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Magnetocapacitance in $CdCr_{1.8}In_{0.2}S_4$ single crystal annealed in cadmium vapor

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$CdCr_2S_4$ single crystal was reported by Hemberger et al. to be multiferroic with evidences of relaxor ferroelectricity and colossal magnetocapacitance (CMC), but whether these effects are intrinsic is under debate. Recently, we reported a one-to-one correlation between CMC and colossal magnetoresistance (CMR) in $CdCr_2S_4$ polycrystalline samples, and argued that CMC could be explained by the superposition of CMR and Maxwell-Wagner effects. In this paper, we further examined magnetic, dielectric and electric transport properties of $CdCr_2S_4$ and $CdCr_{1.8}In_{0.2}S_4$ single crystal before and after annealing in cadmium vapor. $CdCr_2S_4$ single crystal sample has no relaxor ferroelectricity and CMC, in contrast with $CdCr_2S_4$ single crystal reported by Hemberger et al. Only the annealed $CdCr_{1.8}In_{0.2}S_4$ displays CMC, but still does not exhibit relaxor behavior. At the same time, it also shows CMR. All these results are in accord with results of our polycrystalline samples, and further confirm the resistive origin of CMC in $CdCr_2S_4$ system.

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I. INTRODUCTION

Multiferroics which combine coupled electric and magnetic dipoles have attracted special interest in recent years.[1-3] $CdCr_2S_4$ single crystal was reported to be multiferroic with evidences of relaxor ferroelectricity and colossal magnetocapacitance (CMC).[4] However, the emergence of these effects is sensitive to sample preparation. Annealing the single crystal in vacuum or sulphur atmosphere led to a suppression of relaxation features and no remanent polarization was found at low temperatures.[5] Moreover, these magnetoelectric effects are absent in the undoped polycrystal,[5] but present in the indium doped one.[6] First principles calculations exclude softening of the polar modes as an origin of the anomalous dielectric responses.[7] Catalan and Scott suggested that the multiferroic behaviors in $CdCr_2S_4$ were extrinsic, which resulted from the residual chlorine impurities in single crystals.[8] Nevertheless, Hemberger et al. replied that they had excluded any inhomogeneous impurity distribution by electron probe microanalysis and X-ray studies.[9] Raman spectra on $CdCr_2S_4$ single crystal shows some phonon anomalies that are evidences for Cr off-centering, and the resulting enhanced electronic polarizability of displacements that modulate Cr-S distance is proposed as a microscopic mechanism for CMC.[10] High-resolution X-ray diffraction of $CdCr_2S_4$ polycrystal established the dynamical off-centering of Cr ions caused by the presence of simultaneous polar and magnetic nanoclusters.[11] These results are in favor of the viewpoint that the multiferroic behaviors in $CdCr_2S_4$ were intrinsic. However, recently we reported an one-to-one correlation between CMC and colossal magnetoresistance (CMR) in $CdCr_2S_4$ polycrystalline samples,[12] and argued that CMC is extrinsic due to the superposition of CMR and Maxwell-Wagner effects.[13] Furthermore, thermoelectric-power and electronic spin resonance spectra reveal that the magnetic polaron is responsible for CMR, and the existence of magnetic polarons in the paramagnetic insulating matrix forms an intrinsic Maxwell-Wagner system, leading to the appearance of CMC.[14]

One may suspect our experimental results due to the use of polycrystalline samples, so we further studied magnetic, dielectric and electric transport properties of $CdCr_2S_4$ and $CdCr_{1.8}In_{0.2}S_4$ single crystal before and after annealing in cadmium vapor. Neither as grown and annealed $CdCr_2S_4$ nor as grown $CdCr_{1.8}In_{0.2}S_4$ have relaxor ferroelectricity and CMC, in contrast with $CdCr_2S_4$ single crystal reported by Hemberger et al.[4] Only the annealed $CdCr_{1.8}In_{0.2}S_4$ displays CMC, but still shows no relaxor behavior. At the same time, it also exhibits CMR. All these results are in consistent with results of our polycrystalline samples, and further confirm the resistive origin of CMC in $CdCr_2S_4$ system.

