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Comparative study on the NMR features of bulk polycrystalline and nanocrystalline $EuMnO_3$ ceramics

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ABSTRACT

The purpose of this paper is to study the effect of size-variation of $EuMnO_3$ particles on Nuclear Magnetic Resonance (NMR) phenomenon. The $EuMnO_3$ particles have been synthesized through solid state reactions resulting in micrometer (μm) particle sizes (designated as bulk). The particles have also been synthesized through sol-gel combustion resulting in nanometer (nm) particle sizes which have been designated as 'nano'. NMR spectral measurement, SEM & TEM imaging were used to characterize the resultant manganite ceramics. We compared both bulk and nanoparticle samples using NMR spectroscopy. In general, the NMR spectral line width showed a general broadening trend as the size decreased. But there was also evidence of a size dependent effect in chemical shift and in the spin-spin relaxation. The investigated details include the structure, homogeneity and particle size.

Key words: nanostructure, nuclear magnetic resonance (NMR), ceramics, manganite, europium

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INTRODUCTION

Transition metal and rare-earth manganites given by the generic formula $RMnO_3$, with 'R' representing the rare-earth or transition metal-ions, have attracted great interest for their fascinating properties and applications viz., dielectrics, metals, ferro/anti-ferromagnetics, multiferroics, magneto-electrics, magnetocaloric or giant magneto-resistive materials [1-7]. In this study we have investigated a manganite system with 'R' being europium and the material crystallizing in orthorhombic structure with Pbnm space group. In recent years, lot of work has been done on nanocrystalline materials of these manganites because of their unusual properties of bulk materials [8]. Also perovskite type oxides (with the general forrmula ABO_3) have been in the limelight for more than two decades owing to their potential commercial applications as catalysts [9] and technological importance owing to their electronic & magnetic properties [10-11].

Also the perovskite manganite compounds have received significant attention owing to their interesting Colossal Magneto-Resistance (CMR) property [12-14] which results from the presence of Mn^{4+} ions and charge ordering [15]. Of these manganites $EuMnO_3$ crystallizing in orthorhombic Pbnm space group turns-out to be more interesting in terms of cycloidal spin ordering and with half-filled electron configuration for the lanthanide ion.

Europium manganite as a perovskite can be an appropriate host lattice for substitution of other rare-earth ions, alkaline metal ions and alkaline earth metal ions, leading to alterations in the characteristics of the host. The tolerance factor are given by -

$$\tau = \frac{r_{(A-O)}}{\sqrt{2}r_{(M-O)}} \longrightarrow (1)$$

Here A-O (Eu-O is 2.3781 Å) and M-O (Mn-O is 1.9662 Å) are the bond lengths for the different metallic elements which are responsible for providing the perovskite structure in the ceramic [16]. Recent research has shown that the substitution of Mn or Eu by another ion directly modifies the chemical and physical properties of the compound by altering the interactions between the metals and oxygen (A-O and M-O respectively) in particular anti-ferromagnetic ordering at low temperatures [17].

Our earlier study on the bulk manganite system has yielded some clues on the charge build-up and dispersion processes under magneto-optical perturbation (~ 5ev) near Curie temperature T_C [18]. The nano counterpart of the europium manganite gives some clues on the modification of the electron-spin structure centering Mn sites in size restricted geometry. In this report, we have compared the magnetic properties, in particular the magnetic moment of the nuclei of bulk and nano $EuMnO_3$ systems. Also these magnetic properties depend on many factors such as the particle size, shape and morphology of structurally inhomogeneous particles [19].

NMR analysis can provide wealth of information on local magnetic states, such as chemical shifts, line-width, spin-spin relaxation time measurements etc. NMR technique is very useful in probing the individual crystallographically/magnetically nonequivalent atomic constituents [20]. However, the relation between hyperfine parameters and magnetic moment is usually not straight-forward. Also NMR spectroscopy enables the analysis of properties of magnetic materials at a microscopic level via the hyperfine interactions, which are probed using the resonance response of nuclear magnetic moments (here quadropolar nuclei I = 5/2) at individual atomic sites. It should be noted that for manganites, the spin-spin relaxation time (T_2) is often very short and frequency dependent [21]. Here we present ^{55}Mn and ^{153}Eu NMR spectral data collected for bulk and nano europium manganite ceramics.

MATERIALS AND METHODS

The poly crystalline europium manganite sample was prepared through conventional solid state reaction method. While the nano-analouge was synthesized using a sol-genl thermolysis with urea and PVA respectively as fuel and dispersing medium. Phase purity of the synthesized sample was confirmed through powder XRD analysis.

