on top of the aperture (where the lithium was placed) after the process. The iridium powder placed at the bottom is partially oxidized to IrO2.

Single crystals of dimensions larger than 1 mm were obtained (Fig. 3a). A good sample quality is inferred from Laue-back-reflection (Fig. 3b): the diffraction pattern shows the (nearly) three-fold rotational symmetry of the honeycomb layers (along the c* direction). The spot-size of the X-ray beam was similar to the sample dimensions. Figure 3c shows the temperature dependent specific heat measured on the same single crystal in comparison with polycrystalline material that was grown by calcination7. The improved sample quality of the single crystal is apparent from a sharper transition to the antiferromagnetically ordered state at \( T_N = 15 \) K. Temperature-dependent magnetic susceptibility for field applied parallel (\( \chi_{ab} \)) and perpendicular (\( \chi_{c} \)) to the honeycomb layers is shown in Fig. 3d. An easy-plane behavior with a sharp decrease of \( \chi_{ab} \) at \( T_N \) is observed, whereas \( \chi_{c} \) decreases only slightly. A measurement performed on polycrystalline material is included for comparison and can be roughly described by \( 1/3 \chi_{ab} + 2/3 \chi_{c} \) for \( T > T_N \).

The structural order in the grown crystals was probed using X-ray diffraction and representative patterns are shown in Fig. 4a–d. The data are fully consistent with the expected monoclinic crystal structure21 of alternate stacking of honeycomb Li1/2IrO3 and hexagonal Li layers with space group \( \text{Na}_2\text{IrO}_3 \) and \( \text{RuO}_3 \).

Figure 4c. Rods of diffuse scattering with the same selection rule were also observed in the iso-structural materials shown in Fig. 4a–d. The data are fully consistent with the expected monoclinic crystal structure 21 of alternate stacking of honeycomb Li1/2IrO3 and hexagonal Li layers with space group \( \text{Na}_2\text{IrO}_3 \) and \( \text{RuO}_3 \).

The iridium powder placed at the bottom is partially oxidized to IrO2. Only small amounts of Li2O are found on top of the aperture (where the lithium was placed) after the process.

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Author Contributions
F.F. and A.J. developed the crystal growth technique. F.F. grew the single crystals and measured specific heat and magnetization. S.C.W., R.D.J. and R.C. performed and analyzed the X-ray diffraction experiments. F.F., S.C.W., P.G. and A.J. wrote the manuscript with the help of all authors.

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