Floating-zone growth and characterization of triangular lattice antiferromagnetic $\alpha$-SrCr$_2$O$_4$ crystals

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The triangular $S=3/2$ antiferromagnetic $\alpha$-phase MCr$_2$O$_4$ ($M=\text{Ca, Sr, or Ba}$) family has received increasing attention for their low dimensional geometrically frustrated magnetism. For the first time, the single crystals of $\alpha$-SrCr$_2$O$_4$ were successfully grown by the floating-zone method. The plate-like crystals are highly $\alpha$-axis oriented with a 60° twinning structure in the $bc$ plane. We also investigated the magnetic susceptibilities, specific heat and dielectric properties systematically. Our results confirm a long range magnetic ordering emerging in $\alpha$-SrCr$_2$O$_4$ below about 43 K. These crystals are suitable for the future neutron scattering experiments and other in-depth physical measurements.

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1. Introduction

Frustrated magnetism has been of long-term interest for the variety of quantum magnetic ground states and unusual excitations arising from the competing interactions [1]. One of the simplest cases in the frustrated magnets is the nearest-neighbor Heisenberg antiferromagnets on some special geometries like two-dimensional (2D) triangular or kagome lattices. The competing neighboring magnetic interactions lead to the extra degeneracy in ground state over and above the non-frustrated systems, which give rise to the emerging of new physics. In these systems, the short-range ordering, spin fluctuation, rich phase diagrams and novel critical phenomena emerge at low temperatures, providing a fertile ground for condensed matter physicists [2]. For an ideal 2D triangular arrangement of isotropic classical vector spins that are coupled antiferromagnetically with each other, theoretically, there are degenerate solutions for the lowest energy of the system in which each given spin vector is arranged at 120° to its nearest neighbors. The highly degenerate ground states lead to exotic physical magnetic behaviors, such as with short-range ordered spin liquid states and long-range chiral magnetic ordering. In a real triangular antiferromagnet with quasi-2D layered structure, the interlayer magnetic exchange interactions, the possible structural distortions from an ideal regular triangular lattice, and the anisotropy of magnetic ions (of easy-axis or easy-plane type) can all act as important additional terms, leading to different types of magnetic structures. There are still many open questions about the physics in the triangularly frustrated magnets [3].

The $\alpha$-phase MCr$_2$O$_4$ family as investigated in this paper can be viewed as a prototypical example of the 2D triangular antiferromagnets with slight lattice distortion, where M stands for alkaline earth metal ($M=\text{Ca, Sr, or Ba}$) [4–6]. As shown in Fig. 1, $\alpha$-phase MCr$_2$O$_4$ has a quasi-2D layered structure with triangular sheets of CrO$_2$, which made up of edge-sharing CrO$_6$ octahedra. These stacking CrO$_2$ sheets are well separated by intercalated M$_2$O$_3$ ions. In each CrO$_2$ layer, the short neighboring Cr$^{3+}$–Cr$^{3+}$ distance (close to 3 Å) results in a strong direct antiferromagnetic exchange interaction. The exchange interaction between interlayer Cr$^{3+}$ ions is much weaker due to much longer distance. And the different nonmagnetic M$^{2+}$ ions primarily manifest in the different separations between the CrO$_2$ layers. The structure of $\alpha$-MCr$_2$O$_4$ resembles the hexagonal delafossites closely, with a slight rectangular distortion in the CrO$_2$ layers from the ideal regular triangular lattice. This kind of distortion results an overall orthorhombic symmetry in $\alpha$-MCr$_2$O$_4$ with two in equivalent Cr$^{3+}$ sites as shown in Fig. 1(b). Compared with other Cr$^{3+}$-containing triangular antiferromagnets as the delafossite-structure MCrO$_2$ (M=Cu, Ag) and the rock-salt-type LiCrO$_2$ [7,8], $\alpha$-phase MCr$_2$O$_4$ possesses the slight rectangular distortion and the facile tunability of the spacing between CrO$_2$ sheets (as M changes from Ca to Ba), which provides a fantastic arena to study the low dimensional frustrated magnetism.

