Enhanced RCP and large inverse magnetocaloric effect of CoFe$_2$O$_4$ nanoparticles synthesized by auto-combustion method

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Abstract:
This work focuses on the microstructure, magnetic properties and magnetocaloric effect of CoFe$_2$O$_4$ (CFO) nanoparticles elaborated by sol-gel auto combustion method. The XRD investigation indicates that CFO is crystallized in a cubic spinel structure with the $Fd\bar{3}m$ space group and the SEM micrograph shows a fine quasi-spherical with an average grain sizes of 160 nm. The temperature dependence of the Raman spectra reveals the ferromagnetic to paramagnetic (FM-PM) transition started from 723 K and the magnetization versus temperature measurements shows the Curie temperature located at $T_c$= 785 K. Large value of magnetocaloric temperature change of $\Delta T$ =11.2 K with a high RCP of 687.56 J Kg$^{-1}$ are achieved indirectly via the Maxwell approach making our CFO nanopowder suitable candidate for both environmentally friendly magnetic refrigeration and medical applications at ambient temperature.

Keyword:

Introduction:
Recently, the magnetocaloric effect (MCE) has attracted much interest from researchers for its use in a variety of industrial applications. It was discovered by a German physicist Emil
Warburg in 1881[1]. Scientists are now devoting many efforts on ecological and friendly magnetic materials used in heating and cooling technologies[2], [3]. The MCE is an intrinsic property of magnetocaloric materials in which a reversible and adiabatic temperature change is caused when they are exposed to a varying magnetic field[4], it can be evaluated as an isothermal entropy change $\Delta S$ and/or as an adiabatic temperature change $\Delta T$[4].

In the literature, several classes of magnetic materials displayed a magnetocaloric effect including perovskite manganites, manganite alloys and spinel ferrites. Recently, the perovskite manganite $\text{La}_{0.5}\text{Ca}_{0.5-x}\square_x\text{MnO}_3$ (LCMO) exhibiting an interesting MCE, with a $\Delta T$ of 5.6 K is reported [5]. Meanwhile, in several researches, spinel ferrites with a second order magnetic transition have been shown to be effective instruments for magnetic refrigeration (MR) applications. In this regards, Oumezzine et al observed an important magnetic entropy change $\Delta S_M$ of 1.61 J kg$^{-1}$ K$^{-1}$ at 50 kOe in $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$ with a Relative Cooling Power (RCP) of 289 J kg$^{-1}$[6]. Moreover, $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ showed a moderate (-$\Delta S_M$) of 1.39 J kg$^{-1}$ K$^{-1}$ at 25 kOe with a high adiabatic temperature change $\Delta T$ of 68 J kg$^{-1}$ as reported by Anwar et al [7].

Among spinel ferrites, cobalt ferrite ($\text{CoFe}_2\text{O}_4$) has gained great scientific interest owing to its moderate saturation magnetization, high coercivity, good magnetostrictive properties, high Curie temperature ($T_C=520 \degree\text{C}$), electrical insulation with low eddy current loss, and chemical stability [8]–[10]. Benefiting from these properties, $\text{CoFe}_2\text{O}_4$ (CFO) find variety of applications in several domains such as data storage, sensors, microwave devices, high-frequency applications, catalysis, magnetic refrigeration and biomedical field [8], [11]–[14]. More particularly, in refrigeration applications, CFO intended to replace carbon-technology in order to limit global warming and reduce greenhouse gas emissions[15], [16]. For biomedical applications, CFO nanoparticles are used in cancer therapy by hyperthermia (cancer treatment). In fact, CFO nanoparticles were inserted into tumor tissue and subsequently heated after being exposed to an external alternating magnetic field [17], [18].

