Strong Role of Calcination Temperature for Improving Magnetocaloric Effect in Nd_{0.5}Sr_{0.5}MnO₃ Prepared via Combustion Technique

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Strong role of calcination temperature for improving magnetocaloric effect in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ prepared via combustion technique

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Abstract

In this work, phenomenological model (PM) is used to simulate the magnetocaloric effect (MCE) of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (NSMO) sample synthesized at various values of temperature of calcination (T_{cal}). The results showed that MCE of NSMO samples depends strongly on T_{cal} , achieving that a conventional MCE for nanocrystalline NSMO samples. However, the thermomagnetic behavior of bulk NSMO sample NSMO contains both conventional MCE and inverse MCE. MCE of NSMO improves powerfully with increasing T_{cal} . The calcination process is concluded as a powerful tool for improving MCE for NSMO. Especially, NSMO parameters in MCE of some published works are better, with a value equal to or greater than the corresponding MCE parameters in the same value of ΔH . MCE of NSMO system, particularly for nitrogen and hydrogen liquefaction, covers an excellent temperature range is of interest for MR.

Keywords:

Phenomenological model; Magnetocaloric effect; $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

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1. Introduction

With rapid steps, increased refrigeration efficiency, reduction in weight, greater mechanical stability, lower environmental impact, greater efficiency, lower noise levels and high cost-effectiveness, magnetocaloric refrigerator (MR) has developed into a strong alternative to gas refrigeration by magnetocaloric effect (MCE) [1-6]. In space applications, medical appliances, aerospace applications and food cooling, MR is a fundamental requirement [7-14]. In the range of temperatures near the temperature of a magnetic phase transition (T_{MPT}), MR uses the idea to apply MCE on magnetocaloric (MC) material [15-20]. The researchers looked into a variety of magnet materials, such as magnetic alloys, manganites and others in order to develop and improve MR [29-34]. In traditional MCE, a reaction of adiabatic demagnetization occurs as the cooling action in MC material, which is carried out with sudden removal of H_{ex} [35-37]. Quite opposite way, adiabatic magnetization can cool MC materials that increases by sudden increasing H_{ex} applied on MC materials. It is referred to as an inverse MCE [38]. In antiferromagnetic (AFM) materials, this inverse MCE is obvious over AFM transition temperature range.

The unusual magnetic arrangement such as AFM and spinal orientation leads to a highly interesting study of the rare earth-manganites [39-41].

These types of manganese have significant electronic, electrical and magnetic properties such as colossal magnetoresistance of ferromagnetic and antiferromagnetic, negligible eddy current, semiconducting, metallic and insulating states related to ferromagnetic and antiferromagnetic ordering [39-41]. They also showed great promise as electronic equipment materials, solid oxides fuel cells, magnetoresistive, infrared detectors, magnetic recording devices, and radiometers [42, 43]. Chen et al. discovered a large ΔS_M of 7.5 J/kg. K in polycrystalline Nd_{0.5}Sr_{0.5}MnO₃ (prepared by the sol-gel) under H_{ex} of 1 T at the charge-ordered state transition temperature [44]. Liu et al. succeed in tailoring MCE of Nd_{0.5}Sr_{0.5}MnO₃ (NSMO) epitaxial films via controlling the lattice-mismatch-induced-strain [45]. Sande et al. reported that the amount of $|\Delta S_M|$ of NSMO around this first-order transition is around three times larger than that obtained around the second-order transition (ferromagnetic-metallic-to-paramagnetic-insulator) in the same sample [46]. Xu et al. prepared NSMO nanoparticles via sol-gel method, observing the coexistence of an inverse MCE and a conventional MCE, depending on particle size [47]. Venkatesh et al. used the floating zone methodology to grow single NSMO crystals, revealing that the value of ΔS_M is found to be much higher than ΔS_M reported in polycrystalline ones [48]. Shankar et al. investigated bulk

and nanocrystalline NSMO ceramic samples were prepared via the combustion technique and calcined at various temperatures showing broadly second order ferromagnetic-paramagnetic phase transitions for all samples beside antiferromagnetic-paramagnetic phase transition for bulk sample [49]. Since, the powder of NSMO was divided into several parts and calcined at 600°C, 900°C, and 1300°C for 6 h to obtain the samples of various particle sizes, labeling by C600, C900, and C1300, respectively, in this research. From this practical point, the MCE of NSMO samples is recommended to be investigated in this work. In this research, phenomenological model (PM) is used to study the thermomagnetic properties through the work of simulated magnetization temperature curves for NSMO, concluding ΔS_M , heat capacity change ($\Delta C_{P,H}$), and relative cooling power (RCP).

