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Synthesis, structure and magnetic properties of crystallographically aligned CuCr$_2$Se$_4$ thin films

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Abstract

We report the low temperature synthesis of highly textured CuCr$_2$Se$_4$ thin films using the modulated elemental reactant (MER) method. The structure of CuCr$_2$Se$_4$ is determined for the first time in its thin film form and exhibits cell parameters that are smaller than found in bulk CuCr$_2$Se$_4$. X-ray diffraction and precession electron diffraction show a strong degree of crystallographic alignment of the crystallites, where the <111> axis is oriented perpendicular to the substrate surface, while being rotationally disordered within the plane. Temperature and field dependent in-plane and out-of-plane magnetization measurements show that the film is ferromagnetic with a Curie temperature of 406 K. CuCr$_2$Se$_4$ synthesized utilizing the MER method shows stronger magnetic anisotropy (effective anisotropy: 1.82×10^6 erg cm^{-3}; shape anisotropy: 1.07×10^6 erg cm^{-3}), with the easy axis lying out of plane, and a larger magnetic moment (6 μ_B/f.u.) than bulk CuCr$_2$Se$_4$.

1 Introduction

Information technology can be considered one of the key drivers of modern society. With its increasing penetration of modern life comes an ever increasing demand for higher storage capacities, faster data processing and data transmission speeds, and increased information storage lifetimes. [1] Spin-based electronic applications, spintronics, are a promising technology to supply these demands, making research on spin-polarized thin films an important area of research. [1,2] Ideally, spintronic materials exhibit a Curie temperature considerably above room temperature and strong spin polarizability. [1,2] Because of their relatively high Curie temperatures and good spin polarizability, many oxide materials have been investigated for their magnetic properties and their potential application in spintronic materials. [3,4] Other chalcogenides, however, have only received limited attention as potential spintronic materials.

Chalcogenide chromium spinel materials, ACr$_2$X$_4$ (A = Cd, Co, Cu, Fe, Hg, Zn; X = S, Se, Te), are especially interesting due to their relatively high Curie temperatures and the capability to accommodate a large variety of atoms in the structure, which has resulted in a large versatility in magnetic, magnetoresistive and electrical properties. [5–26] CuCr$_2$Se$_4$ is a ferromagnetic compound at room temperature (T$_C$ > 430 K [11,13]) and has the highest Curie temperature among non-oxide chalcospinels. It also exhibits metallic transport properties, which makes it an interesting candidate for spin-polarized electronics applications.

Most of the research on CuCr$_2$Se$_4$ was conducted on bulk or nanocrystalline compounds, but in order to be technologically relevant approaches to prepare thin films of these compounds need to be developed. [11,13,24,27,28] Thin films of CuCr$_2$Se$_4$, however, have proven to be difficult to synthesize. The first to report films with the composition close to CuCr$_2$Se$_4$ were Berzhansky et al., yet without structural

characterization. [29] Bettinger et al. successfully prepared $CuCr_2Se_4$ films with Cr_2Se_3 as a secondary phase. [30] Recently, Anderson et al. published a method to synthesize highly textured $CuCr_2Se_4$ films by depositing Se-Cr-Cu-Cr-Se multi-layer precursors, but with limited structural characterization and without properties reported. [31]

Here, we report the synthesis of $CuCr_2Se_4$ films using multilayer precursors, the structural characterization of the resulting highly textured films and the correlation of the observed ferromagnetic behavior with the structure. The $CuCr_2Se_4$ films were synthesized using the method employed by Anderson et al. [31] Rietveld refinement of specular X-ray diffraction scans shows that the compound crystallizes in a regular spinel structure similar to the bulk material. Specular X-ray diffraction and precession electron diffraction reveal strong crystallographic alignment with the <111> direction perpendicular to the substrate. Random orientation of the crystallites about the <111> axes was observed in the plane of the film. The magnetic properties of the films show anisotropy with an easy axis out of plane. The saturation magnetization is higher than in other $CuCr_2Se_4$ films and the bulk compound.