Crystallographically, CFO has inverse spinel structure where octahedral sites are occupied by $\text{Co}^{2+}$ cations, while $\text{Fe}^{3+}$ cations are equally shared between tetrahedral and octahedral sites[19]. It is known that the magnetic properties are sensitive to the distribution of these cations which is influenced by the preparation method of CFO nanoparticles [20], [21]. Furthermore, ferrite properties are greatly dependent on grain size and microstructure which also can be monitored by the synthesis route [22], [23].For example, the saturation of magnetization ($M_s$) of $\text{NiFe}_2\text{O}_4$ was shown to be increased with increasing ferrite grain size as
reported by Li et al [23]. Furthermore, several studies reported that the MCE of magnetic nanoparticles was tuned by the particle size [24], [25]. Yin et al reported that the $\Delta S_M$ in HoCrO$_3$ decreases ($\Delta S_M = 8.73, 7.22, 7.77, \text{ and } 6.70 \text{ J kg}^{-1} \text{ K}^{-1}$) and the refrigerant capacity (RC = 388, 354, 330, and 310 J kg$^{-1}$) for the 60 nm, 190 nm, 320 nm, and 425 nm size particles. Accordingly, the synthesis methods are crucial in controlling magnetic properties of ferrites powders and their applications. CFO are typically elaborated using various methods including co-precipitation sol–gel, ceramic techniques and auto combustion utilizing different fuels [26]–[28]. Researchers have recently focused on the coupling between sol gel and auto combustion method, as it produced ferrite samples with high chemical homogeneity, good purity, and high crystallization. In addition, it demands a basic equipment and simple preparation process as well as a short processing time and low external energy consumption [29], [30].

It is worth to note that the magnetic characteristics of most CFO have been examined over a wide range of temperatures, from room temperature to as low as 4 K. However, the majority of ferrite’s applications are suitable at room temperature or above, for example, medical application in which magnetocaloric properties can induce local hyperthermia at cancer sites [31]. Note that there are very few reports that describe the MCE properties of cobalt ferrite at high temperature. Herein, we present an investigation at high temperature range from 300 K to 900 K on structural, magnetic and magnetocaloric of CoFe$_2$O$_4$ elaborated by combining sol-gel auto combustion using ammonia as a neutralizer agent, ethylene glycol as polymerizing agent and acetic acid as fuel.

**Chemical synthesis:**

CoFe$_2$O$_4$ nanoparticles were prepared using sol-gel self-combustion method as follows: stoichiometric amounts of Cobalt Nitrate Co(NO$_3$)$_3$.6H$_2$O and Ferric Nitrate Fe(NO$_3$)$_3$.9H$_2$O were dissolved in 2-Methoxyethonal under constant magnetic stirring for 30 mn. Then ammonia was slowly dropped to the solution to adjust the $pH$ to 10. Separately, 1:1 molar ratio of acetic acid (fuel agent) and ethylene glycol (polymerizing agent) mixture was prepared and added to the solution. After four hours of continuous stirring at 90°C, the brown solution was completely turned into a dark, puffy and porous gel. Then, the gel was transferred to a furnace and by heating at 120 °C, it simultaneously burnt in a self-propagating combustion until it was completely transformed into fine powder. Finally, the powder was annealed at 700 °C for two hours using a controlled heating rate of 2 °C/min under air atmosphere.
**Materials and methods:**
The XRD patterns of CFO ceramic were obtained by X-ray diffraction using the Panalytical X-Pert Pro with Cu-Kα radiation (λ = 1.54059 Å) at room temperature. The grain morphology of the ceramic was examined using a scanning electron microscope (SEM, Philips XL30). The Raman spectra were recorded using a micro-Raman Renishaw spectrometer equipped with a CCD detector. Magnetic properties were performed by using a Physical Property Measurement System (PPMS-DynaCool) Quantum Design apparatus in the 300-900 K temperature range under a magnetic field range of 0-25 kOe. The magnetization was measured by using vibrating sample magnetometer (VSM) method integrated in the system. The magnetocaloric study was carried out by the indirect method using the recorded $M-H$ hysteresis loops.

**Results and discussion:**

**Morphological and structural analysis:**
The SEM image of the as-prepared CoFe$_2$O$_4$ nanoparticles shows agglomerates of regular near-spherical particles with average grain sizes of 160 nm, estimated by ImageJ® software as shown in Fig.1. The obtained large particle sizes are due to the high heating temperatures released during the combustion process[9]. It should be noted that the magnetic properties of cobalt ferrites are very sensitive to the grain sizes.

