The Inverse and Conventional Magnetocaloric Effects in $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$ Nanoferrites Over an Extraordinary Temperature Range

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Abstract

The magnetocaloric effect (MCE) of $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$ ($x = 0.02, 0.03, \text{and} 0.04$) nanoferrites is simulated using a phenomenological model. The analysis indicates that the MCE of $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$ nanoferrites is strongly influenced by Dy content in both conventional and inverse MCE. For conventional MCE, the full-width at half-maximum ($\Delta T_{\text{FWHM}}$) has significant values, ranging between 200 K and 258 K for $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$ nanoferrites. However, for inverse MCE, $\Delta T_{\text{FWHM}}$ ranges between 25 and 55 K. The MCE of the $\text{Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4$ system covers an extensive temperature range and is a particularly interesting prospect for nitrogen and hydrogen liquefaction.

Keywords Phenomenological model · magnetocaloric effect · nanoferrites

Introduction

The magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon that arises in the absorption or generation of heat by such magnetically ordered material when the applied magnetic field ($H_{\text{exc}}$) is changed.\textsuperscript{1–5} Because of the advantages of magnetic refrigeration (MR) including environmental safety, higher efficiency, and the ability to be implemented in a wide range of temperatures, it has become an appealing replacement for traditional refrigeration systems.\textsuperscript{6–11} Many decades have been spent studying a broad range of materials that demonstrate acceptable magnetocaloric (MC) characteristics at ambient or even low temperatures.\textsuperscript{9,12–18} MR could be used for gas liquefaction, specifically helium, nitrogen, and hydrogen liquefaction, as well as for research activities and low-temperature space applications.\textsuperscript{19} MR reflects the concept of applying MCE to MC material at temperatures near that of a magnetic phase transition.\textsuperscript{14–19} An initial response of adiabatic demagnetization occurs in traditional MCE as a cooling action in MC material, which is carried out with the abrupt removal of the $H_{\text{exc}}$.\textsuperscript{20–24} However, adiabatic magnetization can cool MC materials that experience a sudden increase in the $H_{\text{exc}}$, which is called an inverse MCE.\textsuperscript{4} This inverse MCE is seen in antiferromagnetic (AFM) materials over the AFM transition temperature range.

Magnetic nanoparticles (MNPs) are an excellent replacement for bulk MCE materials due to the ease of assembly in the form of thin film and other desirable features, including their influence over the $\Delta S_M$ throughout the superparamagnetic–blocking transition.\textsuperscript{24} Theoretically, decreasing the particle size to nearer the single magnetic domain enhances $\Delta S_M$ by many orders of magnitude when contrasted with $\Delta S_M$ in bulk materials.\textsuperscript{24} Furthermore, the high surface area of nano-materials would enhance the exchange of heat with the surroundings, and it would be possible to modify the exchange of heat between MNPs and the surroundings by carefully designing core structures. Furthermore, different MNP sizes have the potential to achieve a broader range of cooling.\textsuperscript{25,26}

The Ni-Cu-Zn ferrite is a soft ferrite with high $T_{MPT}$, large electrical resistivity and extreme permeability in the radio-frequency range. Ni-Cu-Zn ferrites are used primarily as...
transformer cores, inductors, recording heads, and deflection yokes.\textsuperscript{27,28} Optimizing NiCuZn ferrites by modifying the portions of metal ions in the formula or doping with new metals has recently been investigated. When the ferri cement was partially replaced with RE ions (Gd\textsuperscript{3+}, Eu\textsuperscript{3+}, Sm\textsuperscript{3+}, and Pr\textsuperscript{3+}), a distortion in the crystal structure of the Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4} ferrite was noted, as was an improvement in its magnetic properties.\textsuperscript{29}

Almessiere et al. used the sol-gel method to prepare Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} (x \leq 0.04) nanoferrites, which showed superparamagnetic behaviour and broadly second-order FM–paramagnetic phase transitions for all samples, along with an AFM–paramagnetic phase transition at extremely low temperatures.\textsuperscript{30} We were thus highly motivated to investigate the MCE of Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} nanoferrites in this work, based on this useful point. In this research, a phenomenological model (PM) is used to investigate the thermomagnetic properties of Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} nanoferrites using simulated magnetization temperature curves, resulting in $\Delta S_M$, heat capacity change ($\Delta C_P$), and relative cooling power (RCP).

