

RELATIVE COOLING POWER OF $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($0.0 \leq x \leq 0.03$)

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ABSTRACT

Manganite perovskite has a wide variety of potential applications as an advanced material, for example, in magnetic random access memory, spintronics, magnetoelectric, magnetic field sensors and cooling technology, based on magnetism and magnetic materials. In work on cooling technology, magnetic materials show a magnetocaloric effect. Manganite perovskite has some fundamental properties, such as Curie temperature, magnetic entropy change, temperature span and relative cooling power. Current works report detailed properties of manganite perovskite in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ doped with Cu, which show magnetocaloric effects. The samples were synthesized by a conventional solid state reaction. A small amount of doping Cu 1%~3% at a Mn site maintains the First-Order Magnetic Transition (FOMT) without leading into the Second-Order Magnetic Transition (SOMT). Maximum magnetic entropy change increased as the Cu-doped decreased. Introducing a small percentage of Cu-doped on $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ also implies decreasing the Curie temperature, T_C . For all samples under external application in a field of 10 kOe, these resulted in a slightly wider temperature span and the Relative Cooling Power (RCP) of about 39 J/kg to 47 J/kg as the Cu-doped decreased. The small amount of Cu-doping on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ keeps the rate of relative cooling power in a wider temperature range. It may be beneficial for cooling technology based on magnetism and magnetic materials.

Keywords: Cu-doped manganites; Magnetocaloric effect; Relative cooling power

1. INTRODUCTION

With a formula of $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R= rare earth La, Nd, Pr, etc. ; A = Ba, Ca, and Sr) around a ferromagnetic-paramagnetic phase transition temperature (the Curie temperature), manganite perovskite has been attracting attention among researchers for almost two decades (Mira et al., 1999; Wang et al., 2001; Phan et al., 2005a; El-Hagary et al., 2009; Koubaa et al., 2009; Wang et al., 2011). One well-known composition of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) with a transition metal on Mn site has attracted many investigations due to the tuneable $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, which implies easy achievable magnetic properties, especially a Magnetocaloric Effect (MCE). The doped Mn site also is tuned to the magnetic phase transition from a First-Order Magnetic Transition (FOMT) to a Second-Order Magnetic Transition (SOMT) (Phan et al., 2005a; Phan et al., 2012). Simply, the definition for FOMT is a phase transition that involves a discontinuity in the first derivative of free energy with respect to a thermodynamic variable, while on the other hand SOMT is a phase transition with continuous first derivatives of free energy, but

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discontinuous second derivatives (Franco et al., 2012).

The MCE of FOMT is able to concentrate in a narrow temperature range, whereas SOMT transitions are usually spread over a broad temperature range, which is preferable for Active Magnetic Refrigeration (AMR) (Gschneidner Jr et al., 2005; Brück, 2005; Phan et al., 2005b). A large magnetic entropy change in the Cu-doped manganites of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.05, 0.1$) leading to a FOMT show a sharp magnetization jump against temperature (Phan et al., 2005a). Although some authors did not mention in detail whether the magnetic phase transition of a small doped Cu in manganite perovskite leads to SOMT or FOMT; however, one can see how the magnetization jumps sharply versus the temperature of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ which leads to a FOMT (Phan et al., 2005a). Meanwhile, $\text{La}_{0.77}\text{Sr}_{0.23}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ and $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.85}\text{Cu}_{0.15}\text{O}_3$ lead to a SOMT (Phung et al., 2012a; El-Hagary et al., 2009). Obviously, $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$ leads to a SOMT (Phan et al., 2012).

Phan et al. (2005a) describe some advantages of the polycrystalline Cu-doped manganese perovskite materials. First, the samples are easier to fabricate and they possess a higher chemical stability as well as a higher resistivity than non-manganese perovskite materials. Second, the sample has a high resistivity, which is beneficial to lower the eddy of current heating. Thus, the advantages of the polycrystalline Cu-doped manganese perovskite materials also comply with the criteria for selecting magnetic refrigerants (Phan & Yu, 2007).