![Fig.1 SEM micrograph of CFO nanoparticles, the inset to the image shows the particle size distribution](image)

Fig. 2 shows the room temperature XRD spectra of the CFO powder calcined at 700 °C for 2h. The obtained diffraction peaks are well-defined which proves that our sample is well crystallized. All the diffraction peaks can be indexed to the cubic crystal structure of cobalt.
ferrite (JCPDS card no. 22-1086) and no peak from the impurities was detected. The experimental XRD pattern of CFO was refined using the Rietveld refinement program via FullProf software and indexed by a cubic spinel structure with the space group ($Fd\bar{3}m$), and the output data proved an excellent fit between the calculated and observed diffractograms. The “a” lattice parameter of CFO is found to be 8.4013 Å. According to Scherrer’s equation[12], [33], [34], the average crystallite size (D) was estimated from the full width at half-maximum of the conspicuous (311) reflection and found to be 57.6 nm and the grain size of 160 nm determined using ImageJ® software. Table 1 lists the refined structural parameters of CFO powder.

![Fig.2a X-ray diffraction patterns of CFO powder; b Rietveld fitted X-ray diffraction patterns of CFO nanoparticles](image)

**Table 1 Refined structural parameters for CFO nanoparticles at room temperature**

| Structure | Unit cell parameters | Average crystallite size(nm) by XRD | Average grain size(nm) by SEM |
|-----------|----------------------|----------------------------------|------------------------------|
| Spinel $Fd\bar{3}m$ | $a=\alpha=\beta=\gamma=90$ | 592.9792 | 57.6 |
|           | $a=\bar{a}=(4.806\pm0.008)$ Å | 160 | |

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Raman spectra were collected in the temperature range of 303-823 K to study the temperature effect on the spinel structure of the CFO, as shown in Fig.3. For the spinel structure, the group theory analysis predicts the following ten optical phonons: $5T_{1u} + A_{1g} + E_g + 3T_{2g}$. The five $T_{1u}$ modes are IR active, while the other modes ($A_{1g} + E_g + 3T_{2g}$) are Raman active assigned to the motion of oxygen ions, A-site and B-site in the spinel structure[35]. Moreover, the $A_{1g}$ mode is assigned to symmetric stretching of the oxygen anions along the Fe-O (Co-O) in the tetrahedral sub-lattice, $E_g$ and first $T_{2g}(1)$ modes belong to the symmetric and asymmetric bending of the oxygen anions, the second $T_{2g}(2)$ mode arise due to asymmetric stretching of the Fe-O (Co-O) bonds and third $T_{2g}(3)$ corresponds to the translational shift of the entire FeO$_4$ tetrahedron.

At room temperature, $A_{1g}(1)$ and $A_{1g}(2)$ modes located at frequencies of 616 and 693 cm$^{-1}$ are assigned to the stretching vibrations of the Fe–O and Co–O bonds in tetrahedral sites respectively. At the frequencies below 600 cm$^{-1}$, the Raman modes (~208, ~303, ~468, and ~568 cm$^{-1}$) correspond to $E_g$ and $T_{2g}$ revealing the vibration of the spinel structure[36].

By heating, the $A_{1g}(1)$ and $A_{1g}(2)$ become softened and broad, resulting on the thermal effect on cation distribution in ferrite systems. In addition, the $A_{1g}(1)$ mode shifts to lower frequencies that related to the migration of cations in tetrahedral structure. At the same time, $E_g$ and $T_{2g}(3)$ phonon modes show the blue-shifting tendency associated with the cation migration in octahedral sites. In reality, the Fe$^{3+}$ cations move from O-site to T-site, while the Co$^{2+}$ cations move in the opposite direction from T-site to O-site. This dislocation of cations causes a disorder in CFO structure that makes an inequality between these two valances.
This phenomenon increases with the increase of the temperature leading to disruption of the order of the cations. Thus, the magnetic properties of the CFO might be destroyed giving rise to the paramagnetic phase at high temperature[37], [38].