II. EXPERIMENTAL

$CdCr_2S_4$ and $CdCr_{1.8}In_{0.2}S_4$ single crystal samples were grown by chemical vapor transport method using $CrCl_3$ as transport agent. The annealing treatment was performed by heating the sample together with some cadmium metal particle in the quartz tube at 380 °C. The chemical compositions of these samples were determined using an energy-dispersive x-ray spectrometer (EDXS). The magnetic properties were measured using a superconducting quantum interference device (MPMSXL-7) magnetometer. Dielectric measurements were performed using an LCR meter (TH2828S) integrated to MPMS. Electric field was applied perpendicular to the magnetic field. The resistivity of the annealed $CdCr_{1.8}In_{0.2}S_4$ was measured by Keithley 2400 source meter integrated to physical properties measurement system (PPMS).

III. RESULTS AND DISCUSSION

The EDXS results of these samples reveal almost ideal stoichiometry and no chlorine doping is detected. The temperature dependence of the normalized magnetization M(T)/M(5K) in zero-field-cooled (ZFC) process under an external magnetic field of 100 Oe for all samples are shown in Fig. 1. It can be found that, after annealing in cadmium vapor, the magnetic properties of both $CdCr_2S_4$ and $CdCr_{1.8}In_{0.2}S_4$ polycrystal are nearly unchanged.

For $CdCr_{1.8}In_{0.2}S_4$ samples, the temperature dependence of magnetization shows a step-like transition at about 12 K. Below this temperature, the magnetization decreases with decreasing temperature. The Curie temperature T_C, defined as the temperature at which |dM/dT| reaches maximum, is about 76 K for $CdCr_{1.8}In_{0.2}S_4$. This value is lower than the corresponding one (about 87 K) for $CdCr_2S_4$. All these features are in consistent with previous reports about indium doped $CdCr_2S_4$.[15,16]

Figure 2 displays the temperature dependence of dielectric constant ε' at four different frequencies for the as-grown and annealed $CdCr_2S_4$ samples. The as-grown $CdCr_2S_4$ has a similar magnitude of ε' as $CdCr_2S_4$ polycrystal reported in Ref. 5. ε' increases with temperature monotonously and does not show any anomaly around T_C. This monotonic behavior is in contrast with $CdCr_2S_4$ single crystal reported by Hemberger et al,[4] and suggests our as-grown $CdCr_2S_4$ single crystal has no CMC. Compared with the as-grown sample, the annealed one has a much larger ε', but ε' still increases with temperature as in the case of the as-grown sample.

Figure 3 shows the temperature dependence of ε' at four frequencies for the as-grown and annealed

CdCr1.8In0.2S4 samples. Both the magnitude and the temperature dependence of the as-grown $CdCr_{1.8}In_{0.2}S_4$ are similar to those of the as-grown $CdCr_2S_4$. The monotonic temperature dependence of ε′ suggests the as-grown $CdCr_{1.8}In_{0.2}S_4$ still does not have CMC. In contrast, for the annealed $CdCr_{1.8}In_{0.2}S_4$, a strong upturn of ε′ is clearly observed with decreasing temperature near T_C. As can be seen in Fig. 4(a), the magnetic field of 4.5 T does not change the shape of ε′~T curve, but makes the upturn of ε′ shifting towards a higher temperature. Magnetocapacitance, defined as MC=(ε′(4.5T)-ε′(0T))/ε′(0T), reaches up to 140% and 1320% for 100 Hz and 600 kHz, respectively (Fig. 4(b)). These results are in accord with the experimental results reported in Ref. 4. However, similar to $CdCr_2S_4$ single crystal reported by Sun et al,[17] our annealed $CdCr_{1.8}In_{0.2}S_4$ sample does not show the relaxor behavior as reported in Ref. 4.