2 Experimental

Multi-layer precursors were prepared using a custom-built physical vapor deposition chamber modeled after a similar chamber described previously. [32] Cr and Cu were evaporated using an electron beam source, and Se was deposited using an effusion cell under a vacuum of less than 5×10^{-7} mbar. Relative thicknesses of the elements were calibrated to yield compositions close to that of the desired $CuCr_2Se_4$ stoichiometry. (100)-oriented Si was used as substrate material. The total film thickness of the precursors according to X-ray reflectivity were approximately 50 nm. The unit thickness of the repeated Se-Cr-Cu-Cr-Se layers was approximately 1.6 nm.

The precursors annealed on a custom-made hot plate under a nitrogen atmosphere (< 0.6 ppm) at temperatures ranging from 400 °C to 600 °C yielded samples of poor quality due to Se loss. Samples were therefore annealed in a sealed fused silica tube ($p \approx 10^{-5}$ mbar) at 400 °C for 24 h, 48 h, and 96 h. CuSe powder (99.5%, *Alfa Aesar*) was added to generate a positive Se vapor pressure in order to prevent the evaporation of Se off the film.

The structure of the films was probed using X-ray diffraction (XRD) and electron microscopy techniques. XRD patterns were collected under specular and off specular conditions using a Rigaku Smartlab. Off specular scans were done in grazing incidence (GIXRD) and grazing incidence in-plane geometry (in-plane XRD). The lattice parameters of the samples were determined from the specular XRD pattern with a least square refinement method using WinCSD software suite. [33] The structure of the sample annealed for 24 h was also refined using the Rietveld method and the FullPROF software suite. [34,35] In order to determine a map of the crystallographic alignment of the crystallites in the film, precession electron diffraction measurements were performed at the Pacific Northwest National Laboratory using a JEOL JEM-3000SFF.

Magnetic properties were measured using a Quantum Design MPMS3. Temperature-dependent magnetization measurements were carried out for the sample annealed for 24 h from 4.2 K to 400 K. The sample annealed for 24 h was additionally measured from 300 K to 450 K. Magnetization hysteresis curves were recorded as a function of external field strength at 300 K.

3 Results and Discussion

3.1 Structural Characterization

Representative diffraction patterns for the synthesized compounds are shown in Figures 1 and 2. The specular XRD scans, shown in Figure 1, contain three reflections that can be indexed with (hhh) (h = 1, 2, 4) indices of the spinel structure, suggesting a crystallographically aligned structure. The samples annealed for 24 hours are the most crystallographically aligned. Rocking curves around the (222) reflection show an increase of the FWHM as annealing time is increased from 24 h (5.3°) to 48 and 96 h (5.6°). The FWHM of all samples are slightly smaller than the thin films synthesized by Anderson et al., indicating stronger crystallographic alignment.[31] The specular scan for the sample annealed for 24 hours has the highest intensity with a weak reflection with h = 3. In the diffraction patterns for the samples annealed for 24 h and 48 h, only reflections of normal spinel $CuCr_2Se_4$ ($Fd\bar{3}m$) are observed. Thus, according to x-ray diffraction, the films are pure $CuCr_2Se_4$. The sample annealed for 96 h also shows an additional reflection, which is consistent with the (111) reflection of cubic Cu_2Se. The in-plane XRD and GIXRD patterns (Figure 2) can all be indexed to the regular spinel structure ($MgAl_2O_4$-type, $Fd\bar{3}m$).