Scanning Electron Microscopy (SEM) images were recorded using a Hitachi scanning electron microscope, working at 25 kV.

Morphology and chemical purity of the nano sample has been verified using TEM and SAED pattern taken at 200KV using Icon analytical instrument.

The NMR spectra were recorded using a Bruker 400 MHz NMR spectrometer at a field strength of 9.4 Tesla with the sample spinning at a speed of 10 kHz and at a resonance frequency of 98.65 MHz (for ^{55}Mn) and also at 43.80 MHz (for ^{153}Eu). A MAS probe was deployed with a 4 mm solid sample rotor. The experiment was carried out at room temperature. Spin-spin relaxation time (T_2) was measured in seconds and was tabulated for both bulk and nano ceramics using the Bruker 'Solid Echo. Av' pulse sequence.

RESULTS AND DISCUSSION

Phase purity of the synthesized sample was confirmed through powder XRD analysis and the least squares refined crystallographic unit-cell parameters for $EuMnO_3$ sample (space group-*Pbnm*) has been tabulated (Table -1).

Table-1

Least squares refined crystallographic unit-cell parameters for $EuMnO_3$ sample (space group-*Pbnm*).

System	**Refined cell parameters (Å)**			**Standard deviation (σ)**
	a	b	c	
JCPDS #26-1126; # 25-0335	5.336	5.842	7.451	
EuMnO3 – bulk	5.332	5.833	7.461	$\alpha_c = \pm 0.004$ $\alpha_b = \pm 0.009$ $\alpha_c = \pm 0.010$
EuMnO3 – Nano	5.334	5.830	7.443	$\alpha_a = \pm 0.002$ $\alpha_b = \pm 0.012$ $\alpha_c = \pm 0.008$

From the SEM image given in Figure 1, we have that the bulk samples show uniform distribution of grains having particles (average size ~ 2 μm) with well-defined polyhedral morphology. Also this suggests the homogeneous chemical composition, uniform density and porous morphology of the sample. The surface granules forming the ceramic are isotropic (i.e., a spherically symmetric morphology).

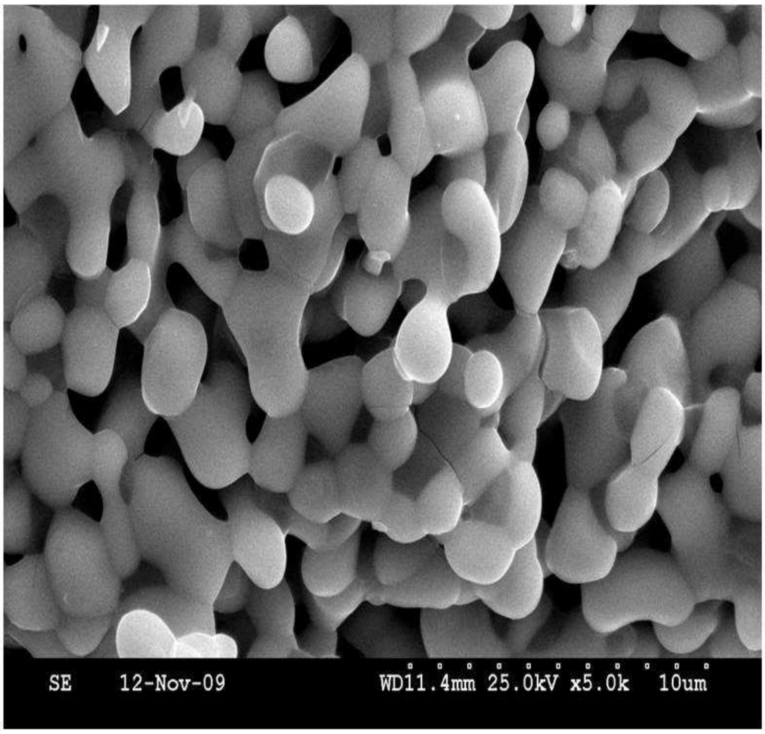

Figure 1 SEM micro image of EuMnO$_3$ bulk ceramics

From the TEM micrograph given in Figure 2, for the nano-ceramics, it can be found that the average particle size is around 5 nm. Also the corresponding systemic spotty SAED pattern corroborates the nanocrystalline nature of the sample under study. Further, TEM image indicates the agglomerated nature of the nanoparticles with the particles having asymmetric morphology and size distribution (with a size of around 5 nm).