Recently, we reported an one-to-one correlation between CMC and CMR in a series of $CdCr_2S_4$ polycrystalline samples,[12] and argued that CMC could be explained by the combination of CMR and Maxwell-Wagner effects.[13] In order to investigate whether this explanation about CMC is also applicable to the annealed $CdCr_{1.8}In_{0.2}S_4$ single crystal, we measured the DC-resistivity of this sample under external magnetic field of 0 T and 4.5 T, as shown in Fig. 5(a). the zero-field resistivity first increases with decreasing temperature. After reaching to a maximum near T_C, the resistivity decreases abruptly, indicting the occurrence of insulator-metal transition. Being correlated to this transition, the magnetic field of 4.5 T makes the resistivity peak move to a higher temperature and dramatically depresses the peak value. Magnetoresistance, defined as MR=(ρ(0T)-ρ(4.5T))/ρ(0T), reaches up to about 99%, as can be seen in Fig. 5(b).

From the above-mentioned experimental results, we can know that dielectric and electric transport properties of $CdCr_2S_4$ single crystals are also quite sensitive to the detail of sample preparation and chemical doping as our previous reported $CdCr_2S_4$ polycrystalline samples. Similar to the case of polycrystal, in a series of $CdCr_2S_4$ single crystal samples reported in this paper, only the indium doped sample after annealing possesses CMC. This similarity indicates that the magnetocapacitance of $CdCr_2S_4$ is due to a magnetoresistive artifact and is unrelated to multiferroicity. One may suspect that exchange striction could be the origin of CMC as proposed in Ref. 17, because $CdCr_2S_4$ shows negative thermal expansion[18-20] and magnetostriction[20]. However, $CdCr_2S_4$ single crystal which does not display these phenomena also have CMC,[21] revealing that exchange striction is not suitable to explain CMC in $CdCr_2S_4$ system.

IV. CONCLUSIONS

In summary, we studied magnetic, dielectric and electric transport properties of $CdCr_2S_4$ and $CdCr_{1.8}In_{0.2}S_4$ single crystal before and after annealing in cadmium atmosphere. $CdCr_2S_4$ single crystal samples have no relaxor ferroelectricity and CMC, in contrast with the sample reported by Hemberger et al. The annealed $CdCr_{1.8}In_{0.2}S_4$ displays both CMC and CMR, but still does not show relaxor behavior. All these results are in accord with results of our polycrystalline samples, and further confirm the resistive origin of CMC in $CdCr_2S_4$ system.

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Figures and Captions:

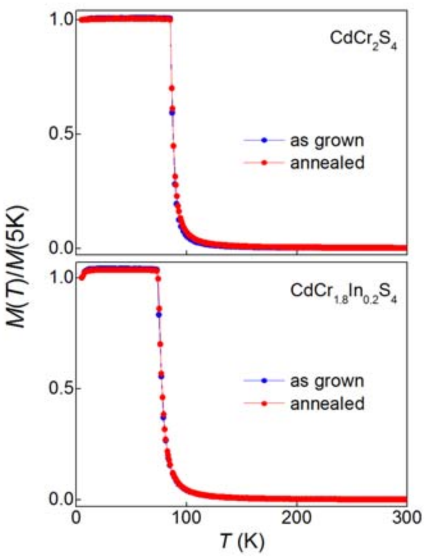

Figure 1. Temperature dependence of the normalized magnetization M(T)/M(5K) in zero-field-cooled (ZFC) process under an external magnetic field of 100 Oe for $CdCr_2S_4$ (upper frame) and $CdCr_{1.8}In_{0.2}S_4$ (lower frame).

