# Relaxation Behavior of Néel Temperature in Micro and Nanosized Particles of $CaMnO_3$

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**Abstract**

Micro and Nanosized powders of $CaMnO_3$ were prepared by the conventional solid state- reaction and sol-gel procedures, respectively. The X-ray patterns indicated that both types of the powders have orthorhombic symmetry structure at room temperature. Further characterizations of the samples were preformed employing SEM and TEM techniques. The oxygen content in the prepared powders were determined by EDS which revealed that the amount of oxygen in the samples synthesized via the sol-gel method is less than that of the samples prepared by the solid-state reaction. The phase transition temperature from antiferromagnetic to paramagnetic was found to be slightly higher in sintered O ring samples made from nanopowders. These results can be due to the double exchange $Mn^{3+}$-O-$Mn^{4+}$ interaction and also electron hopping mechanism which occurs more in the samples made from nanopowders. The frequency dependence of the Neel temperature and the shape of the hysteresis loop, observed in both types of the samples, can be attributed to the reduction of relaxation time with increasing the frequency.

***Keywords**: Antiferromagnetic, Néel temperature, Hysteresis loop, Oxygen deficiency, Relaxation*

## 1. INTRODUCTION

In the past two decades the manganese oxides, because of their interesting electrical, magnetic and thermoelectric properties have been studied extensively. They exhibit large magnetoresistance and unusually charge and magnetic ordering. These effects are believed to arise due to the strong coupling among the charge, lattice, and spin_magnetic_degrees of freedom [1]. $CaMnO_3$ is a so called parent compound for many manganese oxide systems exhibiting colossal magnetoresistance such as $Ca_{1-x}La_xMnO_3$ and $Ca_{1-x}Sr_xMnO_3$ [2]. The $CaMnO_3$, crystallizing in a perovskite type structure with space group Pnma, is a G-type antiferromagnetic (AFM) insulator with additional weak ferromagnetic component in its ground state [3]. When oxygen content decreases, the $CaMnO_{3-x}$ phases show stronger double exchange interactions with ferromagnetic ordering and increasing the $T_N$

[4]. For example, $CaMnO_{2.5}$ shows an antiferromagnetic transition to paramagnetic around $T_N$~350K [5]. This effects are explained by the incorporation of $Mn^{3+}$cations when the oxygen are reduced, which induces $Mn^{3+}$–O–$Mn^{4+}$ ferromagnetic double-exchange interactions and the increase of the conduction by electron hopping mechanism [6]. In addition, increasing of $T_c$ in manganese oxides by particle size reduction is can be due to compaction of the unit cell of the lattice and reduction of the unit cell anisotropy [7]. However, recently, many works have been published related to structure and magnetic properties of $CaMnO_3$ at high magnetic fields [8-12]. In this paper we have studied magnetic properties of $CaMnO_3$ samples prepared by both sol-gel and conventional solid state reaction methods at low magnetic fields and investigated the relaxation behavior in these samples.

## 2. EXPRIMENTAL

Nano and micro powders of $CaMnO_3$ were prepared by sol-gel and conventional solid state reaction methods from a stoichiometric mixture of Ca $(CH_3COO)_2.XH_2O$ and $Mn(CH_3COO)_2.4H_2O$. All the synthesized powders were calcinated at different temperatures. However the lowest temperature at which manganese oxides perovskite structure was established was found to be 800°C. Both samples were pressed into O ring at pressure 100bar and sintered at 900°C. X-ray diffraction (XRD) analysis was carried out using CuKα radiation. Lattice parameters were obtained from the analysis of the x-ray data. Scanning (SEM) and transmission electron microscopy (TEM) techniques were used to observe the particles morphology as well as nano structures of the sintered samples. The samples prepared as O rings were magnetized, using a coil to produce a magnetic field, and also measured in a magnetic setup, using the Faraday effect with H<30 A/m. The Néel temperature and magnetic permeability of both types' samples were measured, as a function of temperature at three different frequencies. The hysteresis loops were measured at 77K by applying an AC current with frequency values 10 KHz and 100KHZ. The shape of the hysteresis loops observed on the oscilloscope depends on the applied current intensity, which is related to the magnetic field of samples (B) [13]. Finally, AC hysteresis curves of both samples are measured and compared.

## 3. RESULTS AND DISCUSSION

### A-Charachtization

The XRD patterns of $CaMnO_3$ powders calcinated at 800°C are given in Fig.1, which indicate that both samples are single phase with an orthorhombic symmetry. Structure refinements of these samples from x-ray data were performed in the orthorhombic space group Pnma with parameter constants presented inTable 1.