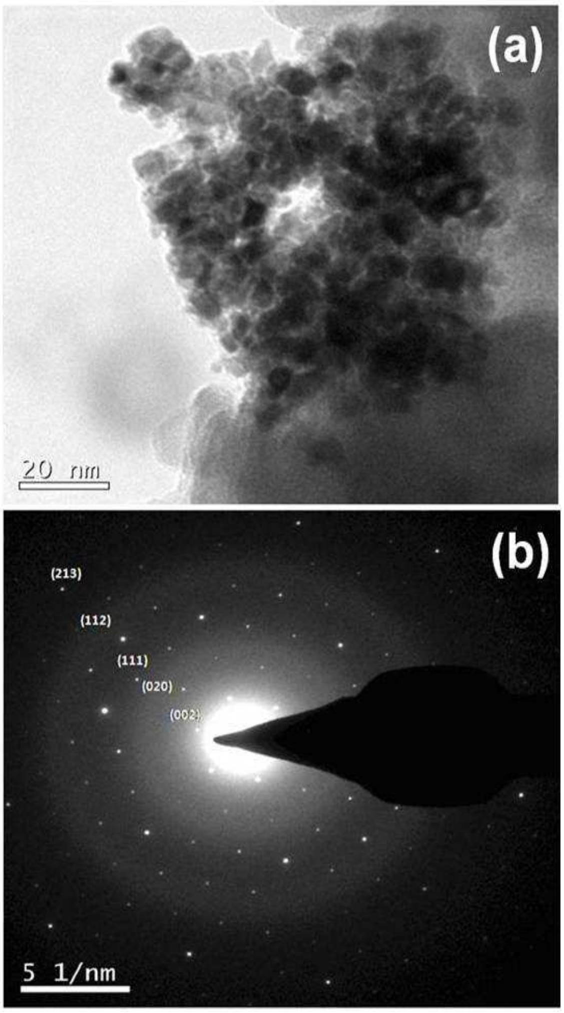

Fig: 2 *(a)* Particle morphology of $EuMnO_3$ nano-ceramics using TEM.
(b) Corresponding SAED pattern of $EuMnO_3$ nano ceramics.

The NMR spectra of the ^{55}Mn nuclei of the bulk and nano-ceramic powder (Figure 3) are rather broad possibly because of ^{55}Mn being a quadrupolar nuclei (I = 5/2) as quadrupole nuclei can display broad resonance lines in NMR spectra [22]. The properties of perovskite oxides (of the general formula ABO_3) depend strongly on the nature of the A and B ions and also on the valence state of these ions. The A site ions are generally catalytically inactive and influence the thermal stability of the perovskite while the transition metal ions at the B sites are from active components. $EuMnO_3$ perovskite crystallizes in the P_{bnm} structure where the manganese atom is surrounded by distorted oxygen octahedron [23]. Therefore there is an oxygen atom between every two manganese atoms. On the other hand, oxygen atoms can directly coordinate with paramagnetic metal centers

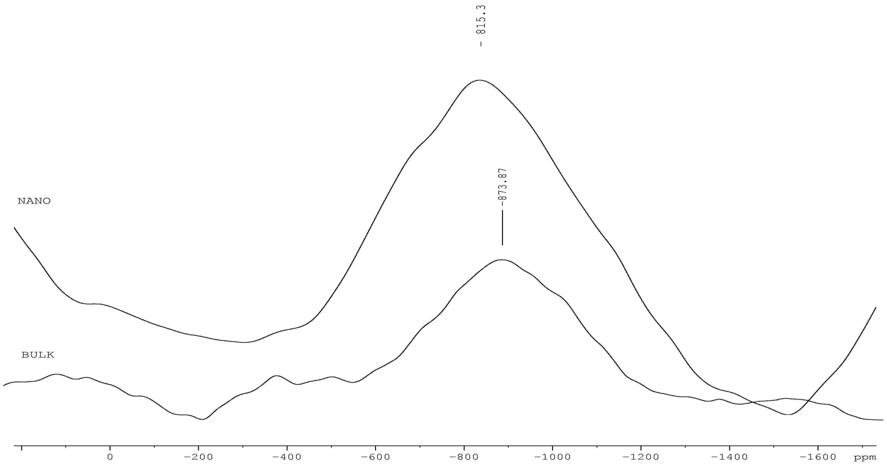

Fig: 3 ^{55}Mn NMR spectra of EuMnO$_3$ ceramics (Bulk & Nano).