**Magnetic properties:**

**Temperature dependence of magnetic properties**

Fig. 4 (a) plots the temperature dependences of ZFC (blue curve) and FC (red curve) magnetization curves obtained in CFO powder under a magnetic field of 0.4 Oe. At 300 K, the magnetization was 8.16 emu g⁻¹ and decreases with increasing temperature. At around 800K, the magnetization drops sharply to zero, which corresponds to the phase transition from ordered (FM) to disordered (PM) state as reported by Franco and Silva [31]. Therefore, our material displays a FM-PM phase transition at Curie temperature $T_c$. The $T_c$ was determined from the derivative $dM/dT$(brown curve) and found to be 785 K Fig.4 (a).

Fig.4 The FC-ZFC curves (a) and magnetic susceptibility $\chi^{-1}$ (T) (b), for CFO sample measured at an applied magnetic field of 0.4 Oe.

The $T_c$ value is confirmed basing on Curie law (equation 1) by fitting the thermally variation of the inverse of the magnetic susceptibility ($\chi^{-1} = \frac{H}{M}$) plotted at 400 Oe:

$$\chi = \frac{C}{T - \theta_p} \quad (Eq \ 1)$$

C denotes the Curie constant, while $\theta_p$ represents the Weiss temperature [39]. From the slop of the linear fit plot of $\chi(T)$ at paramagnetic phase, the C is estimated at 0.30 K emu g⁻¹. The corresponding $\theta_p$ is 789.95 K that is closer to the $T_c$ (785 K) as shown in Fig. 4 (b).
Fig. 5 displays the hysteresis loops (M–H) of CFO nanoparticles, measured under an applied magnetic field of 25 kOe and recorded at different temperatures (300 K - 900 K).

For T<Tc zone, a saturated hysteresis loops are observed which describe the ferro/ferrimagnetic character of CFO. As it can be seen, the saturation of magnetization is attained even at 20 kOe, hence all the spins are oriented in parallel beyond this magnetic field value. At room temperature (300K), CFO sample represents a saturation of magnetization $M_s$ of 83 emu/g that decreases with the increase of temperature and completely disappears at T>Tc, this behavior indicates the appearance of paramagnetic character [5], [39]. Note that, $M_s$, remnant magnetization ($M_r$) and coercive field ($H_c$) decrease as the temperature increases, being equal to zero at close to $T_c$. Nevertheless, this is not a hint of superparamagnetism because the blocking temperature $T_b$ for CFO particles of 160 nm is much higher than $T_c$, ($T_b=KV/25k_B$, where K, V, and $k_B$ are anisotropy constants, particle volume, and Boltzmann constants, respectively) [31]. The details of the hysteresis curve for various temperatures are shown in the inset. The high $M_s$ (83 emu g⁻¹) observed at low $H_c$ (284 Oe) reveals the soft magnetic nature of CFO, this could be useful to design multifunctional devices to change the magnetization with a small external magnetic field [36]. The high obtained $M_s$ is due to the large particle sizes (160 nm) comparing with CFO nanoparticles (35 nm) elaborated by hydrothermal that shows an $M_s$ of 68.5 emu g⁻¹[9]. Indeed, the larger grains tend to consist of more magnetic domains. However, domain wall movement magnetization requires less energy than domain rotation magnetization. The magnetization or demagnetization of the material is easy by the domain wall movement with large grain size. As a result, a sample with large grain size are predicted to have low $H_c$ and high $M_s$ as reported by [23].
Subsequently, our sample shows excellent results than that reported by other works using different synthesis method of CFO as summarized in table 2. In fact, CFO elaborated by sol-gel auto combustion shows an $M_s$ of 69.59 emu g$^{-1}$ under a magnetic field of 10 kOe with a high $H_c$ of 647 Oe [40]. Using solid state method, Rajath Varma obtained an $M_s$ value of 82 emu g$^{-1}$ under a high applied field of 60 kOe [41]. As a result, the different values of $M_s$ and $H_c$ of all reported materials (Table 2) demonstrates the effect of the synthesis method or the microstructure of CFO on their magnetic properties.