The diffraction patterns show small changes as the samples are annealed for longer times. There is a small shift in the lattice parameters when the sample is annealed, changing from 10.315(3) Å to 10.306(1) Å to 10.309(1) Å for the samples annealed for 24 h, 48 h, and 96 h respectively. These values are all smaller than the reported value for single crystalline $CuCr_2Se_4$ (10.337(6) Å). [36] The decrease in intensity of the (hhh) reflections in conjunction with the wider rocking curve widths with increasing annealing time suggests a loss of crystallographic alignment over time. The in-plane XRD patterns (Fig. 2a) confirm the loss of crystallographic alignment. The in-plane diffraction pattern of the sample annealed for 24 h does not show (hhh) reflections. The (440) reflection on the other hand is very intense, showing that the {440} planes, which are perpendicular to the {hhh} planes, are strongly aligned perpendicular to the substrate surface. The strong intensity of the (222) reflection and the absence of the (440) reflection in the specular XRD pattern and vice versa in the in-plane XRD show that the sample is crystallographically aligned along the <111> axes. The in-plane XRD pattern of the sample annealed for 48 h contains the (222) reflection and the intensity of the (440) reflection is decreased. The specular diffraction pattern also contains the (311) reflection, even though only visible in a logarithmic scale. This suggests that the sample is less crystallographically aligned than the sample annealed for 24 h, which correlates well with the decreased intensities in the specular XRD patterns (Fig. 1) and the overall increased intensities in the GIXRD pattern (Fig. 2b). The absence of the (440) reflection in the specular XRD pattern suggests that the sample is still strongly aligned. The sample annealed at 96 h, however, has lower intensities than the sample annealed at 48 h, along with an additional reflection in the specular XRD consistent with the (022) reflection of Cu_2Se. In the in-plane XRD, the (222) reflection is present, but less intense than for the sample annealed for 48 h. We attribute this decrease in intensity to a reduced degree in crystallinity.

Since the $CuCr_2Se_4$ film annealed for 24 h is layered along the [111] direction, and hence, only contains information on the distances between atomic planes along this direction, a simple one-dimensional model can be used to refine the specular diffraction scan. Figure 3 shows the Rietveld refinement of the specular scan of the sample annealed for 24 h. Considering instead of atomic positions only atomic planes, the length of the repeat unit along the [111] direction is $\frac{\sqrt{3}a}{3}$ and in addition contains a mirror plane as indicated in the structural scheme in Figure 3. Using the bulk crystal structure [36] as a model, the only refinable parameter is the position of the plane of the Se-atoms. The structure was modeled in the trigonal space group $P\bar{3}m1$ as this space group has a mirror plane at 0.5 in the z-direction, and detailed results are provided in table S1 in the supplementary material. The structural refinement resulted in low R-values (R_F=0.054 and R_I=0.015) and a reasonable position of the Se-plane (0.2446(2) compared to 0.2426 for the single crystal [36]) confirming the presence of a $CuCr_2Se_4$ structure in the thin film. Converting the

thickness of the repeat unit yields a lattice parameter of the 10.3159(7) Å compared to 10.337(6) Å for the single crystal. This is the first time that cell parameters for a $CuCr_2Se_4$ thin film sample have been reported.

Precession electron diffraction images were taken to qualitatively assess the degree of alignment of the crystallites in the film. The sample was aligned so that the z-direction is parallel to the surface normal of the film. A representative image is shown in Figure 4. The grains exhibit a variety of sizes, but are on average 80 μm across. The color of the grains predominantly show light blue and purple shades, showing that the grains are mostly aligned along or close to the <111> axes. The pole figures show a homogeneous distribution of different crystallographic alignments along the x and y axis (in plane) and a large concentration around the <111> directions along the z axis. The deviations from a pure alignment along the <111> axes are likely due to imperfect sample alignment during the TEM experiment.

The crystallographic alignment may be due to the surface energies in $CuCr_2Se_4$. The natural cleavage surface of single crystal $CuCr_2Se_4$ is the (111) plane, indicating that this surface has the lowest surface energy. [37] Due to the mild reaction conditions, the main driving force of the $CuCr_2Se_4$ formation may be nucleation and Ostwald ripening. In order to minimize their surface energy, nuclei grow in a preferred orientation, forming crystallographically aligned films.