Although the polycrystalline bulk of $\alpha$-phase MCr$_2$O$_4$ had been synthesized and structurally characterized dozens of years ago [4–6], their physical properties at low temperature have not been...
investigated until recently. In 2011, Chapron et al. [9] first investigated the magnetic structure of polycrystalline α-CaCr_2O_4. Their neutron diffraction measurement revealed an interesting helical magnetic structure in α-CaCr_2O_4 below the Neel temperature (T_N) of about 43 K with an incommensurate propagation vector \( \mathbf{k} = (0, -1/3, 0) \) along b-axis. The \( S = 3/2 \) spins of Cr^{3+} ions lie in the ac plane, perpendicular to the \( \mathbf{k} \) vector, a typical “proper-screw-type” spin structure. And the angle between the neighboring spins is about 120°, which is very close to the theoretical expected value for an ideal 2D triangular antiferromagnetic lattice, in spite of the orthorhombic distortion in α-CaCr_2O_4. Later, the similar magnetic structures were found in α-SrCr_2O_4 [10] and α-BaCr_2O_4 samples [11]. Additional, very recently, multiferroicity was discovered in this family [12,13], in which the ferroelectricity occurs concomitantly with the incommensurate helical magnetic ordering below \( T_N \). The corresponding systematical studies will help to clarify the microscopic physical mechanism of multiferroicity and search for new multiferroic materials for future applications in geometrically frustrated triangular magnets [14,15].

Most of previous studies were based on polycrystalline bulk samples, which were synthesized via conventional solid-state reaction. The series of α-MCr_2O_4 (M = Ca, Sr, Ba) have very high melting-points (\( T_{mp} \)) for M = Ca, Sr, \( T_{mp} > 2000 \) °C and for M = Ba, \( T_{mp} > 1600 \) °C [4–6]. Furthermore, there exists a phase competition between two isomers (α- and β-phases) in the MCr_2O_4 system. The preparation of α-phase MCr_2O_4 requires a very high sintering temperature (close to \( T_{mp} \)) while another β-phase is prone to appear in lower temperature, the phase boundary is found much above 1000 °C [16]. Therefore, a rather high sintering temperature (around 1500 °C) is indispensable to obtain pure α-phase samples. Besides, we also have found the controlled atmosphere is very important during the sintering and cooling process to keep chromium in its lowest oxidation state (+3) [13].

Till now, there are only a few studies on CaCr_2O_4 crystals reported by Toth et al. [17,18], without further detailed information on their growth conditions. In principle, the present difficulty of the crystal growth can be overcome by adopting the high-temperature floating zone technique, in which the large temperature gradient and well-controlled atmosphere is facile. The large single crystals of α-MCr_2O_4 is necessary for further in-depth research on this quantum frustrated magnetism with inelastic neutron scattering or other advanced measuring techniques. In this work, we grew the α-SrCr_2O_4 crystals for the first time and the corresponding characterization of their structure, magnetic susceptibilities, specific heat, and dielectric properties are presented.

2. Crystal growth

The growth of α-SrCr_2O_4 crystals of includes the preparation of the precursor oxide powders, sintering of the polycrystalline rods and finally, growing crystals in a high temperature optical floating zone furnace. The details are discussed as follows.

The highly pure powders of Cr_2O_3 (Sterm, 99.5%) and SrCO_3 (Alfa Aesar, 99.99%) with a nominal stoichiometric ratio of 1:1 were well mixed using an agate mortar and pestle. The starting materials were calcined in a continuous high vacuum (\(< 10^{-5} \) Torr) at 1000 °C for 72 h with several intermediate grindings. The final product is light green powder. The X-ray powder diffraction (XRD) measurement (not shown here) revealed that the resulting product mainly consisted of β-phase SrCr_2O_4 and a trace amount of un-reacted Cr_2O_3. The latter may be due to the incomplete solid state reaction or slight loss of volatile strontium oxide during the sintering process in high vacuum.

