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Large magnetocaloric effect at Verwey point in nanocrystalline Fe_3O_4 thin films

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A comparative study of magnetocaloric effect (MCE) near Verwey transition temperature, $T_V = 120$ K, has been reported in two different types of nanocrystalline Fe_3O_4 thin films. These films were laser ablated either directly on pre-heated substrate or they were post heat treated. The dominant ferrimagnetic order over superparamagnetic has been observed in the whole temperature (5–300 K) range. The entropy change, ΔS was derived from the measurements of magnetization, $M(H,T)$ curves at defined temperature intervals across the Verwey transition. These films show maxima $\Delta S_M = 2-12$ J/kg K around T_V at applied field of 1 T. The value of ΔS_M strongly depends upon method of heat treatments, and they are found to be two orders of magnitude higher than those reported in nanoferrites powder and comparable to many conventional giant MCE materials.

1. Introduction

Recent advances in Nano/Micro Electro Mechanical Systems (NEMS/MEMS) [1] have propelled a new interest in miniaturization of the cooling techniques (cooler on a chip). Moreover, the industrial demand to systematically reduce the size of these devices is also fuelling new research at nanoscale [1]. Compressorless refrigeration, namely, solid state based magnetic refrigeration (large thermal changes driven by a magnetic field) is a significant development for energy-efficient and eco-friendly future technologies such as gas liquefaction, space missions and air conditioning applications [2]. Current studies on magnetocaloric effect (MCE) are limited and focussed only onto bulk rare-earth based alloys and perovskite-type manganese oxides [1–3]. The prerequisite for NEMS/MEMS i.e. range of thin film geometries for MCE materials remains yet unexplored [4]. However, it is also very problematic to grow rare-earth binary and ternary alloys that exhibit giant MCE in thin film form while preserving their stoichiometry and anticipated properties [3]. Existing MCE bulk materials mainly rely on the maximum entropy change associated with magnetic transitions (Curie point and Néel point) [2,4], which must be overcome by tuning the coupling between structural, magnetic and electronic degrees of freedom [3] and *via* external strain and growth of artificial geometries [5]. Recently, giant and reversible extrinsic MCE was obtained in ferromagnetic manganite ($La_{0.7}Ca_{0.3}MnO_3$) epitaxial films [5] using strain-mediated feedback from $BaTiO_3$ substrates near a first-order structural phase transition, which inspires the search for giant MCE in a wide range of magnetic materials. In the parallel development, nanostructured samples [4,6] can provide an alternative to conventional bulk MCE materials because of controlled size selection, dispersion, inter-particle interactions and high magnetic moments, which determines entropy change across spin blocking transition. Therefore, there is a constant urge for developing new MCE nanostructured materials with large surface area with a better heat exchanging capability –this infact, is a key factor to boost performance of next generation devices.

Versatile Fe_3O_4 material can be a potential contender for magnetic refrigeration owing to its various temperature driven transitions in between 5 and 1000 K [7–11]. For instant, bulk Fe_3O_4 exhibits paramagnetic to ferrimagnetic phase transition at high temperature of 850 K (T_N: Néel point) and then change of sign of magneto-crystalline anisotropy at low temperature of 130 K (T_S: Isotropic point) [9,10]. Crossing over 120 K (T_V: Verwey point), the ferrimagnetic phase of Fe_3O_4 undergoes structural transition from cubic ($Fd3m$) to monoclinic (Cc) [7–12]. A profound feature of

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