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Multicaloric effect in multiferroic sulpho spinel MCr_2S_4 (M = Fe & Co)

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ABSTRACT

We observe a rare occurrence of multiple caloric effects in multiferroic $FeCr_2S_4$ & $CoCr_2S_4$ compounds having a spinel structure. The significant magnetic entropy changes of ~3.72 J kg^{-1} K^{-1} and 3.99 J kg^{-1} K^{-1} are observed in $FeCr_2S_4$ & $CoCr_2S_4$, respectively, for a magnetic field change of 0–50 kOe at the paramagnetic to ferrimagnetic transition (T_N). At T_N large magnetoresistances are also observed as ~17% and ~10.2% for $FeCr_2S_4$ & $CoCr_2S_4$, respectively, for applied magnetic field 50 kOe. On the other hand, the electrocaloric entropy are also found considerable as ~0.56 J-m^{-3} K^{-1} and 1.24 J-m^{-3} K^{-1} for a small electric field change of 0–100 kV/m at the ferroelectric transition temperature (T_C) for $CoCr_2S_4$ & $FeCr_2S_4$, respectively.

1. Introduction

Correlation between the magnetic and electrical response in a single phase material is crucial for technological applications such as magnetic sensors and read head devices in computer hard disks. Magnetoelectric multiferroics meet the above criterion for magnetoelectric coupling, which is interesting for fundamental interest and applications [1]. Recent advances in materials science have identified a couple of interesting materials that are promising for multifunctional properties including magnetoelectric coupling, magnetoresistance, multicaloric properties, etc. [2,3]. The sulpho spinel compounds are one of those interesting materials, which attract the community for multifunctional properties. For example, coexisting colossal magnetoresistance (CMR) and magnetocapacitance has been first addressed in the sulpho spinel multiferroic compound $HgCr_2S_4$ with spinel structure [4] followed by the observations in $CdCr_2S_4$ [5] and $FeCr_2S_4$ [6,7]. The origin of CMR associated with significant magnetocapacitance in these sulpho spinel compounds are different from commonly observed CMR in the manganite perovskites [7–9]. More studies are required for understanding the origin of these multifunctional properties, apart from that observed in the mixed-valent manganites. Besides the new and interesting CMR mechanism, the coexistence of CMR with multiferroicity in spinel compounds makes them technologically promising and attracts the community for finding new compounds with such diverse physical properties.

The solid state refrigeration technique involving magnetocaloric and electrocaloric effects is recognized as a promising mechanism for efficient cooling process. In multiferroics the coexistence of magnetic and electric ordering has additional advantages because of the cross magnetoelectric coupling, where one can tune magnetic polarization using the electric field and vice versa. Moreover, the occurrence of magnetocaloric effect (MCE) and electrocaloric effect (ECE) together in a chemically single phase material has additional benefits since either caloric effect is enhanced considerably in case of occurrence at the same temperature or the effect is distributed on a wide range of temperature for the appearance of the effects at different temperatures. Considering spinel multiferroic materials only, very few reports are available for caloric effects in $CdCr_2S_4$ [10], $Cd_{0.8}Cu_{0.2}Cr_2S_4$ [11], $MnCr_2O_4$ [12], and MnV_2O_4 [13]. Current interest in this field is centered on searching promising materials with second-order phase transition near room temperature where magnetization can be reversed by varying temperature and magnetic field. Analogous to the MCE effect, ECE is also promising for next-generation cooling technologies without emitting greenhouse gases that can replace conventional gas compression/expansion refrigeration. Furthermore, generating an electric field is not as difficult as producing a magnetic field. Thus ECE provides an effective platform for fabricating compact solid-state devices with high cooling power densities for on-chip thermal management of microelectronic, optoelectronic and biomedical devices [14–16]. Unlike MCE, ECE is not much explored till date, the application of ECE is mainly centered on

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