Table 2 Comparison of magnetic properties $M_s$ and $H_c$ at 300K of CoFe$_2$O$_4$ particles obtained by various synthesis processes

| Synthesis method                     | Particle size (nm) | Magnetic field (kOe) | $M_s$ (emu g$^{-1}$) | $H_c$ (Oe) | References |
|--------------------------------------|--------------------|----------------------|---------------------|------------|------------|
| Sol-gel auto combustion              | 160                | 25                   | 83                  | 284        | This work  |
| sol–gel auto combustion              | 25                 | 10                   | 69.59               | 647        | [40]       |
| Wet chemical route                   | 21                 | 15                   | 68                  | 1250       | [26]       |
| Co-precipitation                     | 34-40              | 15                   | 74                  | 650        | [9]        |
| Hydrothermal                         | Rods (length : 139.63 / width : 35.23) | 15 | 68.5 | 1250 | [9] |
| Solid state                          | 290                | 60                   | 82                  | 304        | [41]       |
| Sol–gel                              | 36.5               | 30                   | 66.7                | 1163.9     | [12]       |
| Polymer complex                      | 32                 | 60                   | 67                  | 1625       | [41]       |

To have a better insight of the nature of the magnetic phase transition in our CFO, the Arrott plots ($M^2$ vs H/M) obtained from M(H) curves are extrapolated, as plotted in Fig. 6.

Fig. 6 Arrott plots at different temperatures under an applied magnetic field of 25 kOe
The slope signs of the linear fit indicate the order of the transition, when the slope is negative, a first order transition occurs, and when it is positive, a second order transition exists. Following Banerjee's criterion [42]. In our case, a positive slope value is identified, suggesting that our sample represents a second order FM-PM phase transition, and exhibiting the same behavior shown in nickel–zinc ferrites [7].

**Magnetocaloric properties**

In order to investigate the magnetocaloric effect of our material, the indirect method based on M(H) measurement was performed. The magnetic entropy change $\Delta S$ and the adiabatic temperature changes $\Delta T$, versus the magnetic field (H), are given by the Maxwell equations 2 and 3. Using the upper branches of all the recorded M(H) curves at each measurement temperature, the polynomial fits allows us to determine the variation of magnetization as a function of temperature ($\frac{\partial M}{\partial T}$) under various applied magnetic fields between 5 and 24 kOe. The resulting curves of $\Delta S$ and $\Delta T$ are plotted in the fig.7 (a) and (b) respectively.

$$\Delta S(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH \quad (Eq 2)$$

$$\Delta T(T, H) = \int_{H1}^{H2} \frac{T}{C_p} \left( \frac{\partial M}{\partial T} \right)_H dH \quad (Eq 3)$$

![Fig. 7 Magnetic entropy change $\Delta S$ and the adiabatic temperature changes $\Delta T$ as a function of temperature under various magnetic fields for CoFe$_2$O$_4$ powder](image)

Both curves reveal two magnetic anomalies. The anomaly occurred at 700 K corresponds to the FM-PM phase transition. However, the first anomaly that observed at 600 K on the $\Delta T$ curves and at 450 K on the $\Delta S$ curves can be attributed to lattice distortion and domain walls.
dynamics or pinning of domains. This process is activated by temperature, leading to the maximal reorientation at Curie temperature. Moreover, we can observe also on the M(H) measurement (Fig.5) the vertical jump straight up of the magnetization M as showed on the $\Delta T$ reordered curve at 600 K. Maximal entropy of 6.2 J.kg$^{-1}$K$^{-1}$ is observed at the FM-PM phase transition temperature that corresponds to an adiabatic electrocaloric temperature change of 11.2 K. The high value obtained can be attributed to the grain size as reported by [24], [25]. In another way, smaller particle sizes have less magnetic hysteresis, resulting in less energy lost in the thermal process, and thus the electrocaloric effect is greater.

For industrial refrigeration applications, the performance of MCE of CFO sample is evaluated using the Relative Cooling Power (RCP) defined by Equation 4:

$$RCP = -\Delta S_M^{max} \times \delta_{FWHM} \quad (Eq \ 4)$$

Here $\Delta S_M^{max}$ refers to the maximum value of the magnetic entropy, and $\delta_{FWHM} = (T_{hot} - T_{cold})$ is the full width at half maximum of the curve $\Delta S_M^{max}$.