The precursor powder was then packed into the latex sleeves with 10 mm in diameter and pressed under a hydrostatic pressure of more than 100 MPa. The resulting rods were sintered at 1100 °C in vacuum for 24 h. The sintered rods were about 9 mm in diameter and 10–15 mm long, which were ready for the floating zone growth.

Because of its refractory nature (\( T_{mp} > 2000 \) °C) and absence of approximate flux, the α-SrCr_2O_4 crystals were grown in a high temperature optical floating zone furnace (FZ-T-12000-X-VPO, Crystal systems Corp., Japan), which is equipped with four 3-kW
Xenon lamps and four elliptical mirrors. After the installation of two rods (the feed and seed ones with the same composition), a rotation rate of 10–20 rpm is maintained. To keep chromium in its lowest oxidation state (+3) in $\alpha$-SrCr$_2$O$_4$, a pure argon flow of 100 sccm was adopted as ambient environments.

As aforementioned, there exists a two-phase competition in SrCr$_2$O$_4$ system. The unwanted $\beta$-phase is prone to appear in lower temperature. According our previous experience in the preparation of bulk $\alpha$-SrCr$_2$O$_4$, the phase boundary is around 1400 °C. Therefore, a rapid cooling of the crystallized boule from high temperature melt is also necessary to avoid the appearance of the unwanted $\beta$ phase impurities. Therefore, an alumina shielding surround the enclosed quartz tube was used to increase the temperature gradient, which is about 1.5 cm below the growth front.

Since the $\alpha$-SrCr$_2$O$_4$ is highly refractory ($T_{mp} > 2000 °C$), the melt zone begun to appear only as the power of the 4 Xenon lamps reaches above 90% of the maximum limit according our growth experience. The melting zone was suspended by surface tension between the upper feed rod and the lower seed one. Both rods with identical compositions were counter-rotated at the same rate (10–20 rpm). As lowering both rods slowly, the crystallization process could occur at the growth front between the lower rod and the melt zone. The large temperature gradient was further enhanced by the set-up of an alumina shielding, and prevented the $\alpha$-phase SrCr$_2$O$_4$ crystals from converting into $\beta$ phase during the cooling process.

Although we have tried many runs with different growth parameters, two severe problems have not been completely overcome till now, which prevent us from achieving long-time continuous stable growth process. The biggest problem is low viscosity of the melt at this extreme high temperature. The low viscous melting zone lacks surface tension and is very hard to be kept stable. At present, the careful and agile manual adjustments (including rotation and translation rates, the heating power) in real time are necessary to maintain the melt zone and prolonging the growth time as possible as one can. Otherwise, the melt can flow easily down the lower rod and the crystal growth is interrupted. This is why we cannot acquire long crystallized rod. In our later runs, the crystal growth was controlled at a translation rate of around 3 mm/h with an optimal rotation rate of around 13 rpm. It is hard to acquire long crystallized rods by prolonging the growth time or increasing the translation rate at present.

Another severe problem is the light green deposit on the inside surface of the quartz tube during the growth process. The deposit came from the volatilization of the melt at high temperature. The accumulation of the deposit decreased the transmittance of the quartz tube and lowered the effective heating power on the melting zone. Correspondingly, we had to increase the power of lamps manually in the floating zone furnace to maintain the melt till our equipment had reached its powder limit, and then the growth process had to be stopped because of too much deposit in the quartz tube.