The TEM image of the $CaMnO_3$ nanopowders shown in Fig. 2 indicates that the nanoparticles shape is spherical. The average particles size is about 85 nm.

**B-SEM and EDS Analysis**

The SEM images of the $CaMnO_3$ samples sintered at 900°C, prepared from conventional solid state reaction and sol-gel techniques, are shown in Fig.3. The grains size of $CaMnO_3$ sample made from the nanopowders synthesized via sol-gel method, Fig.3 (a), are about 100–200 nm and are highly homogeneous in comparison with the grains of the sample prepared from micropowders, Fig.3 (b).

The Oxygen content determined by EDS analysis for the $CaMnO_3$ sample prepared by sol-gel method is less than that of the sample prepared by conventional solid state reaction.

**C-Magnetic properties**

Plotting the magnetic permeability of $CaMnO_3$ samples versus temperature helps to determine the Néel temperature and test the homogeneity of the samples. Permeability was obtained by measuring the inductance of the samples in a coil on an impedance bridge at different temperatures [13, 14]. Samples were cooled in liquid nitrogen and warmed up gradually with a constant rate. The variation of relative magnetic permeability versus temperature is shown in Fig.4, which shows that above $T_{Néel}$, permeability decreases with increasing temperature. This can be due to disturbing the domains magnetic ordering, by increasing thermal energy more than the exchange interaction. So at $T_{Néel}$, transition from antiferromagnetic to paramagnetic occurs. The values of $T_{Néel}$ obtained at different frequencies for both types of the sintered samples are given In Table 2. The Néel temperature of the sample made from nanopowders are slightly higher than that of the sample made from micropowders. This result can be due to more double exchange interaction $Mn^{3+}$–O–$Mn^{4+}$ and electron hopping which occur in the first sample. The hysteresis curves of the samples are shown in Fig. 5, which are obtained for two frequencies (10KHZ and 100KHZ).Although, the eddy currents are weak, the widening of the hysteresis loops may be due to the increase of eddy currents in our case, since $Mn^{3+}$–O–$Mn^{4+}$ double exchange and electron hopping mechanism have increased with increasing the frequency, leading to the increase of the electrical conductivity. Another way to understand the frequency dependence of $T_{Néel}$ and the coercivity is considering the forces that act on the domain walls. The state of the system, given by domain wall configuration, is driven by the applied field (varying at a given dH/dt),to relax at lower energies. Coercive and remanence magnetic field measured in both types of the samples are summarized in Table.3. The increase of the coercivity with increasing the frequency in both samples is remarkable. Widening of hysteresis loop is well known in the conductive magnetic materials and it can be attributed to eddy current losses [15, 16]. However, in such low magnetic fields eddy current is negligible. In this case we can use the other theory that at low frequency, dH/dt is low and the system has more time to relax to lower energies, which results in the lowering $H_C$. With increasing frequency dH/dt increases and the system has less and less time to relax. This effect can be observed as an increase of the domain wall pinning [17].

## 4. CONCLUSION

The $CaMnO_3$ nano and micropowder samples have been synthesized by sol-gel and conventional solid state reaction methods, respectivly. The X-ray analysis indicates that both structures have orthorhombic phases. The single phase of $CaMnO_3$ starts to form at calcination temperature of 800°C in both procedures. The average particles size of the synthesized powders is estimated from TEM image and was found to be about 85nm. $CaMnO_{3\ O\ ring}$ pressed sintered sample made from nanopowders has slightly higher phase transition temperature to paramagnetic state and also wider hysteresis loop than that of bulk samples. This result is due to the double exchange interaction of $Mn^{3+}$–O–$Mn^{4+}$ and electron hopping which occurs more in the samples made of nanopowders synthesized via sol-gel technique. It was also found that if the hysteresis loop is obtained in an AC magnetic field, the measured Néel temperature and the shape of the hysteresis loop both depend on the frequency of the measuring magnetic field, which can be interpreted by domain wall pinning.

