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Research articles

Possible observation of Griffith phase over large temperature range in plasma sintered $La_{0.67}Ca_{0.33}MnO_3$

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ABSTRACT

We report on the possible observation of Griffith phase in a wide range of temperature (>272–378 K) in the 2.5 min plasma sintered $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) as deduced from careful electron spin resonance studies. This is 106 K higher than the paramagnetic to ferromagnetic transition (Curie transition ~272 K) temperature. The indication of Griffith phase in such a wide range is not reported earlier by any group. We purposefully prepared LCMO samples by plasma sintering technique so as to create a disordered structure by rapid quenching which we believe, is the prime reason for the observation of Griffith Phase above the Curie transition temperature. The inverse susceptibility curve represents the existence of ferromagnetic cluster in paramagnetic region. The large resonance peak width (40–60 mT) within the temperature range 330–378 K confirms the sample magnetically inhomogeneity which is also established from our electron probe microstructure analysis (EPMA). EPMA establishes the presence of higher percentage of Mn^{3+} cluster in comparison to Mn^{4+}. This is the reason for which Griffith state is enhanced largely to a higher range of temperature.

1. Introduction

The understanding of spin dynamics, magnetic interactions and spin correlation on a microscopic level could be well explained in colossal magnetoresistance (CMR) manganites through electron spin resonance studies [1–4]. The interplay between spin and charge degrees of freedom in colossal magnetoresistance manganites have been generated a lot of attention for the potential applications of these materials in magnetic sensors, bolometers, magnetic refrigeration and micro-magneto electronics (micro-spintronic devices) [5–8]. The prime interest in manganites is also to observe the low-field sensitivity of large magnetoresistance (MR) response around Curie temperature (T_C) close to room temperature. The Curie temperature observed in $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) is 250 K whereas it could be enhanced to 260 K in LCMO sintered at partial melted stage [9]. The micrographs of partial-melt samples exhibit an excellent connectivity between grains, suggesting the enhancement of percolation current transport by opening new conduction channels and disappearance of magnetic phase boundary at elevated temperatures by the ordering of Mn spins blocked at the grain boundary of sintered samples [9]. This new phenomena prompts us to sinter the sample by thermal plasma technique within a short sintering time, which leads to the enhancement of Curie transition temperature from 260 K to 280 K [10]. Thermal plasma techniques forbids the grain growth and as well creates inter-grain and intra-grain connection between them which is the prime reason for the enhancement of Curie transition temperature. In addition to this, the understanding of Griffith phase in the paramagnetic region is an interesting issue in manganites. However, ESR studies confirm the presence of Griffith Phase [11] in the paramagnetic region upto higher temperature than the Curie transition temperature in manganites [1,5,12–22] and in particular LCMO [1,8,14,17]. The quenched disordered structure and clusters of magnetic domains on sample surface is the origin of enhanced Griffith phase to higher temperature [11,16]. It is reported that Griffith phase is observed within a temperature range of 20–30 K higher than the paramagnetic to ferromagnetic transition temperature. Moreover, the investigations suggest that the mixture of Mn^{3+}/Mn^{4+} ions and the arrangement of both the ions are responsible for the observation of enhanced Griffith phase at large temperature above than Curie transition temperature. Again the presence of some form of magnetic clusters is also responsible for the enhancement of ferromagnetic signal above

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room temperature [16]. The higher value of transition temperature is also depending upon the content of oxygen and the oxygen deficiency helps in increasing the transition temperature [14]. The purpose of our research work is to prepare LCMO samples by plasma sintering technique and to create intentionally a disordered structure by rapid quenching. As there is a drastic fall of temperature from thousands K to hundreds K during processing within a small span of time, the system does not get enough time for the relaxation and possibly, this is the mechanism for the creation of disordered structure [10]. Again, the sample is prepared at argon atmosphere, oxygen deficiency is also one of the factors for the enhancement of paramagnetic to ferromagnetic transition temperature and metal-insulator transition temperature [10]. As discussed above, the quenched disordered structure also creates existence of Griffith like phase in the paramagnetic region. This prompts us to study the plasma sintered samples by electron spin resonance technique. The electron spin resonance studies on plasma sintered LCMO shows Griffith like phase at much higher than the Curie transition temperature obtained from SQUID studies. Attempt has also been undertaken to understand the role of magnetic domains and the role of magnetic domain boundary for the existence of Griffith phase in the paramagnetic region. The possible observation of Griffith phase in the plasma sintered LCMO upto 378 K is a surprising feature which is 106 K higher than the Curie transition temperature.