2. Theoretical Considerations

According to PM, the magnetization (M) vs. temperature (T) is provided by [50, 51]:

$$M(T) = \left(\frac{M_i - M_f}{2}\right) [\tanh(\alpha(T_{MFT} - T))] + \beta(T - T_{MFT}) + \left(\frac{M_i + M_f}{2}\right), \quad (1)$$

where M_i is an initial value of magnetization at ferromagnetic (FM) or AFM-paramagnetic transition and M_f is a final value of this transition as

shown in Fig. 1, where $\alpha = \frac{2(\beta - \gamma)}{M_i - M_f}$,

$$\beta = \left(\frac{dM}{dT} \right)_{average} \text{ for FM or AFM phase, and } \gamma = \left(\frac{dM}{dT} \right)_{T=T_{MFT}}.$$

3. Results and Discussion

To simulate MCE of NSMO, PM parameters for NSMO were directly determined from experimental data (magnetization vs. temperature), as described in Ref. [49]. Fig. 2 depicts the magnetization vs. temperature for the bulk (C1300) and nanocrystalline (C600) and (C900) NSMO samples measured at 0.05T, with the experimental data from Ref. [49] represented by symbols and the simulated data represented by dashed lines. According to Fig. 2, there is a satisfactory agreement between the experimental and theoretical values of $M(T)$ for NSMO samples under 0.05 T, indicating that PM is a suitable model for fitting magnetization vs. temperature for FM-paramagnetic and AFM transitions.

Interestingly, it is expecting the existence of an inverse MCE plus conventional MCE for C1300 sample as we will show later.

ΔS_M of NSMO samples under adiabatic magnetic field shift (ΔH) of 0.05 T is formulated by

$$\Delta S_M(T, \Delta H) = 0.05 \times \left(-\alpha \times \left(\frac{M_i - M_f}{2} \right) \times \text{sech}^2(\alpha \times (T_{MPT} - T)) + \beta \right). \quad (2)$$

A maximum of ΔS_M (ΔS_{Max}) can be determined as follows:

$$\Delta S_{Max} = 0.05 \times \left(-\alpha \times \left(\frac{M_i - M_f}{2} \right) + \beta \right) \quad (3)$$

Fig. 3 shows simulated temperature dependence of ΔS_M for NSMO samples under ΔH of 0.05 T, calculated by using Eq. (2). Interestingly, ΔS_M of NSMO depends strongly on temperature of calcination (T_{cal}), concluding that the thermomagnetic behavior of NSMO characterizes as a conventional MCE over investigated range of temperatures for nanocrystalline (C600) and (C900) NSMO samples. However, the thermomagnetic behavior of NSMO characterizes as an inverse MCE of bulk (C1300) NSMO sample as the result of FM to AFM transition below the temperature of FM to AFM transition ($T_N \sim 225K$). But, above T_N , the thermomagnetic behavior of NSMO characterizes as a conventional MCE with negative value of ΔS_M as result of FM transition. Therefore, C1300 sample can be utilized in MR that exploits both positive and negative magnetic entropy changes via magnetization and demagnetization processes, respectively. With increase T_{cal} , $|\Delta S_{Max}|$ is enhanced strongly due to increase particle size of NSMO. This increase particle size of

NSMO leads to bigger crystallite size, leads to decrease the possibility of creating of spin disorder in the surface.

An effectiveness for NSMO samples as MC material can be evaluated by RCP. This parameter is accounted by the absolute value of ΔS_{Max} and full-width at half-maximum (δT_{FWHM}) of the ΔS_{M} curve by following formula:

$$\text{RCP} = \left| \Delta S(T, H_{\text{max}}) \right|_{\text{Max}} \times \delta T_{\text{FWHM}}, \quad (4)$$

where δT_{FWHM} can be obtained as follows

$$\delta T_{\text{FWHM}} = \frac{2}{\alpha} \times \cosh^{-1} \left(\sqrt{\frac{2(M_i - M_f) \times \alpha}{(M_i - M_f) \times \alpha + 2\beta}} \right) \quad (5)$$

Table I indicates that δT_{FWHM} has significant values and are ranged between 44 and 171 K for NSMO samples under ΔH of 0.05 T. Furthermore, RCP changes nonmonotonically with T_{cal} as a result of competition between δT_{FWHM} and ΔS_{M} with T_{cal} .