We have tried tens of runs with different growth parameters, the above two severe problems have not been completely overcome. At present we could only acquire rods with short crystallized regions. The photograph of one good crystallized rod is shown in Fig. 2(a). The well crystallized section (black part) is less than 3 cm (usually 1–2 cm for most of our rods). The growth direction was perpendicular to the $a$-axis, i.e. parallel to the $bc$ plane, according our X-ray diffraction measurements. The crystallized section was cut with a diamond saw. Due to the layered structure of $\alpha$-SrCr$_2$O$_4$, it can be easily cleaved along the rod direction with the aid of a razor blade. And the dark green

![Fig. 2. (a–c) Optical photographs. (a) An typical as-grown SrCr$_2$O$_4$ rod with a nearly 3-cm-long crystallized region (black part), (b) the splitting of a crystallized section cut from the rod (the cleavage plane along the rod), and (c) two typical cleaved sheet-like crystals. (d) The SEM image of the cleaved crystal surface.](image-url)
sheet-like crystals with shining facets could be acquired, as shown in Fig. 2(b) and (c).

The present growth method without flux seems very hard to acquire larger single crystals. According to our experience, the most promising way is developed a suitable melt to avoid conversion into a two-phase boundary. But for $\alpha$-SrCr$_2$O$_4$, the temperature of melt must be still higher than the two-phase boundary (around 1400 °C) to avoid converting into $\beta$-phase. And above all, the melt with flux at such high temperature must have enough surface tension to form stable melting zone, and low volatility to decrease possible contamination on the quartz tube used in FZ growth. Now, we have not found such appreciate flux which can meet aforementioned demands, but it is the most possible way to acquire large perfect single crystals in the further studies by us or other groups working on this $\alpha$-MCr$_2$O$_4$ system.

3. Structural characterization

Because of its layered lattice structure, the thin-plate-like $\alpha$-SrCr$_2$O$_4$ crystal can be easily cleaved from the crystallized sections of the rods. The crystal samples with large shiny cleavage surfaces more than 5 mm$^2$ with the thickness of 0.1–0.3 mm can be easily obtained. The $a$-axis is perpendicular to the plate.

The surface morphology is measured by scanning electron microscopy (SEM). A typical SEM image is shown in Fig. 2(d). We observed a large flat and clean surface with a few terraced steps, consistent with the layered structure of $\alpha$-SrCr$_2$O$_4$. The corresponding energy dispersive X-ray spectra (EDX) measurement confirmed that the atomic ratio of Cr and Sr is very close to the nominal stoichiometric ratio (2:1).

To verify the phase purity, some crystals were pulverized for characterization by X-ray powder diffraction measurements. A Panalytical X’pert Pro diffractometer with CuK$\alpha$ radiation was used. As shown in Fig. 3(a), no diffraction peaks of the $\beta$-phase or other possible impurities as Cr$_2$O$_3$ can be observed. All the Bragg peaks can be indexed in the 14H space group, confirming that the sample are of the single $\alpha$-phase. The XRD pattern has been refined using the GSAS software [19]. Because of the layered crystal structure of $\alpha$-SrCr$_2$O$_4$, the strong preferred orientations exist even in powder sample, which have to be taken into account during the Rietveld refinement of the XRD patterns. The final refinement pattern for $\alpha$-CaCr$_2$O$_4$ is also shown in Fig. 3, which yields $R_p=5.9\%$, $R_w=7.7\%$. The calculated lattice constants and atomic coordinates are consistent with the previous reports [5].

We also measured a typical thin plate-like crystal with dimensions of 2.5 mm $\times$ 3 mm $\times$ 0.15 mm. The XRD pattern of an out-of-plane 20-$\theta$ scan is shown in Fig. 4(a). Only the sharp (2l 0 0) Bragg peaks can be observed, confirming its highly $a$-axis orientation. That is, the $a$-axis is perpendicular to the surfaces (bc-plane). To further characterize the mosaic structure in the bc plane, we performed a phi-scan around the (202) Bragg reflection of this crystal, using a four-circle diffractometer (Pananalytical X’pert MRD). Because of the overall two-fold symmetry in the orthorhombic $\alpha$-CaCr$_2$O$_4$, only two peaks with 180° can be observed for a single domain. However, there are six Bragg peaks emerges with equal 60° separation with respect to their nearest neighbors, as shown in Fig. 4(b).