3.2 Magnetic Properties

Temperature-dependent magnetization curves (Figure 5) show Brillouin-type behavior. The Curie temperature of the sample annealed for 24 h is 406 K, which is comparable to Bettinger et al. ($T_c = 405 - 410$ K), but lower than the Curie temperature found in bulk ($T_c > 430$ K). [11,13,30] In-plane and out of plane magnetization curves of $CuCr_2Se_4$ films were measured at room temperature (Figure 6). They show the hysteresis behavior characteristic of a ferromagnetic compound.

The magnetization shows saturations at an external magnetic field of 2 kOe. At 4.2 K, the saturation magnetization of the samples annealed for 24 h and 48 h are 413 emu/cm^3 and 448 emu/cm^3, respectively, which corresponds to 6.1 μ_B/f.u. and 6.6 μ_B/f.u., respectively. These values are higher than in bulk and in the thin films found by Bettinger (4.5 – 5.0 μ_B/f.u.). [11,13,30] Colminas predicted a moment of 6 μ_B/f.u. under the assumption that Cr is present as Cr^{3+} and Cu is present as Cu^+.[38] DFT calculations conducted by Bettinger et al. suggest that the increase in the magnetization may be due to Se deficits.[30] Doping experiments with Br^- ions also showed that a decrease in the Se concentration correlates with stronger magnetization due to a decrease in Cu^{2+} concentrations and thus an increase in the Cu^+ concentration.[37] Thus, our films may have a significant amount of Cu^+ ions and defects on Se sites. Another factor for this increased magnetization may be the orbital momentum of the chromium ions. A not fully quenched orbital angular momentum, would increase the magnetization per formula unit compared to the spin-only magnetism. A stronger influence of the orbital angular momentum would also contribute to magnetic anisotropy. However, this effect is expected to be very small. The saturation magnetization is significantly lower for the sample annealed for 96 h (253 emu/cm^3 or 3.7 μ_B/f.u.), which is probably due to the Cu_2Se impurity or lower degree of crystallization.

The saturation moment, coercitivity and remanence are larger out of plane than in plane, suggesting anisotropy in the films. The effective anisotropy for the sample annealed for 24 h is 1.82×10^6 erg cm^{-3} with the easy axis being out of plane, i.e. along the <111> axes. The sample annealed for 48 h shows a stronger effective anisotropy with 2.6×10^6 erg cm^{-3}. Due to higher magnetization, the shape anisotropy is also higher for the sample annealed at 48 than for 24 h with 1.26×10^6 erg cm^{-3} and $1.07 \times$

10^6 erg cm^{-3}, respectively. The anisotropy shown is stronger than in the single crystals and may be due to strain inside the sample or a stronger influence of the orbital angular momentum, which is typically stronger along the easy axis of magnetization.[13] This is the first time, magnetic anisotropies are published in $CuCr_2Se_4$ thin films, so no comparison with other films can be made.