![Graph showing RCP vs. H(Oe)](image)

Fig. 8Magnetic field dependence of the RCP

The RCP value increases proportionally with the applied magnetic field (Fig. 8). The good RCP value of 687.56 J Kg$^{-1}$ obtained under low applied magnetic field (24 kOe) leads to state that such sample could be considered as potential candidate for magnetic refrigeration application at 600 K - 800 K temperature range.

It should be mentioned that the obtained values of $\Delta S$, $\Delta T$ and RCP are much higher than those reported in the literature in the ferromagnetic oxide systems (table 3). Moreover, even with a high applied magnetic field, cobalt ferrites doped with copper show a moderate $\Delta S$ value of 0.6 J Kg$^{-1}$ K$^{-1}$ with a RCP of 62.55 J Kg$^{-1}$[39]. For Mg$_{0.6}$Cu$_{0.4}$Fe$_2$O$_4$ nanoparticles elaborated by the sol-gel technique, the maximum MCE value reported was 1.09 J kg$^{-1}$ K$^{-1}$ under an applied field of 50 kOe. In our previous work [5], a high RCP of 79.19J Kg$^{-1}$ with a $\Delta T$ of 5.6 K under 60 kOe was achieved in perovskite manganite La$_{0.3}$Ca$_{0.5-x}$□$_x$MnO$_3$. 
This comparison makes our CFO nanopowder a good candidate for the magnetic heating and cooling applications.

Table 3. Magnetocaloric properties of ferromagnetic oxides.

| Material                  | \(T_C\) (K) | Magnetic field (kOe) | \(\Delta S\) (J Kg\(^{-1}\) K\(^{-1}\)) | \(\Delta T\) (K) | RCP (J Kg\(^{-1}\)) | References |
|---------------------------|--------------|----------------------|------------------------------------------|-----------------|---------------------|------------|
| CoFe\(_2\)O\(_4\)        | 785          | 24                   | 6.15                                     | 11.24           | 687.56              | This work  |
| CoFeCuO\(_4\)            | 688          | 50                   | 0.6                                      | --              | 62.55               | [39]       |
| Zn\(_{0.2}\)Ni\(_{0.8}\)Fe\(_2\)O\(_4\) | 705          | 50                   | 1.61                                     | --              | 233                 | [6]        |
| NiFe\(_2\)O\(_4\)        | 845          | 25                   | 0.75                                     | --              | 60                  | [7]        |
| Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) | 481          | 25                   | 1.15                                     | --              | 161                 | [7]        |
| Mg\(_{0.6}\)Cu\(_{0.4}\)Fe\(_2\)O\(_4\) | 630          | 50                   | 1.09                                     | --              | 136                 | [44]       |
| La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) | 364          | 1                    | 1.6                                      | --              | 0.4                 | [45]       |
| La\(_{0.5}\)Ca\(_{0.5-x}\)\(\square\)\(_x\)MnO\(_3\) | 254          | 60                   | 2.70                                     | 5.6             | 79.19               | [5]        |
| EuTi\(_{0.9}\)Cr\(_{0.1}\)O\(_3\) | --           | 20                   | 30                                       | 4.2             | 125                 | [46]       |
| EuDy\(_2\)O\(_4\)        | -17.4        | 80                   | 25                                       | 16              | 415                 | [47]       |

**Conclusion:**

In conclusion, we investigated the structural, magnetic, and magnetocaloric properties of CoFe\(_2\)O\(_4\) ferrite (CFO) nanoparticles elaborated by sol-gel auto combustion. According to X-ray diffraction analysis and Raman spectra the CFO crystallizes in a cubic spinel structure with space group of \(Fd\overline{3}m\). Magnetic measurements reveal that our CFO exhibits a second order PM - FM phase transition with a Curie temperature of 785 K. The maximal magnetic entropy change and relative cooling power (RCP) are both enhanced, making our CFO suitable candidate for both environmentally friendly magnetic refrigeration and medical applications that need temperatures above 300 K.

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