**Theoretical Considerations**

The PM provides the relationship between magnetization ($M$) and temperature ($T$) as follows\textsuperscript{31,32}:

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

(1)

where $M_i$ is an initial value of magnetization at the FM–paramagnetic or AFM–paramagnetic transition, and $M_f$ is a final value of this transition as shown in Fig. 1, where $\alpha = \frac{2(\beta - 1)}{M_f - M_i}$ for FM or AFM phase, and $\beta = \left(\frac{dM}{dT}\right)_{average}$

$\gamma = \left(\frac{dM}{dT}\right)_{T=MFT}$

**Results and Discussion**

To simulate the MCE of Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4}, PM parameters for Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} were obtained directly from experimental results (magnetization vs temperature), as described in Almessiere et al.\textsuperscript{30} The magnetization versus temperature for Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} nanoferrites measured at 0.01T is depicted in Fig. 2, with experimental data from Almessiere\textsuperscript{30} expressed by symbols and simulated data expressed by dashed lines.

There appears to be reasonable agreement between the experimental and theoretical values of $M(T)$ for Ni\textsubscript{0.4}Cu\textsubscript{0.2}Zn\textsubscript{0.4}Fe\textsubscript{2-x}Dy\textsubscript{x}O\textsubscript{4} nanoferrites, implying that PM is an appropriate model for fitting FM–paramagnetic and AFM

\[\text{Fig. 1 The dependence of isofield magnetization vs temperature.}\]

\[\text{Fig. 2 Magnetization vs temperature for Ni}_{0.4}\text{Cu}_{0.2}\text{Zn}_{0.4}\text{Fe}_{2-x}\text{Dy}_x\text{O}_4\text{ nanoferrites in } H_{exe} \text{ of 0.01 T. The dashed curves are modelled results and symbols represent experimental data from Ref. 30.}\]
transitions. Interestingly, it seems that, in addition to conventional MCE, an inverse MCE for Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites is present at very low temperatures, as we will later explore.

$\Delta S_M$ of Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites under an adiabatic magnetic field shift ($\Delta H$) of 0.01 T is formulated by

$$\Delta S_M(T, \Delta H) = -0.01 \times \left( \alpha \times \left( \frac{M_i - M_f}{2} \right) \times \text{sech}^2(\alpha \times (T_{MPT} - T)) + \beta \right).$$  \hspace{1cm} (2)

The maximum $\Delta S_M$ ($\Delta S_{Max}$) can be determined as follows:

$$\Delta S_{Max} = -0.01 \times \left( \alpha \times \left( \frac{M_i - M_f}{2} \right) + \beta \right)$$  \hspace{1cm} (3)

The simulated temperature dependence of $\Delta S_M$ for Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites is depicted in Fig. 3. Importantly, the thermomagnetic behaviour of Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites is strongly dependent on Dy content, leading to the conclusion that the thermomagnetic behaviour of Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites is characterized as a conventional MCE over temperatures higher than 78, 62, and 39 K for doping levels $x = 0.02$, 0.03, and 0.04, respectively. However, the thermomagnetic behaviour of Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites is characterized as an inverse MCE at lower temperatures. As a result, Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites could be operated in MR that uses magnetization and demagnetization processes to exploit both positive and negative magnetic entropy variations. $|\Delta S_{Max}|$ is significantly reduced when the Dy content is high. The fact that Dy$^{3+}$ ions are favoured to exist in the B sites, which can be attributed to their large ionic radii, could explain this decreasing trend. As a result of the Fe$^{3+}$ replacement by Dy$^{3+}$, the crystal symmetry is reduced, implying that the distance between Dy–O will be smaller than the distance between Fe–O. Consequently, some of the corresponding ions display aligned antiparallel moments with respect to others in these sites, causing a drop in net magnetic moments just on B sites. As Dy$^{3+}$ content increases, further cations on B sites exhibit antiparallel moments. To put it another way, the decrease in $|\Delta S_M|$ at high content in samples is due to surface spin effects and cation distribution on various sites. Despite the fact that magnetic moments are no longer directed linearly, nonlinear spins of magnetic ions exist due to spin frustration. The increase in migration of Fe$^{3+}$ cations from tetrahedral to octahedral sites with the goal of occupying the increasing Dy$^{3+}$ ions causes the reduction drop in the $|\Delta S_M|$. The increased presence of Fe$^{3+}$ cations in octahedral B sites due to site preference causes an increase in spin canting and antiparallel spin coupling, reducing the $|\Delta S_M|$ and weak super-exchange interactions between tetrahedral and octahedral sites, lowering the magnetization. Furthermore, the ionic radii for various elements, and also the critical A–B super-exchange interactions between many magnetic ions, could be used to deduce the influence of Dy$^{3+}$ ions on magnetic characteristics. Dy$^{3+}$ ions have an ionic radius of 0.912 Å, indicating that they prefer to be found on B sites. The ionic radii that are subjected to substitution differ greatly, causing disorder in the electronic states and internal strains in the crystal structure. This has an impact on the A–B super-exchange interactions between metal sites A and B. Furthermore, variations in the drop in $|\Delta S_M|$ at high Dy$^{3+}$ content can be explained by crystallite size variation. Indeed, as the Dy$^{3+}$ content increases, the crystallite size decreases, resulting in a reduction in magnetization and, as a result, a decrease in $|\Delta S_M|$.