As illustrated in Fig. 1(b), the structure of $\alpha$-SrCr$_2$O$_4$ in bc-plane is very close to ideal triangular lattice with hexagonal symmetry. The rectangular ordering of interlayer Sr$^{2+}$ ions lead to a slight distortion of CrO$_2$ layer, resulting in a overall orthorhombic symmetry in $\alpha$-SrCr$_2$O$_4$. This structural characteristic makes $\alpha$-CaCr$_2$O$_4$ very apt to form a 60° twinning structure naturally with three different kinds of crystallographic domains whose $b$-axis rotates 60° with respect to each other and their $a$-axes align in the same direction. The FWHM (full width at half

![Fig. 3. Rietveld refinement of the powder XRD pattern of pulverized $\alpha$-SrCr$_2$O$_4$ crystal. The observed (points), background (green dash), calculated (black line) and the difference curve (blue) are plotted. The vertical bars (green) mark the positions of Bragg peaks for the $\alpha$-CaCr$_2$O$_4$ phase. The refinement is carried out using GSAS software. The corresponding parameter is also shown in the inset. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)](image1)

![Fig. 4. (a) The XRD pattern of a typical thin-plate-like $\alpha$-SrCr$_2$O$_4$ crystal sample and all the Bragg peaks are indexed. (b) The (202) phi-scan of the crystal measured on a 4-circle diffractometer. The upper right inset is the rocking curve (red circles) around the (202) Bragg reflection peak of one domain with the corresponding Gaussian fit (blue line). The FWHM is 0.4°. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)](image2)
maximum) of the rocking curves around the (202) Bragg reflection is about 0.4°, as shown in the inset of Fig. 4(b).

4. Physical properties (magnetization, specific heat and dielectric)

We studied the physical properties of our crystals, including magnetization, specific heat and dielectric characterization.

4.1. Magnetic properties

The magnetic properties were measured with a SQUID magnetometer (MPMS-5S, Quantum Design Inc.) in the temperature range between 2 and 380 K. The linear behavior in the field-dependent magnetization (\(M-H\) curve) is observed up to \(H=5\) T (as shown in the inset of Fig. 5) at several different temperatures below and above the magnetic transition and no hysteresis behavior can be found, suggesting the absence of ferromagnetic impurities in our sample.

The temperature dependent magnetic susceptibilities measured in \(H=0.3\) T is shown in Fig. 5. The field was applied parallel (\(H_z\)) and perpendicular (\(H_\perp\)) to the crystal surface (bc plane) and the corresponding susceptibility is denoted as \(\chi_z\) and \(\chi_\perp\). A broad hump occurs with the maximum around 50 K, which is quite common in low dimensional systems with short-range antiferromagnetic ordering. As temperature decreases further, both \(\chi(T)\)'s drop abruptly at around 40 K. The kink-like features indicate the emerging of a long-range antiferromagnetic ordering (as confirmed in the corresponding specific heat measurements discussed later). For clarification, we take the temperature derivatives of \(\chi_z\) and \(\chi_\perp\) as plotted in the upper right inset. The sharp peaks both occur at the Néel temperature (\(T_N\) = 43 K).

Above \(T_N\), the behavior of \(\chi(T)\) deviates considerably from the Curie–Weiss law. We just fit the data of \(\chi_{\perp}\) and \(\chi_z\) in the high-temperature range(200–380 K) to the Curie–Weiss formula, \(\chi = C/(T-\theta)\). The effective magnetic moment (\(\mu_{\text{eff}}\)) calculated from the fitted \(C\) parameter is 4.11 and 3.64 \(\mu_B\) for \(H_z\) and \(H_\perp\). Both values are close to the expect moment value 3.87 \(\mu_B\) for paramagnetic spin 3/2 Cr\(^{3+}\) ion, also consistent with the previous results on polycrystalline samples [12,13] and confirming the 3+ valence state of Cr ions in our crystals. The considerable difference between \(\chi_z\) and \(\chi_\perp\) can be attributed to the strong anisotropic magnetic interaction in layered structure \(\alpha\)-SrCr\(_2\)O\(_4\).