leading to increased electron spin density around these nuclei. As a result, the contact mechanism between the metal ion (^{55}Mn) and oxygen nuclei (^{17}O) becomes dominant. Theoretically for paramagnetic complexes, the rate of nuclear relaxations are expressed by

$$1/T_2(I) = R_2(I) = R_2(I)^{DIP} + R_2(I)^{CON} + R_2(I)^{CURIE} \text{ ----------------------(2)}$$

Here $R_2(I)^{DIP}$, $R_2(I)^{CON}$, $R_2(I)^{CURIE}$ are the dipolar, contact and curie temperature contributions, respectively. Solomon's equation[24] shows that the influence of unpaired electrons on nuclear relaxation depends on the target nuclei. Since the nuclei (^{55}Mn) possess much smaller magnetic moments when compared to protons, their dipolar interaction with unpaired electrons will be consequently weaker [24]. In this system the only contributing factor is $R_2(I)^{CON}$. The contact contribution which arises from delocalization of the unpaired spin density in a metal-oxygen complex is given by

$$1/T_2(I) = R_2(I)^{(CON)} = (1/3)\, S(S+1)\, (A/\hbar)^2\, (\tau_{E1} + \tau_{E2} /(1+\omega_E^2\, \tau_{E2}^2)) \text{ ------------------- (3)}$$

Here “S” is the electron spin, “A” is the hyperfine coupling constant characterizing the scalar electron-nucleus interactions, with τ_{E1} and τ_{E2} being the longitudinal and transverse electron spin relaxation times respectively. For nuclei such as ^{15}N, ^{19}F or ^{17}O the A/h values are particularly big [24]. Hence the contact mechanism become dominent and ^{55}Mn NMR spectral line become broad.

From the ^{55}Mn NMR spectral data, much larger line-width is observed for nanoparticles compared to the bulk counterpart (Figure 3). Spectral shift between the bulk sample and nanoparticle is obvious (- 873.87 ppm to - 815.3 ppm). Chemical shift is the manifestation of modifaction in electronic environments of the ions indicating change in the local magnetic fields experienced by different nuclei. These local fields are anisotropic and a source of the relaxations. There may be more contributing factors in the determination of NMR chemical shifts [25] viz.

- The valence charge density on the central ^{55}Mn nuclei.
- The immediate oxygen environment of that atom.
- The more distinct neighbour around it.
- The anisotropic effect.

From the SEM images it is quite evident that the bulk particles are comparitively isotropic in nature, having uniform narrow grain size distribution when compared to the nano-analogue which has an agglomeration of particles as evidenced by the TEM micro-image. The bulk and nano samples prepared by completely different methods: high temperature solid state reaction method and low temperature sol-gel method. As a result the oxygen deficient samples especially in the case of sol-gel method could be obtained. As it is known in $EuMnO_3$ system the magnetic moments goes only from the $Mn3^+$ ions. Thus the appearance of oxygen defects in crystal structure can induce the valence change from $Mn3^+$ to $Mn2^+$ that in turn will broaden the NMR resonance lines and shift it. It is the characteristic of the randomly oriented magnetic moments and the hyperfine fields subjected to the external field in paramagnetic $EuMnO_3$ system at room temperature. It can give rise to the relaxation rate (T_2) as well a two fold increase in rate for the nanoparticles when compared to the bulk particles; 0.02 ms and 0.01 ms as presented in Table-2.

Table -2

T_2 Measurements of ^{55}Mn nuclei of $EuMnO_3$ ceramics.

Sample	T_2 (m sec)
Bulk	**0.020**
Nano	**0.012**

The NMR spectra of ^{153}Eu in both its' bulk and nano material are depicted in Figure 4. At first sight it may appear that there is no line broadening effect for both types of particles even though it is a quadrupolar nuclei having I = 5/2. In $EuMnO_3$, electrons around the europium nuclei are highly symmetrical [26]. Owing to this highly symmetrical arrangement of electrons, the field (electric field gradient) experienced by the ^{153}Eu nuclei is expected to be isotropic leading to sharp spectral line.

