Effects of Fe^{2+} substitution on magnetic and dielectric properties of $CdCr_2S_4$*

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(Received 18 March 2011; revised manuscript received 19 April 2011)

The magnetic and dielectric properties of polycrystalline $Cd_{1-x}Fe_xCr_2S_4$ ($0 \leq x \leq 0.9$) are investigated. Upon substitution of Cd by Fe, the Curie temperature (T_C) is increased while the saturation magnetization is decreased. A low doping level of Fe increases the permittivity, while a high doping level decreases the permittivity, which is explained by the internal barrier layer capacitor model. Kinks are observed in the temperature-dependent permittivity and loss tangent near T_C for the samples with $x = 0.5$, 0.7, 0.9, implying the existence of the magnetodielectric effect. Furthermore, with the increase of Fe content, a decrease of anomaly deviation rate induced by internal molecular field is revealed in the permittivity, while an increase is observed for the loss tangent.

Keywords: $Cd_{1-x}Fe_xCr_2S_4$, solid state reaction, magnetism, permittivity

PACS: 75.80.+q, 77.84.–s, 75.50.Gg, 75.30.–m **DOI:** 10.1088/1674-1056/20/9/097503

1. Introduction

Multiferroic materials in which more than one ferroic order (magnetic, electric or elastic) coexist and couple with each other, have recently attracted a surge of attention due to their potential applications in novel magnetoelectric (ME) and magneto-optical devices.[1−7] In particular, in magnetic order induced ferroelectrics, coupling between the magnetic and dielectric properties is expected. A large magnetodielectric (MD) effect can be expected in such materials. However, few magnetic ferroelectrics have been found since the conventional mechanism of ferroelectricity in perovskites, an off-centering structure distortion corresponding to the d^0 nonmagnetic electron configuration, is incompatible with the magnetic ordering which requires active d electrons.[8] In 2006, Catalan[9] proposed a scenario where the magnetocapacitance (MC) effect could also be achieved through a combination of magnetoresistance (MR) and the Maxwell–Wagner effect without ME coupling.[9] Many MC materials such as some mixed-valence manganites[7,10] and relaxor-like selenides,[11,12] have been assumed to belong to this group.

Among the MC materials, ACr_2S_4-type chalcogenide-chromium spinels, such as $CdCr_2S_4$ and $HgCr_2S_4$, are interesting in that they exhibit the simultaneous occurrence of colossal magnetocapacitance (CMC) and colossal magnetoresistance (CMR)[12−14] effects. Their CMC effect was attributed to a speeding up of the dielectric relaxational dynamics during the magnetic phase transition.[15] One cannot rule out a possible contribution to the CMC effect from the combination of the Maxwell–Wagner effect and the CMR effect observed in this system.[11,12] It is reported that Fe doped $CdCr_2S_4$ shows a modified CMR effect due to the introduced charge carriers.[16] Thus, we could reasonably speculate that the Fe^{2+} substitution for Cd^{2+} will considerably modulate the permittivity and CMC effect in $CdCr_2S_4$. Our previous study already indicated the large MD effect induced by the internal molecular field in the Fe^{2+} doped $CdCr_2S_4$ ($x = 0.5$).[17] It exhibited an enhanced Curie temperature (T_C) compared with that of the undoped polycrystalline $CdCr_2S_4$ and was assumed to have a possible resistive origin of the MD effect due to its CMR effect.[16] Here, we present a detailed study of the influence of A-site Fe^{2+} doping

*Project supported by the National Natural Science Foundation of China (Grant No. 10874228) and the National Basic Research Program of China (Grant No. 2010CB833102).

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on magnetic and dielectric properties by substituting Fe^{2+} for Cd^{2+} in $CdCr_2S_4$.

2. Experiment

The cubic spinels $Cd_{1-x}Fe_xCr_2S_4$ with $x = 0$, 0.1, 0.3, 0.5, 0.7, 0.9 were synthesized by a solid state reaction. A stoichiometric powder mixture of FeS (99.9%), CdS (99.9%), and Cr_2S_3 (99%) from the Alfa Aesar company was well ground, then pressed into pellets and sealed into evacuated quartz tubes. The tubes were heated to 750 °C and maintained for a week. The samples were characterized by X-ray diffraction (XRD), type Rint 2400, with graphite monochromatized Cu $K\alpha$ radiation. DC magnetizations were recorded by a physical property measurement system (PPMS, Quantum Design). To perform the electric measurements, the samples were polished into thin plates with a typical thickness of about 0.4–0.6 mm. Ag was used to make the electric contact for the dielectric measurements. Dielectric measurements were performed on an Agilent 4294A precision impedance analyzer in a frequency range of 30 kHz–1 MHz.