In order to investigate the magnetocaloric effect, it is preferable to determine the magnetic entropy change, ΔS_M , by an indirect method. This technique calculates isothermal magnetization rather than through the adiabatic temperature change, ΔT_{ad} , which is the temperature change of the material when adiabatically magnetized/demagnetized. From isothermal magnetization one can obtain magnetization measured at a discrete field and temperature intervals and the magnetic entropy change ΔS_M can be assessed as shown in Equation 1:

$$\left| \Delta S_M \right| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i, \quad (1)$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} under external field H , respectively. Figure 4 shows the maximum entropy change of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$ with a tendency to incline as the Cu-doped decreased.

In addition to the MCE behavior, another important property related to MCE is the Relative Cooling Power (RCP). RCP is the product of the $\Delta S_{M \max}$ and the full-width at half-maximum ($\delta T_{FWHM} = T_2 - T_1$) as shown in Equation 2:

$$RCP = -\Delta S_M(T, H) \times \delta T_{FWHM} \quad (2)$$

where T_1 and T_2 are the cold and the hot end temperature of a refrigerator in an ideal thermodynamic cycle (Franco et al., 2012; Phan & Yu, 2007). Here, we used non-linear fitting of a Gaussian function to define the working temperature (ΔT_{FWHM}) of the samples as the temperature span corresponding to the full width at half maximum of $\Delta S_{M \max}$.

Introducing Cu-doped on the LCMO decreased the Curie temperature, T_C , and led to a wider temperature span. Therefore, the RCP has a strong relation with 1%~3% of Cu doping to the Mn site of the LCMO. Thus, it is important to investigate the correlation between $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ with both its Relative Cooling Power and magnetic phase transition. Hereinafter, we report in detail.

2. EXPERIMENTAL METHODS

In this work, we investigated $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ (LCMCuO) with ($0.0 \leq x \leq 0.03$) which was synthesized by a conventional solid state reaction method. We used high-purity powders of La_2O_3 , CaCO_3 , CuO and MnCO_3 as precursors. Furthermore, the powders were combined in stoichiometric quantities, which were ground and mixed well, and then calcined at 900°C for 6 hrs. The mixtures obtained were pressed into pellets and sintered at 1300°C for 48 hours in the air with several re-grinding and sintering times. The crystal structure of the final products was examined by an X-ray diffractometer (Bruker AXS, D8 Discover) using $\text{Cu-K}\alpha$ radiation at room temperature. Magnetic properties of the samples were investigated by using a Vibrating Sample Magnetometer (VSM) in an applied field of 10 kOe.

3. RESULTS AND DISCUSSION

Figure 1 shows that the X-Ray Diffraction (XRD) of the crystal pattern structure of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($0.0 \leq x \leq 0.03$) was within an angle range of $20\text{--}90^\circ$ at room temperature. It appears that the XRD patterns from all of the samples have the same features in the XRD shape. There is no tendency for additional peaks, implying that the Mn site has been completely substituted by Cu. The Cu-doped resulted in a slight shift of the XRD intensity to a larger 2θ compared to the non-doped LCMO. Our work is similar to Zhang et al. (2012) in that diffraction peaks resulted in a shift to a higher angle as Cu-doped. Structural analysis demonstrates the samples to be single phase in an orthorhombic structure with a $Pbnm$ space group.

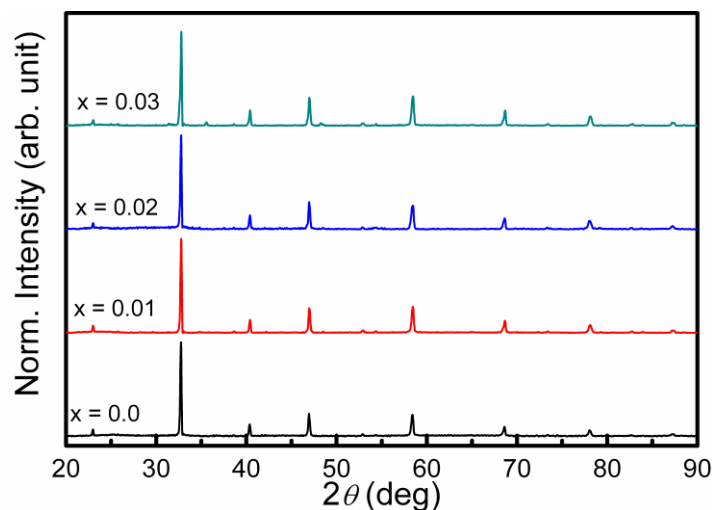


Figure 1 XRD pattern of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$ ($0.0 \leq x \leq 0.03$) at room temperature