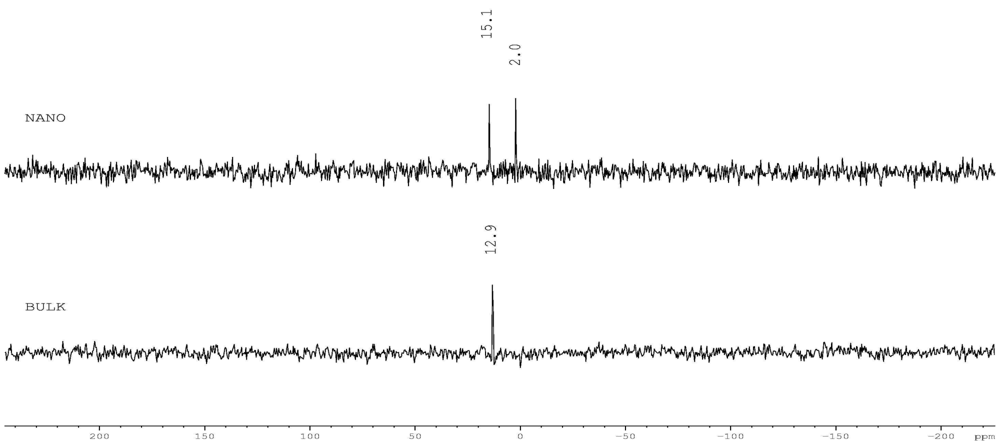

Fig: 4 ^{153}Eu NMR spectra of $EuMnO_3$ ceramics (Bulk & Nano).

Also it is of interest to note here that in addition to the shift in spectral position between the bulk (12.9 ppm) and nanoparticle samples, nano sample gives rise to two sharp resonance signals at different frequencies (as is evident from the peak positions at 2 ppm and 15.1 ppm). Also, as mentioned earlier, the chemical shifts are due to the combined effect of the electronic environments around the target nuclei and the presence of the more distinct neighbours.

Nano objects exhibits unusual physical and chemical properties. The important contributing factor for the change in properties as the particle size decreases is the increase in the ratio of “surface” atoms [19]. Such particles have a larger surface-area to volume ratio than larger particles, affecting the way they react with each other and with other substances. A 10 nm diameter nanoparticle has about 15% of the atoms on the surface; by comparison, this drops to <1% for a bulk solid [26]. The surface-atoms differ from the bulk-atoms in their coordination number, local environmental symmetry etc. which eventually causes a variation in their physical and chemical properties. As a result the properties of the surface and the interior of the nanoparticle are inevitably dissimilar. It can be stated with confidence that any random nanoparticle will have a shell structure but not all will have a clearly defined core. Among many physical properties “magnetic properties” of nano material has special place. If we look at the magnetic properties, the difference between the bulk material and the nano material is clearly pronounced. The magnetic properties of nano particles are determined by chemical composition, particle size, shape and morphology. It has been shown that the magnetism (per atom) and magnetic anisotropy (surface) of nanoparticles can be much greater than those of a bulk specimen [19].

We hoped at the outset for some sign of a separating “surface” europium signal, which, given the known dispersion of europium shifts, would have split-off from the bulk signal. In ^{195}Pt metal dispersions, such separate contributions are identifiable [27]. From our data, it is clear that the surface atomic nuclei resonate at a slightly different frequency in comparison to the rest of the bulk. This may be the cause of two NMR spectral lines in the ^{153}Eu spectra as mentioned already. The electron symmetry around europium nuclei changes in the surface due to oxygen deficient nano samples obtained by sol-gel method, could be the reason to produce this effect.

In the case of the bulk particles the surface structure shows isotropic chemical shifts that are unchanged from isotropic shifts. These observations validate our hypothesis that the nano particles surface is regarded to be localized. Also from Table-3 it is clear that the relaxation rate for both types of particles remains the same (6.7 ms to 6.3 ms), but the side bands show much larger line width.

Table - 3

T_2 measurements of ^{153}Eu nuclei of $EuMnO_3$ ceramics.

Sample	T_2 (m sec)
Bulk	**6.7**
Nano	**6.5**

CONCLUSION

Bulk and nano europium manganite ($EuMnO_3$) ceramics have been synthesized. The poly crystalline samples studied using SEM showed well dispersed fine spherical particles (size ~ 2 µm) with homogeneous distribution.

While the nano ceramics investigated using TEM has shown nano particles with pronounced shape anisotropy and a wide size distribution (size ~5 nm). The NMR spectral analysis on ^{55}Mn revealed that in size restricted geometry, the effect of particle size and distribution (~5nm) is reflected directly in the increased line-broadening for the nano sample. Also the ^{153}Eu NMR spectra has shown sharp peaks for the bulk specimen while two sharp resonance peaks has been observed in the case of the nanoparticle sample that can be attributed to localized surface metal-ions in comparison with rest of bulk. On the other hand the reason for not observing the same phenomenon in the case of ^{55}Mn NMR spectra can be due to line broadening. It has also been observed that the nanoparticles tend to relax much faster than the bulk particles for ^{55}Mn nuclei whereas for ^{153}Eu nuclei the rate of relaxation remains same.

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