3. Results and discussion

As shown in Fig. 1, all the X-ray diffraction peaks of $Cd_{1-x}Fe_xCr_2S_4$ ($0 \leq x \leq 0.9$) can be indexed successfully using a cubic structure (space group: $Fd3m$). The intensity varies in (111) peak with Fe content which can be interpreted as the change in total structure factor due to the substitution of Cd atoms by Fe atoms. Rietveld refinement via Fullprof program[18] also reveals the substitution of Fe^{2+} ions for Cd^{2+} ions. The lattice constant decreases linearly with the increase of Fe concentration (the insert in Fig. 1), which is attributed to the smaller ionic radius of the Fe^{2+}.

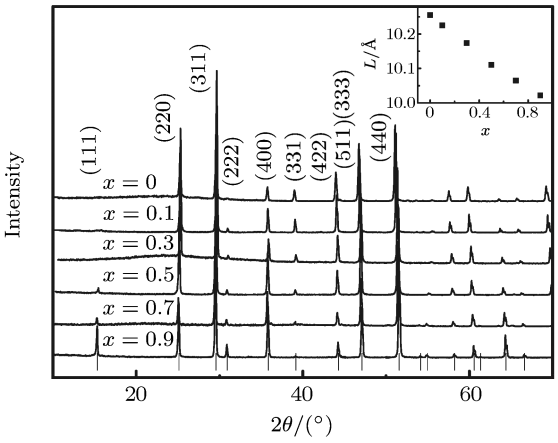


Fig. 1. X-ray diffraction patterns for $Cd_{1-x}Fe_xCr_2S_4$ ($0 \leq x \leq 0.9$). The insert shows the lattice parameters L versus doping level x for all the samples.

Figure 2 shows the temperature dependences of the zero-field-cooled (ZFC) magnetization of $Cd_{1-x}Fe_xCr_2S_4$ in a magnetic field of 1 kOe (1 Oe=79.5775 A/m) from 2 K to 300 K for different doping levels. All the samples undergo a transition from the paramagnetic to ferromagnetic (PM–FM) phase, and the transition temperature T_C increases monotonically with Fe content, from 87 K for $x = 0$ to 163 K for $x = 0.9$ (the insert in Fig. 2). The magnetic field dependent magnetization curves at 2 K (Fig. 3) show that full saturation can be achieved under a field of about 1T for all of the samples. The undoped sample has a saturation value of $6\mu_B$/f.u. (f.u. represents the formula of $Cd_{1-x}Fe_xCr_2S_4$), exactly corresponding to two Cr^{3+} spins at B-sites. For the doped sample, the extracted saturation magnetization decreases linearly at a rate of 4.77 μ_B per Fe^{2+} ion (the insert in Fig. 3), indicating that the spins of Fe^{2+} and Cr^{3+} are aligned to be anti-parallel to each other due to exchange interactions between them. The effective moment of 4.77 μ_B per Fe^{2+}, larger than the theoretical value of 4 μ_B, suggests the formation of Cr^{2+} ions in the low-spin state due to sulfur deficiency during the sintering process.[19–21]

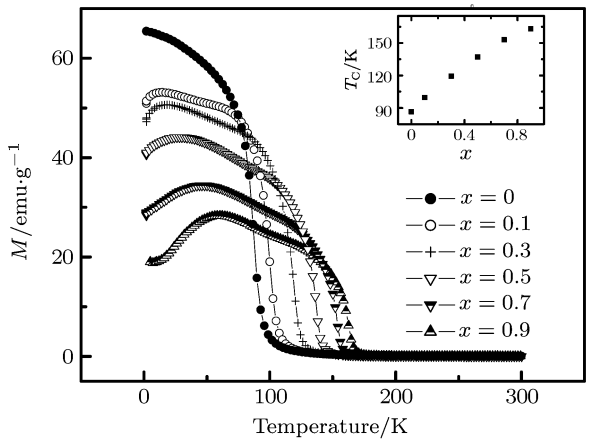


Fig. 2. Temperature dependences of magnetization for $Cd_{1-x}Fe_xCr_2S_4$ ($0 \leq x \leq 0.9$) under a magnetic field of 0.1 T by ZFC for all of the samples (1 emu=10^{-3} A·m^2). The insert shows the Curie temperatures T_C versus the doping x, accordingly.