Anisotropy is also observed in the coercive forces. The insets of Fig. 6 show the coercive force H_c as a function of annealing time and show an increase in the coercive force for the out-of-plane magnetization with increasing annealing time. While the difference between the sample annealed for 24 h and 48 h is rather small (10 Oe), there is a strong increase for the sample annealed for 96 h (60 Oe difference to 48 h). For the in-plane magnetization, H_c is approximately the same for the samples annealed for 24 h and 48 h (65 Oe and 63 Oe, respectively), the sample annealed for 96 h has a much larger H_c (180 Oe). For the samples annealed at 24 h and 48 h, H_c is larger for the out-of-plane than for the in-plane magnetization. This phenomenon can be explained by the different degrees of crystallographic alignment and crystallinity. The coercive force increases with increasing defect and domain wall concentrations. X-ray diffraction has shown that the sample annealed for 96 h is less crystalline and less aligned than the other samples and thus has larger coercive forces than the samples annealed for 24 h and 48 h. The lack of anisotropy in the coercive force shows the reduced degree in crystallinity as there are more defects in the entire film. The in-plane coercive forces for the samples annealed at 24 h and 48 h are approximately the same, whereas they are higher in the out-of-plane magnetization for the sample annealed for 48 h. As shown by PED, the films are aligned along the [111] direction, but are rotationally disordered in the perpendicular plane. The consequence of this rotational disorder are abrupt interfaces between individual $CuCr_2Se_4$ slabs, which are not present within the plane. This and the easy axis of magnetization, which is out-of-plane, elevate the out-of-plane H_c compared to the in-plane H_c. The fact that the in-plane H_c are approximately the same for the samples annealed for 24 h and 48 h and much smaller than for the sample annealed for 96 h shows that both have a similar defect concentrations and are well crystallized within the plane. Lower degree of crystallographic alignment, potentially stronger rotational disorder, and increased magnetization all contribute to a larger H_c, which explains why the out-of-plane H_c for the sample annealed for 48 h is larger than H_c for the sample annealed for 24 h.

4 Conclusion and Outlook

$CuCr_2Se_4$ films aligned along the <111> axes were successfully synthesized at a relatively low temperature of 400°C. The degree of crystallographic alignment decreases with time while annealing at elevated temperatures. These films are ferromagnetic up to a temperature of 406 K. Films exhibit anisotropic magnetism with the easy axis lying along the <111> axes. The saturation magnetization is higher than in bulk $CuCr_2Se_4$ and in other $CuCr_2Se_4$ films. The none-forced preferred orientation and the ability to deposit thin layers may open the pathway to magnetic intergrowth compounds with interesting magnetic properties.

Acknowledgments

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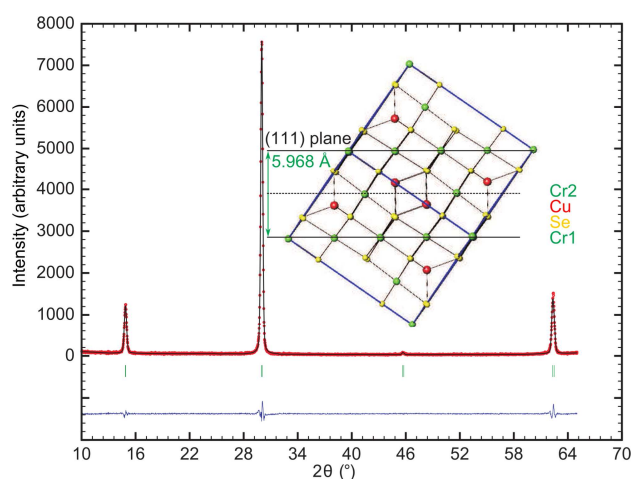
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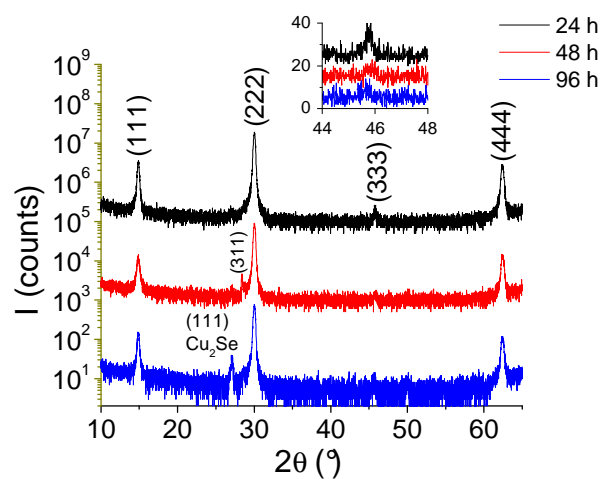