4.2. Specific heat

To confirm the long-range antiferromagnetic ordering in \(\alpha\)-MCR\(_2\)O\(_4\), we measured the specific heat (\(C_p\)) of a \(\alpha\)-SrCr\(_2\)O\(_4\) crystal. The measurements of specific heat were carried out using a standard thermal relaxation calorimetric method in a commercial Physical Property Measurement System (PPMS, Quantum Design Inc.).

The sharp \(\lambda\)-shaped transition in \(C_p(T)\) was observed as in Fig. 6, which were consistent with the reported data on bulk samples [10,13]. The anomalous peak in \(C_p(T)\) at \(T_N\) (~42.9 K) indicates the emerging of the long-range magnetic ordering, also consistent with the aforementioned data of magnetic susceptibilities. It is noticeable that the weak anomalous feature at 35 K reported by Dutton et al. [11] is not observed in our data, which may come from some unknown impurities in the polycrystalline sample prepared via a conventional method.

4.3. Dielectric and ferroelectric properties

At present, only the dielectric constant and electric polarization along \(a\)-axis \((\varepsilon_a)\) can be measured in our experiment because large electrode area is needed in these measurements. Firstly, the silver paint was attached to both sides of the crystal plates (typically 2 mm × 3 mm × 0.15 mm) as electrodes to form a parallel-plate capacitor. The samples are glued on the cryogenic stage of our homemade probe. The dielectric constant was acquired using a high-precision capacitance meter. Different testing frequencies (from 1 kHz to 1 MHz) were adopted to avoid possible extrinsic factors as interface effect and the results on a typical crystalline sample are shown in Fig. 7.

As shown in Fig. 7, in zero field, \(\varepsilon_a(T)\) decreases gradually on cooling. Around \(T_N\), only a very weak hump is observed. This weak anomaly in \(\varepsilon_a(T)\) (independent of testing frequencies) is associated with the multiferroic transition, which has been confirmed on bulk samples in previous work [12,13]. But around \(T_N\), no corresponding anomaly can be observed in the dielectric loss (\(\tan \delta\)), suggesting no ferroelectricity exists along \(a\)-axis in \(\alpha\)-SrCr\(_2\)O\(_4\). We have also measured the electric polarization along \(a\)-axis using pyroelectric method, no net electric polarization \((P_a)\) is observed within the resolution limit of our experimental set-up.

Our observations confirm the absence of ferroelectricity along \(a\)-axis in \(\alpha\)-SrCr\(_2\)O\(_4\). Obviously, the intrinsic ferroelectric polarization, arising from magnetic ordering in multiferroic \(\alpha\)-SrCr\(_2\)O\(_4\), must lie in \(bc\)-plane. According to the new microscopic mechanism proposed by Arima [20] based on the \(d-p\) hybridization modified
by the spin–orbital interactions, the electric polarization should be
along the propagation vector in the “proper-screw-type” helical
spin structure (b-axis in $\alpha$-SrCr$_2$O$_4$). Our results are consistent
with theoretical prediction, as well as the phenomenological
symmetry analysis [9].

5. Summary

In conclusion, for the first time we have succeeded in growing
crystals of $\alpha$-phase SrCr$_2$O$_4$ by the floating zone method. Our
structure characterization manifests that these crystals are highly
$\alpha$-axis oriented with the in-plane 60° twinning structure. The
physical properties of this quasi-2D geometrically frustrated tri-
angular antiferromagnet are investigated. A long range magnetic
ordering emerges below $T_N$, associated with the specific heat and
dielectric anomalies. At present, the main problem is the lack of an
appropriate flux, which prevents us from acquiring larger and un-
twinned crystals. Our present crystals are suitable for further
in-depth measurements such as synchrotron inelastic X-ray scat-
tering or neutron diffraction experiments.

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References

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