After introducing rare earth or alkaline earth ions into the A-sites and based on the charge neutrality, one might expect a difference in $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and also a distortion of the original lattice that could be induced from the valence mismatch and difference of ionic radii. Introducing Cu^{2+} into Mn site then could replace Mn^{4+} due to a similar average ion radius of 0.066 nm between the two (Zhang et al., 2012). A slight shift to higher angles might be from the existence of Cu^{3+} , which has been reported by others (Zhou et al., 2002; Zhang et al., 2012).

Electrons itinerant among the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in an orthorhombic structure might change the magnetic and electrical properties of materials. Zener (1951) proposed a fundamental theoretical explanation of the Double-Exchange (DE) phenomenon, which later become a clear understanding of the MCE (Phan et al., 2004). Double-Exchange is an indirect interaction

achieved by coupling in a parallel alignment of the spin between Mn^{3+} and Mn^{4+} through oxygen ions. Another similar explanation is the so-called, Super-Exchange (SE) closely related to the DE, however, in SE the electrons do not actually move between the two metal positive ions. Therefore, a subsequent insertion of transition metals into the *B*-sites would influence the bonding geometry around the Mn cations that might be tunable. Consequently, the magnitude of the SE and DE interactions can be controlled.

Saturation magnetization versus temperature under a low homogeneous external magnetic field obtained a sharp jump as temperature increased for all samples (Figure not shown). Afterwards, we can compute an extreme point of the first derivative of magnetization versus temperature, which was defined as T_C . The value of T_C tended to decline as the Cu concentration increased. Phan et al. reported that 5% of the attempted Cu-doped resulted in T_C of 197 K (Phan et al., 2012), while in the present work the 3% Cu-doped experiment resulted in a T_C of 217 K which was in agreement with the T_C trend. However, their work already showed a SOMT while the present work maintains a FOMT. The value of T_C on the Cu-doped in our work follows a linear decreasing trend. T_C decreased as the Cu-doped concentration increased, which was also found in other reports (Phan et al., 2005a; El-Hagary et al., 2009). The T_C reduction was presumably due to the weakening of the DE interaction, which is probably because of the replacement Mn ions by the Cu ions that built an antiferromagnetic SE (Zhang et al., 2012; Kim et al., 2005).

The method used by the first derivative in order to distinguish whether the sample has a FOMT or SOMT behavior is not clear enough at the higher concentration of the Cu-doped. Therefore, we used another method known as the Banerjee criterion (Banerjee, 1964). By using the Banerjee criterion one can distinguish FOMT from SOMT by purely magnetic methods. This method consists of observation of the slope of the magnetic isotherm plots of the H/M versus M^2 , where M is the observed magnetization in the experiment and H is the magnetic field. The tendency of a positive or negative slope indicates a SOMT or FOMT, respectively.