Figure 1 Specular diffraction patterns of CuCr$_2$Se$_4$ samples annealed for 24 h, 48 h, and 96 h. The inset shows the intensity of the (333) reflection. Offsets added for clarity.
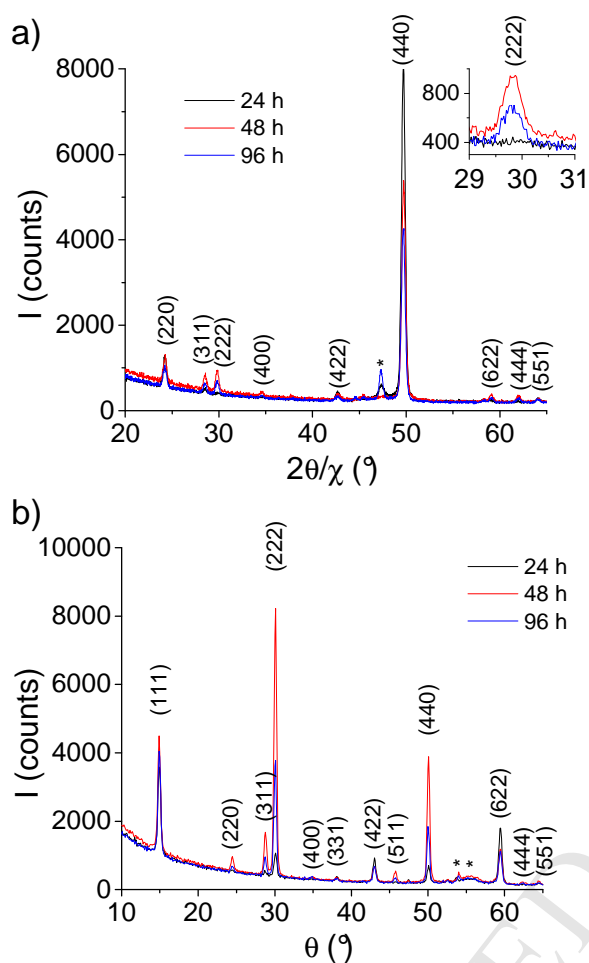
Figure 2 In-plane XRD (a) and GIXRD (b) diffraction patterns of CuCr$_2$Se$_4$ films annealed for 24 h, 48 h, and 96 h. Reflections denoted by an asterisk are reflections from the substrate. The inset shows the intensity of the (222) reflection in the in-plane XRD scan.