The $|\Delta S_{Max}|$ and full-width at half-maximum ($\delta T_{FWHM}$) of the $S_M$ curve are used to account for RCP as follows:

$$\text{RCP} = |\Delta S(T, H_{max})|_{Max} \times \delta T_{FWHM},$$  \hspace{1cm} (4)

where $\delta T_{FWHM}$ can be obtained as follows:

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

For conventional MCE, the calculations show that $\delta T_{FWHM}$ has significant values, ranging between 200 K and 258 K for Ni$_{0.4}$Cu$_{0.2}$Zn$_{0.4}$Fe$_{2-x}$Dy$_x$O$_4$ nanoferrites under $\Delta H$ of 0.01 T. However, for inverse MCE, the range of $\delta T_{FWHM}$ is between 25 K and 55 K. Furthermore, for conventional MCE, RCP is between 0.05 J/Kg and 0.08 J/Kg.
nanoferrites can be explained as follows, according to the PM materials in MR, particularly between 10 and 325 K. Furthermore, they have high resistivity, small hysteresis, low Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites are an interesting demonstration both conventional and inverse MCE. The magnetic behaviour of Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites are fascinating MCs transition, an inverse characterization is observed. Finally, a negative value. However, over the range of the FM transition, an inverse characterization is observed. Finally, Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites are fascinating MC materials in MR, particularly between 10 and 325 K. Furthermore, they have high resistivity, small hysteresis, low loss of eddy current, and the energy loss is negligible. The MCE and the electrocaloric effect both contribute to the future of refrigeration technology.

The characterization of curves for Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites can be explained as follows, according to the PM model:

$$\Delta C_{P,H} = -0.01 \alpha^2 \times T \times (M_i - M_f) \times \tanh(\alpha \times (T_{MPT} - T)) \times \sech^2(\alpha \times (T_{MPT} - T)).$$

(6)

ΔCP,H versus temperature simulations for Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites at ΔH of 0.01 T are shown in Fig. 4. Over the range of the AFM transition, the simulated ΔCP,H of all samples varies from a positive to a negative value. However, over the range of the FM transition, an inverse characterization is observed. Finally, Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites are fascinating MC materials in MR, particularly between 10 and 325 K. Furthermore, they have high resistivity, small hysteresis, low loss of eddy current, and the energy loss is negligible. The MCE and the electrocaloric effect both contribute to the future of refrigeration technology.

**Conclusion**

MCE simulations were performed on Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites synthesized using the sol–gel method. The simulation results show that this PM is an efficient model for calculating the thermomagnetic properties of Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites for both FM–AFM and FM–paramagnetic transitions. The thermomagnetic behaviour of Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites demonstrates both conventional and inverse MCE. The Ni0.4Cu0.2Zn0.4Fe2-xDyxO4 nanoferrites are an interesting possibility for MR because they cover a wide temperature range, especially liquefaction of nitrogen and hydrogen, even at room temperature.
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