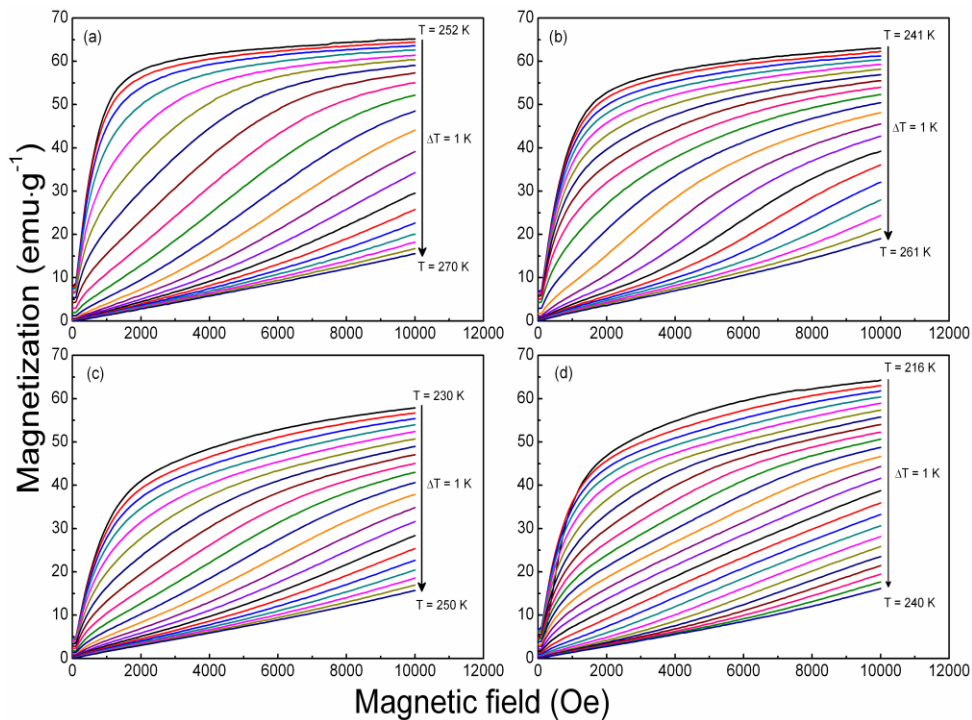


Figure 2 Isothermal magnetization curves for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$ with: (a) $x = 0.0$; (b) $x = 0.01$; (c) $x = 0.02$; and (d) $x = 0.03$

Figure 2 shows the saturation magnetization dependence of the magnetic field at various temperatures below and above T_C . All samples show that the magnetization has not reached saturation yet. The Banerjee criterion described above indicates that the sign of the slope of H/M versus M^2 results in negative slopes near the transition, thus corresponding to a FOMT as shown in Figure 3. Thus, the Cu-doped of 1%~3 % on the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$ resulted in a consistent FOMT.

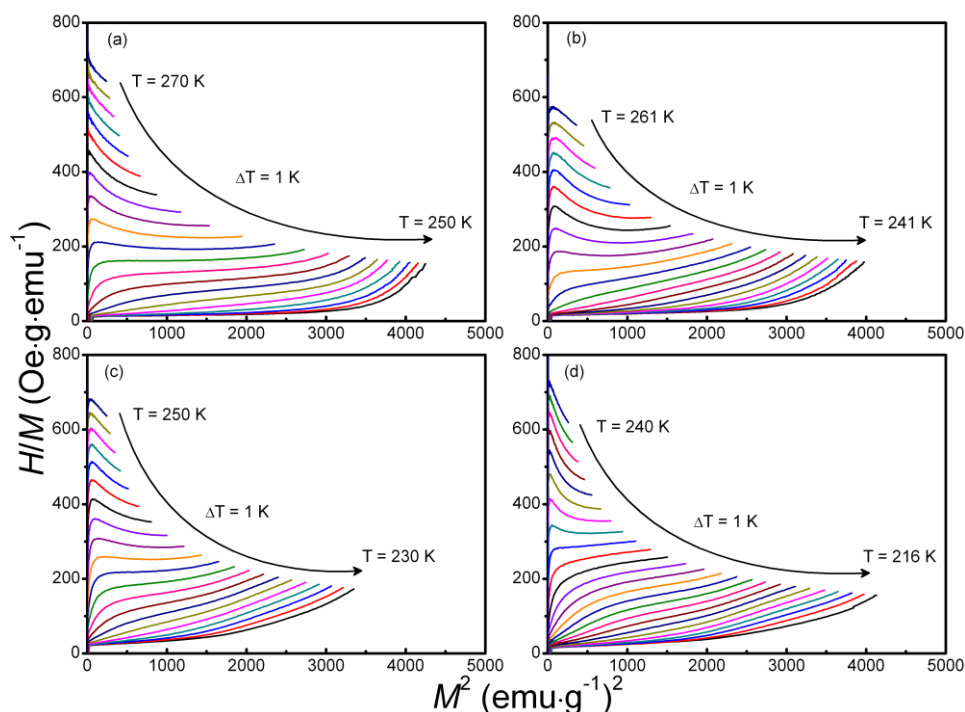


Figure 3 M^2 versus H/M curves for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$ with (a) $x = 0.0$, (b) $x = 0.01$, (c) $x = 0.02$ and (d) $x = 0.03$