Figure 3: Rietveld refinement of the sample annealed for 24 h. The inset shows the layered model that was used for the refinement of the atomic planes along the [111] direction. The solid lines indicate the length of the repeat unit corresponding to $\frac{\sqrt{3}a}{3}$ and the dashed line displays the position of the mirror plane. The red, black and blue line show the measured intensity, the calculated intensity and the intensity difference, respectively.
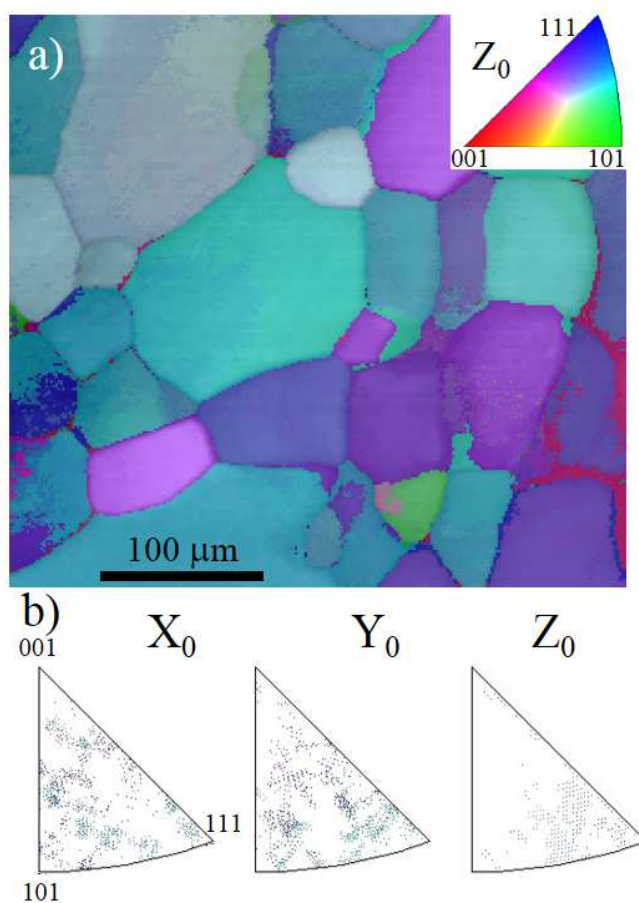
Figure 4 (a) Map of crystallographic orientations from precession electron diffraction. (b) Orientation distribution along the x, y, and z axis (z axis parallel to surface normal of the film).
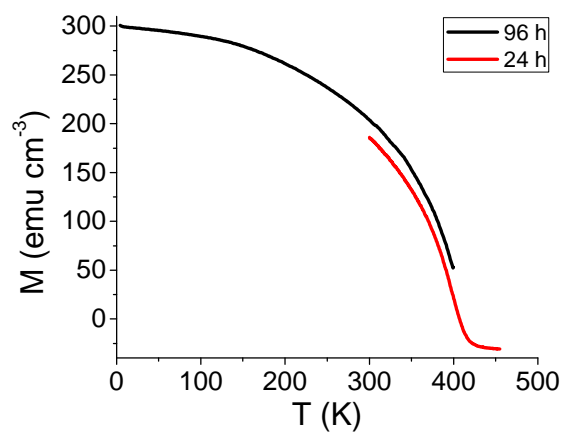
Figure 5 Representative temperature-dependent magnetization curves for samples annealed for 24 h, and 96 h.
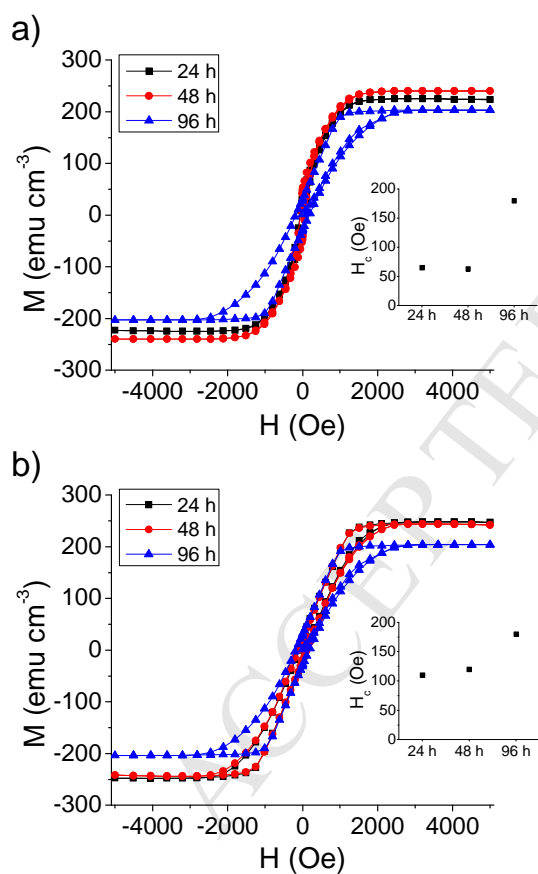
Figure 6 Room temperature magnetization hysteresis (a) in plane and (b) out of plane. The insets show the coercive forces H_c as a function of annealing time.

Highlights

Crystallographically aligned, phase pure $CuCr_2Se_4$ were synthesized.

The degree of alignment decreases with annealing time.

The films are ferromagnetic with the easy axis along the <111> direction.

The magnetization is larger than bulk $CuCr_2Se_4$ or other $CuCr_2Se_4$ films made to date.