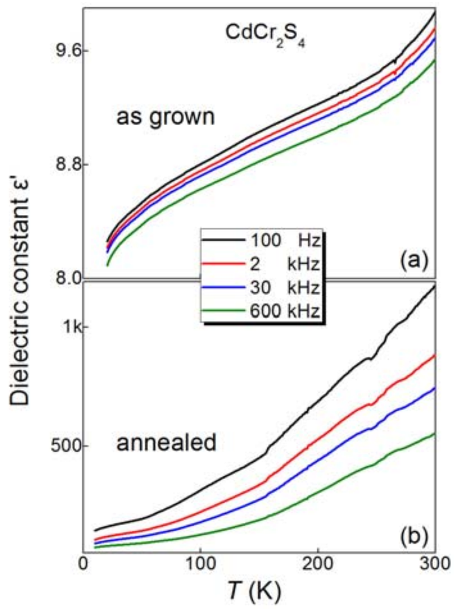

Figure 2. Temperature dependence of dielectric constant ε′ at four different frequencies for (a) as-grown and (b) annealed $CdCr_2S_4$.

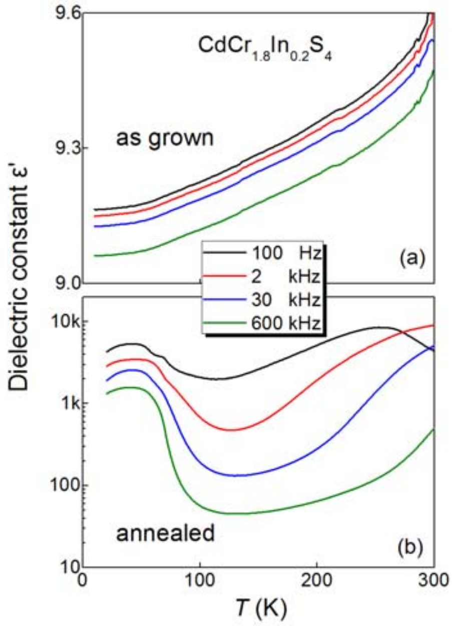

Figure 3. Temperature dependence of ε′ at four frequencies for as-grown (upper frame) and annealed (lower frame) $CdCr_{1.8}In_{0.2}S_4$.

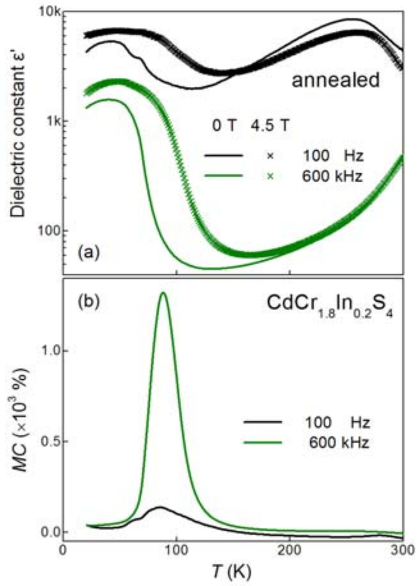

Figure 4. Temperature dependence of (a) ε′ in magnetic field of 0 T and 4.5 T and (b) the corresponding magnetocapacitance defined as MC=(ε′(4.5T)-ε′(0T))/ε′(0T) deduced from (a).

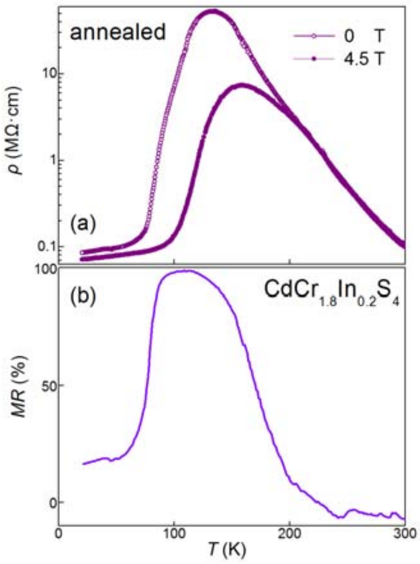

Figure 5. Temperature dependence of DC-resistivity under the magnetic field of 0 T and 4.5 T for the annealed $CdCr_{1.8}In_{0.2}S_4$ (upper frame). The corresponding magnetoresistance defined as MR=(ρ(0T)-ρ(4.5T))/ρ(0T) (lower frame).