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Research Article

Investigations on Transport and Magnetic Properties of Pb (0.1) Doped $LaMnO_3$ Single Crystals

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Abstract

Single crystals of $La_{0.9}Pb_{0.1}MnO_3$ (LPMO) were grown from the flux solution of PbF_2 and PbO. The X ray back reflection Laue pattern and powder diffraction were carried out to determine quality and structure of the grown LPMO single crystals. Surface morphology and the chemical composition of the grown crystals were studied using SEM and EDX. Resistivity measurement was performed in a magnetic field of 0T and 6T and its magneto-resistance value was determined. Hysteresis was measured using magnetic field parallel and perpendicular to 'ab' plane at 10K. DC magnetization was carried out between the temperature ranges 10 K-300 K. The magnetic field dependence of ZFC and FC condition magnetization were measured with the field at 20 Oe and 500 Oe.

Keywords: Olossal magnetoresistance; Single crystals; Surface morphology; Cluster glass.

Introduction

Large magneto-resistance (MR) near the Curie temperature (T_C) in divalent doped rare earth manganese oxides perovskite has created a lot of interest among researchers. The general form of perovskite-type manganese oxides are $R_{1-x}A_xMnO_3$ (R and A being trivalent rare earth and divalent alkaline earth ions respectively). Ferromagnetism in these systems has been explained usually in terms of the double-exchange (DE) mechanism proposed by Zener. However, the double-exchange model alone is not sufficient to explain the colossal magneto-resistance (CMR) effect of the manganite. It has been suggested that a strong spin-phonon interaction arising from the Jahn-Teller splitting of the Mn^{3+} levels plays an important role in the localization of carriers and the origin of the colossal magneto-resistance [1].

The Jahn-Teller effect and the electron-phonon coupling have been proved by optical measurement on $La_{0.7}Pb_{0.3}MnO_3$ single crystal [2] and positron annihilation studies on $LaPbMnO_3$ poly crystals [3,4]. A large number of $R_{1-x}A_xMnO_3$ systems have been studied at ×=0.3 due to the crossover from semiconductor to metal transition at room temperature [5]. The Pb substituted system has attracted great interest because of its large negative magnetoresistance and metal insulator transition at room temperature [4,6]. Peak resistivity, metal insulator transition temperature and magnetic transition temperature are dependent on the quality, processing conditions and amount of doping. The growth of single crystals of rare earth manganite has been carried out using flux growth and floating zone method [7-9].

The flux growth method is one of the most commonly used processes to produce single crystals for incongruent melting and high melting point materials. Most of the polycrystalline colossal magneto-resistance (CMR) materials are synthesized by solid state reaction at approximately 1573K due to the formation of oxide material but, the present study in this case the Pb based material was synthesized below 1573K due to its low melting point and the evaporation of Pb at high temperatures. The growth of Pb doped rare earth manganite single crystals was reported [7-9]. The eutectic composition of PbO-PbF_2 at 1:1.17 gives a low melting point of flux and complete dissolution of charge at low temperatures [10]. In the present work $La_{0.9}Pb_{0.1}MnO_3$ single crystals were grown by flux method and their

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structural, surface morphology, electrical transport and magnetic properties were studied.

Materials and methods

Initially, the poly crystals of $La_{0.9}Pb_{0.1}MnO_3$ were prepared using the solid state reaction method. Stoichiometric amount of La_2O_3, PbO and MnO_2 powders were homogeneously mixed. Then the mixed powder was sintered at 1073k and 1273K for 24 hours with intermediated grinding. The powder obtained was ground and mixed with flux material, the ratio between flux and the crystallizing compound was ~ 6:1. The evaporation and contamination of Pb is a huge problem in Pb based crystal growth. To avoid the evaporation of Pb, 5 weight percentage of B_2O_3 was added to the flux because B_2O_3 is more viscous and hence reduce the evaporation of Pb. For the crystal growth process, PbO-PbF_2 was used in 1:1.15 ratio. The mixture of flux and precursor were transferred to a platinum crucible and covered with a platinum foil. The crucible was kept in an alumina crucible and covered with an alumina lid. The alumina paste was used to tighten the lid to reduce Pb evaporation. The alumina crucible was placed in a resistive heating vertical single zone furnace with Eurotherm controller. The furnace was a 7cm homogeneous temperature zone and the whole crucible was kept in a constant temperature region during growth.