Figure 4 presents the temperature and frequency dependences of permittivity (ε) and loss tangent ($\mathrm{tg}\,\delta$) for the samples with $x = 0.1$, 0.5, 0.7, and 0.9. As can be seen, both the permittivity and the loss tangent decrease with an increase in frequency for all of the

samples. At a low frequency (30 kHz), the relative permittivity increases more than 15 times from 18 at 100 K to 300 at 300 K for $x = 0.1$. This strong low-frequency dispersion is due to the Fe^{2+} dopants in which high densities of thermally activated hopping polarons dominate the permittivity behaviour.[22–24] This is in accordance with the resistance experiments on polycrystalline $Cd_{1-x}Fe_xCr_2S_4$ where the Fe^{2+} doping modulates the carrier density, leading to polarons increasing with the Fe content.[16,25]

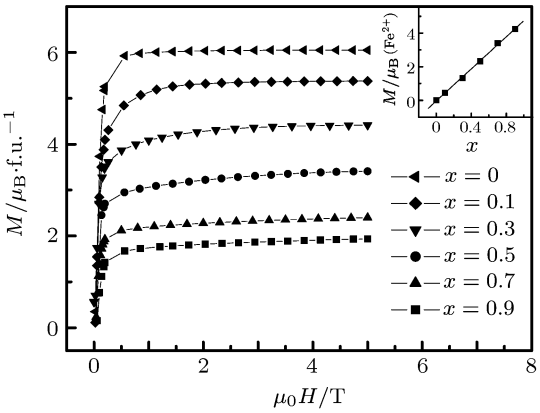


Fig. 3. Magnetic field dependences of magnetization for $Cd_{1-x}Fe_xCr_2S_4$ ($0 \le x \le 0.9$) at 2 K. The insert shows the effective Fe^{2+} contribution to magnetization with x increasing. The solid line is a linear fitting curve to the data.

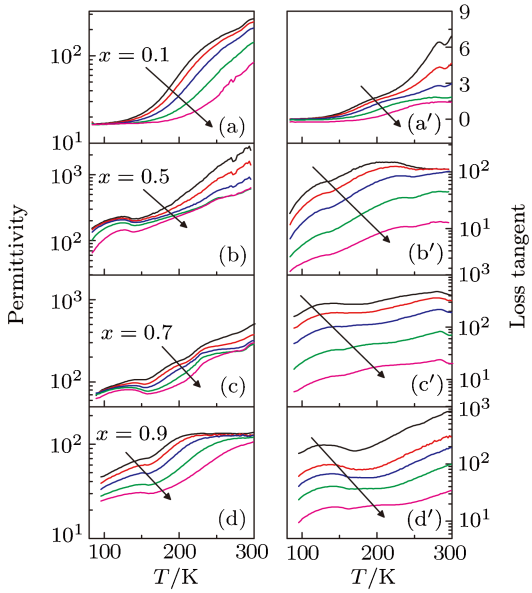


Fig. 4. (colour online) Temperature dependences of permittivity ((a)–(d)) and loss tangent ((a′)–(d′)) of $Cd_{1-x}Fe_xCr_2S_4$ ($x = 0.1$, 0.5, 0.7, and 0.9) at various frequencies (from top to bottom: 30 kHz, 50 kHz, 100 kHz, 300 kHz, 1 MHz). The arrows indicate the directions of increasing frequency.

The Fe^{2+} doping-dependence of the permittivity and loss tangent at 100 K are plotted in Figs. 5(a) and 5(b), respectively. One can see that the increase of Fe content increases the loss tangent while decreasing the permittivity ($0.5 \le x \le 0.9$), which represents the trends of permittivity and loss tangent with Fe content x in a temperature region of 100–300 K. These results might be related to the high density carriers due to the Fe^{2+} substitution for Cd^{2+}.[16] It is well known that the two end member compounds $CdCr_2S_4$ and $FeCr_2S_4$ are insulating and semiconducting, respectively. In between, doped Fe^{2+} enters A-sites randomly, leading to an inhomogeneous distribution of Cd^{2+} and Fe^{2+} ions. Thus, we introduce the internal barrier layer capacitor (IBLC) model to describe our samples' permittivity behaviour.[26–28] In the case of the IBLCs, extrinsic permittivity is generated by boundary capacitance between the spatially separated semiconducting regions (Fe^{2+} rich) and insulating barriers (Cd^{2+} rich) in our samples. Therefore, the permittivity increases with x until $x = 0.5$ where the one-to-one Fe^{2+}/Cd^{2+} ratio produces the maximum IBLC capacitance. The further increase of x leads to a decrease in the number of the insulating regions and correspondingly a reduction in the measured permittivity.