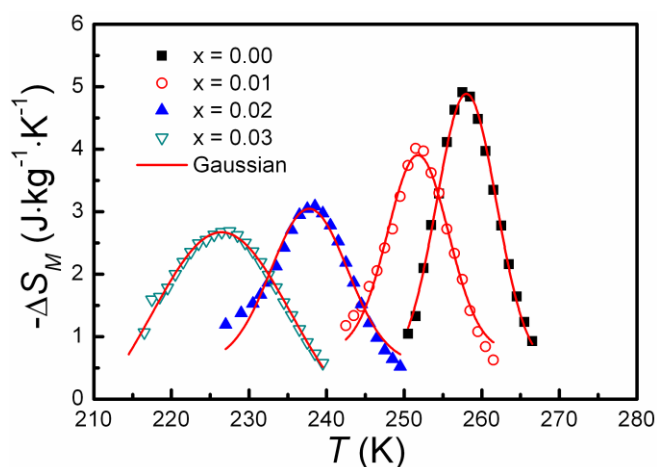


Figure 4 Magnetic entropy change function of temperature for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{MnO}_3$. Gaussian fitting guided determine temperature span for Relative Cooling Power

The small doped 1%~3% of the Cu-doped in the LCMO maintains the sample in a FOMT, which could be comprehended as maintaining the large magnetic entropy change. Moreover, the RCP value does not affect this result as much. Thus, the small Cu-doped on the

$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ system does not destroy the spin-lattice coupling interaction in the magnetic interaction which is responsible in the large magnetic entropy change (Phan & Yu, 2007). We resume in detail our work shown in Table 1, which indicates a comparison among the Cu-doped documented in some previously reported manganite perovskite samples.

Table 1 The magnetic phase transition, curie temperature (T_C), applied external field, maximum magnetic entropy change and relative cooling power

	T_C [K]	ΔH [T]	$-\Delta S_M$ [J/kgK]	RCP [J/kg]	Ref.
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$	350	1.35	1.96	39	(Chau et al., 2003)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.90}\text{Cu}_{0.10}\text{O}_3$	350	1.35	2.07	43	(Chau et al., 2003)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$	345	1.0	3.05	-	(Phan et al., 2005a)
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.90}\text{Cu}_{0.10}\text{O}_3$	347	1.0	3.24	-	(Phan et al., 2005a)
$\text{La}_{0.77}\text{Sr}_{0.23}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$	325	1.0	4.41	90	(El-Hagary et al., 2009)
$\text{La}_{0.77}\text{Sr}_{0.23}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$	293	1.0	2.68	62	(El-Hagary et al., 2009)
$\text{La}_{0.77}\text{Sr}_{0.23}\text{Mn}_{0.7}\text{Cu}_{0.3}\text{O}_3$	242	1.0	3.36	52	(El-Hagary et al., 2009)
$\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.85}\text{Cu}_{0.15}\text{O}_3$	194	1.5	2.10	85	(Phung et al., 2012b)
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	260	1.0	4.32	45	Present
$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Cu}_{0.01}\text{O}_3$	248	1.0	3.46	42	Present
$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.98}\text{Cu}_{0.02}\text{O}_3$	230	1.0	2.98	39	Present
$\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.97}\text{Cu}_{0.03}\text{O}_3$	217	1.0	2.74	47	Present

4. CONCLUSION

Polycrystalline $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($0.0 \leq x \leq 0.03$) is successfully synthesized by a conventional solid state reaction which performs as a first-order magnetic transition. The Curie temperature decrease is relatively small when compared to the other metal doped for example Sn. It is tunable about 35 K in the working temperature range towards a lower temperature. Under an external field of 10 kOe, the 1%~3% Cu-doped in the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ system resulted in a decrease in $-\Delta S_{M \max}$ but almost same RCP within a margin of experimental error because ΔT_{FWHM} became larger.

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