2. Experimental detail

LCMO samples with composition of $La_{0.67}Ca_{0.33}MnO_3$ was prepared by thermal plasma sintering technique for which high-purity oxides (99.99%) of La, Ca and Mn were taken as starting materials. The oxide powders with exact stoichiometric compositions were mixed by repeated grinding, followed by heating and quenching at room temperature. Suitable quantity of polyvinyl alcohol (PVA) was mixed (0.5 M) with the consolidated powder to make circular pellets of 1 cm diameter using hydraulic press with an applied load of 10 tonne/cm^2. All pellets were calcined at 600 °C for 5 h to achieve pre-handling strength of the green pellet for thermal plasma assisted sintering. These calcined pellets were sintered by thermal plasma reactor at plasma power of 15 kW with a plasmagen gas (argon) flow of 1.5 l/min within 2.5 min of sintering time. At the end of the plasma arc, sample was cooled in the normal environment. The details of the plasma reactor and sintering modules were discussed elsewhere [10]. Temperature dependent magnetization studies were carried out using SQUID magnetometer at an applied magnetic field of 50 Oe. To have a further view on the spin dynamics and magnetization, electron spin resonance studies has been carried out using Bruke ESR spectrometer. An electron probe microstructure analyser (EPMA) study of sintered specimen was carried to have the surface morphology and elemental distribution using JEOL-JXA 8100 (Superscope) model.

3. Results and discussion

X-ray diffraction pattern of 2.5 min plasma sintered LCMO is shown in Fig. 1 which presents the polycrystalline nature of the sample. The diffraction peaks are indexed according to the JCPDF # 87-1084. It clearly shows the orthorhombic crystal structure with *Pbnm* space group. However, the higher intensified peak ((112), (020)) is shifting towards the lower 2θ in consideration to the referred value (JCPDF # 87-1084). The lattice parameters are estimated to be "a = 5.499 Å, b = 5.546 Å and c = 7.820 Å" which are slightly higher than the reported values "a = 5.471 Å, b = 5.456 Å and c = 7.711 Å". This evidences the creation of structural disorder of the samples due to the rapid sintering technique. As, the sample is quenched off from higher temperature to room temperature during sintering, the sample does not get enough time for grain growth and to build up a perfect crystal structure. However, the intention of the work is to process high temperature ceramics like LCMO within a short span of time with proper phase and space group. This prompts us to cool this sample in the presence of environmental atmosphere to see the variation in magnetic behaviour through SQUID and ESR spectroscopy.

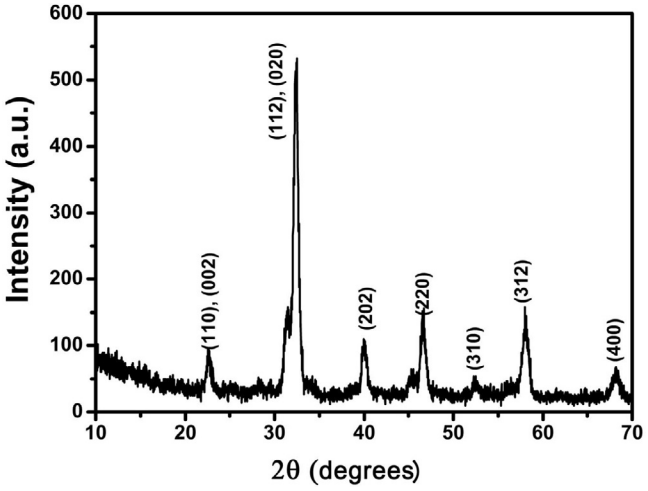

Fig. 1. X-ray diffraction pattern of 2.5 min plasma sintered $La_{0.67}Ca_{0.33}MnO_3$.

Temperature dependent magnetization curve is shown in Fig. 2a. The magnetization measurement has been carried out with the variation of temperature at an applied magnetic field of 50 Oe. A broad transition from ferromagnetic to paramagnetic (T_C) has been observed at around 272 K for the plasma sintered LCMO. The observed ferromagnetic properties of the manganite is well described in terms of the theory of double exchange interaction [23,24] between Mn^{3+} and Mn^{4+} ions. Again, it is observed that the magnetization value decreases with the decrease in temperature below Curie temperature. It indicates the presence of some kind of randomly frozen magnetic clusters [25–28] at lower

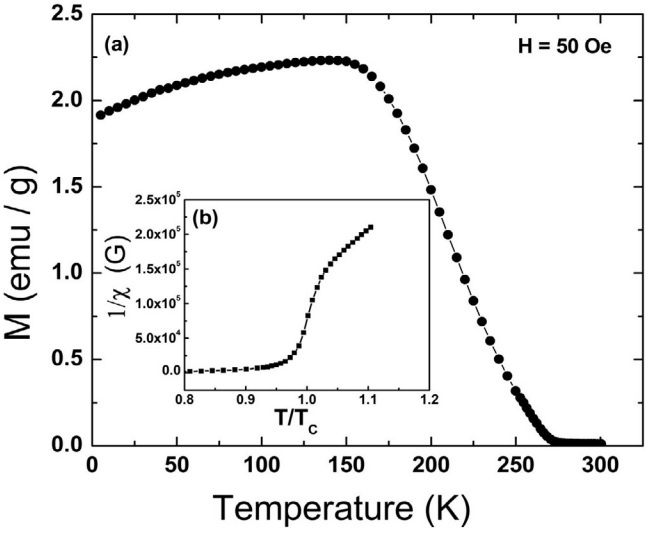

Fig. 2. a. Temperature dependent magnetization curve of 2.5 min plasma sintered $La_{0.67}Ca_{0.33}MnO_3$ and b. Inverse susceptibility vs T/T_C curve of 2.5 min plasma sintered $La_{0.67}Ca_{0.33}MnO_3$.

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