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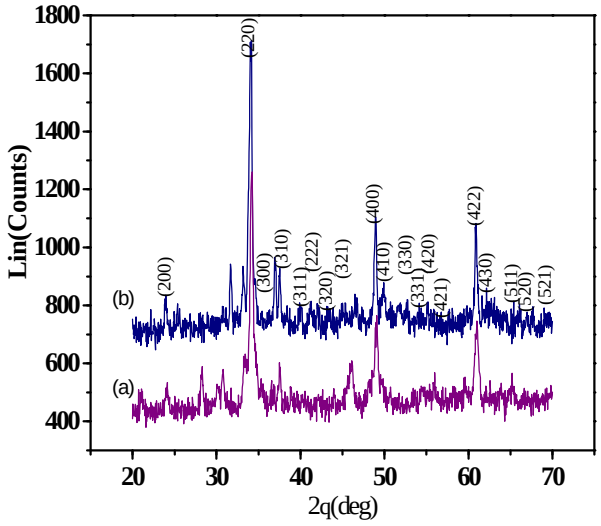


Fig.1 X-ray powder diffraction patterns of $CaMnO_3$ prepared by

(a) sol-gel and (b)conventional solid state reaction techniques.

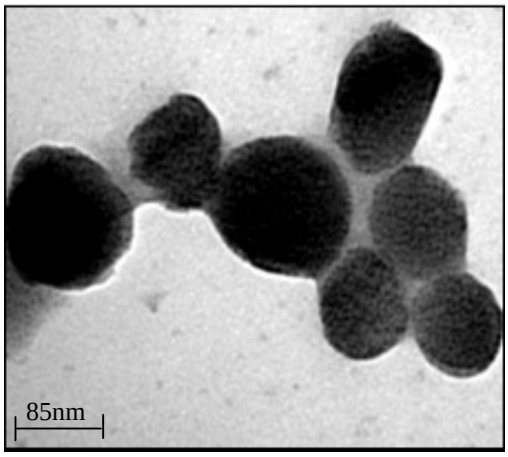


Fig.2 TEM image of the $CaMnO_3$ nanopowder calcinated at 800°C

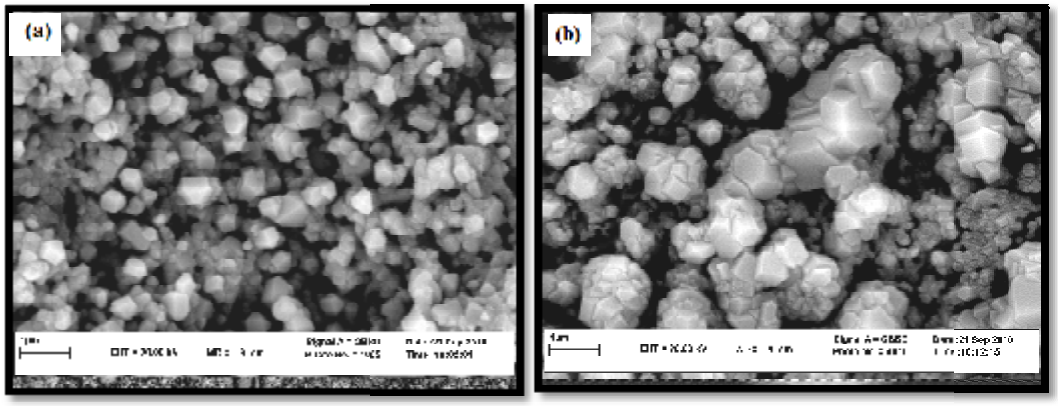


Fig.3 SEM micrograph of the sintered sample, prepared by a) sol-gel and b)conventional solid state reaction methods .

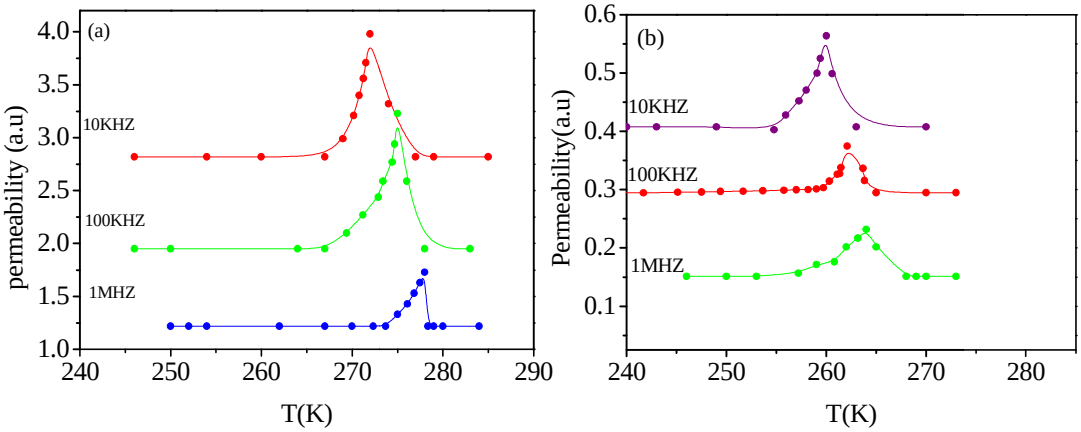


Fig. 4 magnetic permeability of $CaMnO_3$ prepared by (a) Sol-gel and (b) Conventional solid state reaction methods.