According PM model [50], the characterization of $\Delta C_{P,H}$ curves for NSMO samples is expected as follows

$$\Delta C_{P,H} = -0.05\alpha^2 \times T \times (M_i - M_f) \times \tanh(\alpha \times (T_{\text{MPT}} - T)) \text{sech}^2(\alpha \times (T_{\text{MPT}} - T)). \quad (6)$$

Fig. 4 shows simulated $\Delta C_{P,H}$ vs. temperature for NSMO samples under ΔH of 0.05 T. For C600 and C600 samples, the simulated $\Delta C_{P,H}$ varies from negative value to positive one as a result of FM transition.

For C1300 sample, the simulated $\Delta C_{p,H}$ varies from positive value to negative one over range of AFM transition. However, the inversed characterization is observed when over range of FM transition.

To investigate extra details about MCE in NSMO samples, the refrigerant capacity (RC) is well-thought-out to judge the efficiency for NSMO samples as effective MC materials in MR. RC was calculated as follows [51]

$$RC = \int_{T_c - \frac{\delta T_{FWHM}}{2}}^{T_c + \frac{\delta T_{FWHM}}{2}} \Delta S_M dT. \quad (8)$$

Form Table I, RC takes the same behavior of RCP due to the same reasons.

Table II offers a comparative image of MCE parameters of NSMO samples with corresponding ones of several MC materials in same value of ΔH and higher ones in published works [52-55]. Importantly, the MCE parameters of NSMO samples are higher or as good as corresponding MCE parameters of these published works in the same value of ΔH or larger. Finally, NSMO samples are interesting MC materials in MR below room temperature notably over temperature range of nitrogen and hydrogen liquefaction. Furthermore, the loss of eddy current plus loss of

hysteresis energy are disregarded due to high resistivity plus small hysteresis [49].

Conclusion

The simulation of MCE is done for NSMO compounds synthesized and calcined at various values of T_{cal} . The results of this simulation show that this PM is a constructive model for the calculation of thermomagnetic properties for NSMO compounds for both FM-AFM and FM-paramagnetic transitions. The thermomagnetic behaviour of NSMO characterizes as a conventional MCE over investigated range of temperatures for nanocrystalline NSMO samples. However, the thermomagnetic behaviour of bulk NSMO sample NSMO contains conventional MCE and inverse MCE. MCE in NSMO samples is strong tunable with variation of T_{cal} during preparation of NSMO samples. Interesting for MR is the NSMO system covering an outstanding temperature range, particularly of liquefaction nitrogen and liquefaction of hydrogen.

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Figures

Figure 1: dependence of Isofield magnetization vs. temperature.

Figure 2: Magnetization vs. temperature for NSMO samples in $H_{\text{ex}} = 0.05$ T. The dashed curves are modelled results and symbols represent experimental data from Ref. 49.

Figure 3: ΔS_M vs. temperature for NSMO samples in ΔH of 0.05 T.

Figure 4: $\Delta C_{p,H}$ vs. temperature for NSMO samples in ΔH of 0.05 T.

Tables

Table I: The predicted values of MC properties for NSMO under ΔH of 0.05 T.

Sample	$ \Delta S_{\text{Max}} $ (J/Kg.K)	δT_{FWHM} (K)	RCP (J/Kg)	$\Delta C_{\text{P,H(Max)}}$ (J/Kg.K)	RC (J/Kg)
C600	0.0045	171	0.77	0.008	0.55
C900	0.0085	135	1.15	0.027	0.82
C1300	0.006, 0.014	69, 44	0.41, 0.62	0.023, 0.139	0.29, 0.44

Table II: The values of MC properties for NSMO and other MC materials.

Composition	ΔH (T)	$ \Delta S_{\text{Max}} $ (J/Kg.K)	δT_{FWHM} (K)	RCP (J/Kg)	$\Delta C_{\text{P,H(Max)}}$ (J/Kg.K)	Ref.
NSMO	0.05	0.0045—0.0085	69—171	0.41—1.15	0.008— 0.139	This work
$\text{BiFe}_{1-x}\text{Zn}_x\text{O}_3$	1	0.005- 0.006	4.9-6.9	0.27-0.40	0.022-0.038	[52]
$\text{Ni}_{58}\text{Fe}_{26}\text{Ga}_{28}$	0.2— 0.5	0.005—0.013	42—73	0.19—0.94	0.04—0.07	[53]
Ge0.95Mn0.05 Films	0.1	4E-7—3.6 E-6	12.69—17.75	6.3 E-6— 0.451 E-5	7.7 E-6—1.1 E-4	[54]
NdMnO_3	1	3.7 E-3	6.8	0.025	-	[55]