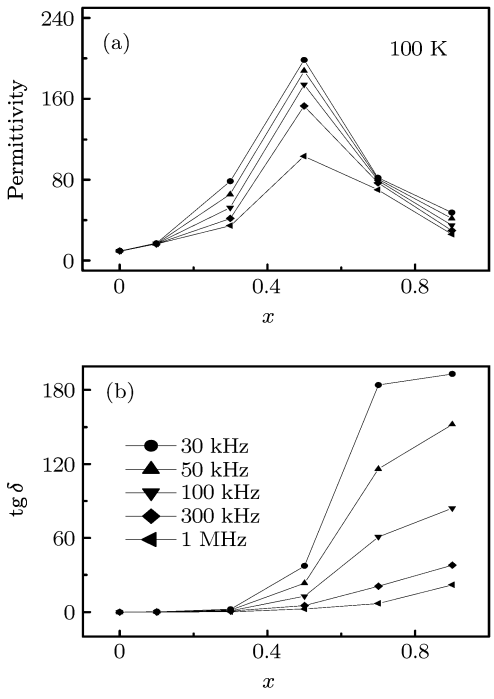


Fig. 5. Permittivity and loss tangent dependences of Fe^{2+} content at 100 K under various frequencies for $Cd_{1-x}Fe_xCr_2S_4$ ($0 \le x \le 0.9$).

On the other hand, the imaginary part of permittivity is mainly from the bulk conductivity, which, in the case of the $Cd_{1-x}Fe_xCr_2S_4$ system, arises from the nearest-neighbour hopping of magnetic polarons.[16]

Therefore, the increase of Fe content causes the decrease of the average distance between Fe^{2+} ions, leading to an increase in the loss tangent. One may evaluate the loss tangent by using the following formula:[26]

$$\mathrm{tg}\delta = 1/(\omega R_{\mathrm{ins}} C_{\mathrm{p}}) + \omega R_{\mathrm{sc}} C_{\mathrm{p}}, \quad (1)$$

where R_{sc} and R_{ins} represent the resistances resulting from semiconducting regions (Fe^{2+} rich) and insulating barriers (Cd^{2+} rich), respectively, and C_{p} is the capacitance of the parallel-plate capacitor made of the disk sample. In a frequency range of 30 kHz–1 MHz, both terms come into play, resulting in an increase of the loss tangent with the increase in Fe^{2+} content. Consequently, according to the resistance experiments,[16] larger resistivity yields larger permittivity and a smaller loss tangent, indicating that the permittivity has a resistive contribution. Furthermore, a Maxwell–Wagner type contribution to the permittivity is possible since the two-point probe method is used for the measurements. Metal–semiconductor contact often exhibits a high ohmic resistance, accompanied by a high capacitance due to the formation of a depletion layer at the metal-to-semiconductor interface.

In the temperature region near T_{C}, the temperature dependent permitivities and/or loss tangents each display an inverse S-shape anomaly for $x = 0.5$, 0.7 and 0.9, similar to those of the polycrystalline $YMnO_3$,[10] implying the existence of the MD effect induced by an internal molecular field (see Fig. 4). The relative deviations of the permittivity $(\varepsilon - \varepsilon_{T_{\mathrm{C}}})/\varepsilon_{T_{\mathrm{C}}}$[16] and loss tangent $(\mathrm{tg}\,\delta - \mathrm{tg}\,\delta_{T_{\mathrm{C}}})/\mathrm{tg}\,\delta_{T_{\mathrm{C}}}$ are calculated, where $\varepsilon_{T_{\mathrm{C}}}$ and $\mathrm{tg}\,\delta_{T_{\mathrm{C}}}$ represent the permittivity and loss tangent at T_{C}. For the samples with $x = 0.5$, 0.7 and 0.9 at a frequency of 30 kHz, the maximum deviations of permittivity are about 16.1%, 4.61%, 1.36% and those of the loss tangent are 0.05%, 0.18%, and 23.4%, respectively. These values reveal that the anomaly deviation decreases in permittivity, but it increases in loss tangent, with an increase in Fe content. It seems that the increase of the deviation rate in loss with the increase of x correspondingly leads to a decrease of the deviation rate in permittivity. Based on the results of the resistance experiments,[16] electron doping via the substitution of Fe for Cd enhances the carrier density and reduces the magnetoresistance. It is interesting that the trend of variation in MD induced by the internal molecular field with x is consistent with that of MR, implying a close correlation between MD and MR effects. For a material with the simultaneous occurrence of MC and MR combined with the Maxwell–Wagner effect, one could expect to find out whether MC has a resistive contribution by measuring the loss tangent and magnetolosses (ML) effect with care. Further studies should be carried out on single crystal samples.

4. Conclusions

The magnetic and the properties are investigated in polycrystalline samples of $Cd_{1-x}Fe_xCr_2S_4$. The permittivity reaches a maximum at the doping level of $x = 0.5$, then decreases with the further increase of Fe content, while the loss tangent keeps rising for all doping levels. In the present paper, an IBLC model is introduced. The samples with $x = 0.5$, 0.7, and 0.9 exhibit anomalies in permittivity and loss tangent, induced by the internal magnetic field near their Curie temperatures. The decrease of the anomaly deviation rate in permittivity and the corresponding increase in the loss tangent with the increase of Fe content are observed.

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