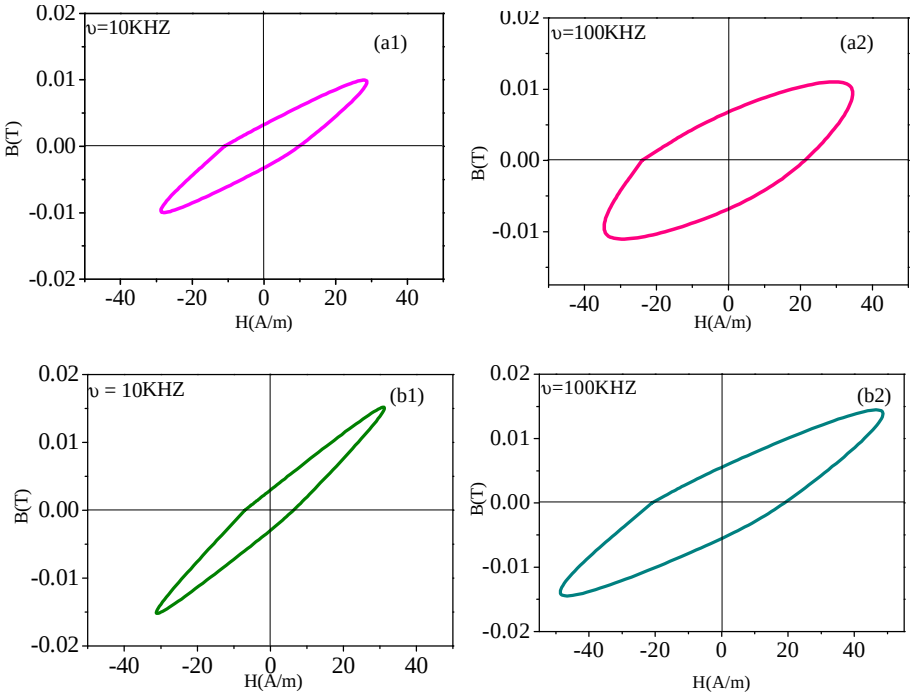


Fig. 5 AC hysteresis curves of $CaMnO_3$ prepared by (a) nano and (b) micro powders

**Table1**

Lattice parameter of $CaMnO_3$ powders

| **Method** | **T (°C) (calcination)** | **2θ (deg)** | **$d_{hkl}$** | **(hkl)** | **Phase** | **Lattice parameter (Å)** |
|---|---|---|---|---|---|---|
| **Solid state reaction** | 800 | 34.17<br>49.07<br>60.98 | 2.62<br>1.85<br>1.51 | (220)<br>(400)<br>(422) | Orthorhombic | a=5. 35<br>b=7. 43<br>c=5.28 |
| **Sol-gel** | 800 | 34. 06<br>48.94<br>60.99 | 2.62<br>1.85<br>1.52 | (220)<br>(400)<br>(422) | Orthorhombic | a= 5.28<br>b=7.45<br>c=5.26 |

**Table2**

Frequency dependence of Néel temperatures

| **Sample Prepared of** | **ν** =10KHZ | **ν=** 100KHZ | **ν=** 1MHZ |
|---|---|---|---|
| **Nano powders** | $T_N$=272K | $T_N$=275K | $T_N$=277K |
| **Bulk powders** | $T_N$=259K | $T_N$=262K | $T_N$=264K |

**Table3**

Coercive and Remanence magnetic field of $CaMnO_3$ samples in ν = 10 and 100KHZ

| | **Sample prepared by Sol-gel** | | **Sample prepared by Solid state reaction** | |
|---|---|---|---|---|
| ν(KHZ) | $H_c$(A/m) | $B_R$(T) | $H_c$(A/m) | $B_R$(T) |
| 10 | 10 | 0.0034 | 7 | 0.003 |
| 100 | 25 | 0.0078 | 21 | 0.006 |