The content of Pb and the size of the crystals were decreased at higher growth temperature (1573K). For the same initial flux composition, and the same cooling rate, the growth of the crystal was terminated at around 1223K [10]. The optimal growth temperature range of 1323K to 1223K was used for the growth of the crystals. During the heating cycle from room temperature, the temperature was allowed to remain at 673K for 5 hours in order to create an oxygen-ambient to reduce the risk of crucible corrosion. At this temperature, PbO was transformed to less corrosive Pb_3O_4, which decomposes by releasing oxygen at higher temperature [11]. The temperature was increased to 1323K at the rate of 50 K/h and crucible was soaked for 24 hours to get a homogenized mixture of flux and precursor. The furnace was then cooled to 1223K at the rate of 0.5K/h. The temperature was maintained at 1223K for 12 hours in order to evaporate the remaining flux and finally the crucible was quenched to room temperature. The crystals were separated mechanically using boiled acetic acid. It was observed that the separated crystals had cubic and rectangular like morphology. Crystals with a maximum of 5x3x3 mm^3 in size were obtained from the growth. Cut and polished crystals are shown in figure 1a &1b. Figure 1c and 1d shows the crucible after the growth and EDAX composition analysis.

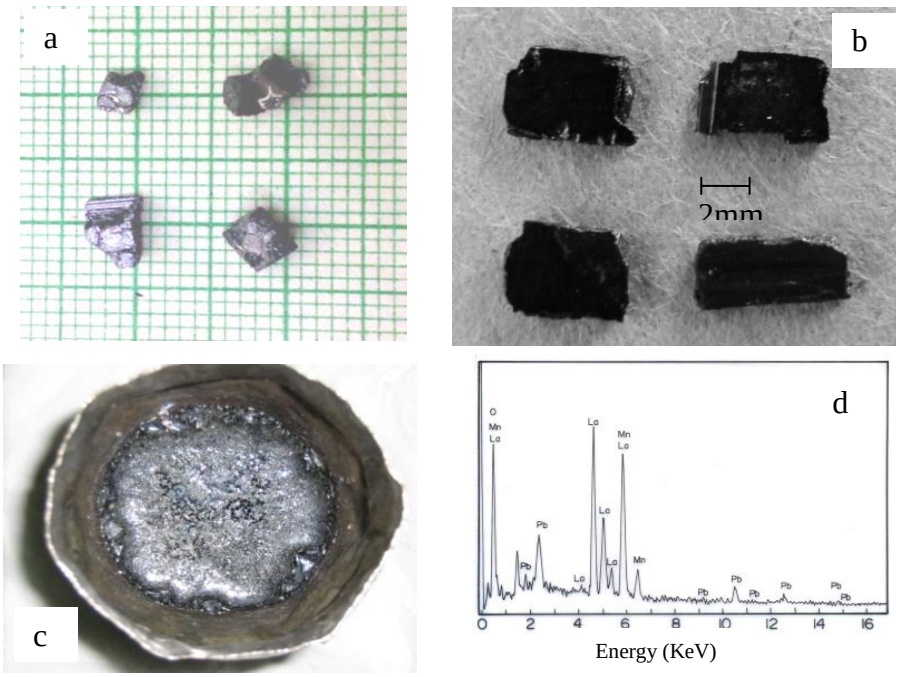

Fig. 1. Photograph of as grown (a) single crystals (b) cut and polished $La_{0.9}Pb_{0.1}MnO_3$ single crystals (c) Crucible after the growth and (d) EDX spectrum of LPMO single crystal

The composition of the crystals measured using EDX was found to be $La_{0.9}Pb_{0.1}Mn_1O_3$. All the measurements were carried out along easy axis 'ab' plane of magnetization of the single crystal. The structure and quality of single crystals were examined by powder XRD. The chemical composition of the crystal was determined by energy dispersive X-ray (EDX) analysis. The surface features were observed using optical and scanning electron microscopes. The electrical resistivity of the sample was measured with DC four probe method and the magnetic properties using physical property measurement system (PPMS).

Result and discussions

The morphology of bulk single crystals provides more information about the habitual faces and growth rates. Crystals start to nucleate at the surface of the melt during slow cooling. After a critical size, the crystals start to deposit at the bottom of the crucible. As a result a strain is produced in the crystals that are at the bottom of the crucible. At the bottom of the crucible, cubic and rectangular shaped crystals are found which were segregated from one another with a dimension varying from 1 mm to 5 mm. This is due to the super saturation and the consequent spontaneous nucleation that starts at two places of the crucible. A slight temperature gradient at the bottom of the crucible may initiate supersaturation and which is likely to be followed by the growth of the crystals. On the melt surface crystals are formed around the wall of the crucible and these have an irregular morphology. Crystals found at the top of the surface near to the wall exhibit in layers growth pattern as is shown in figure 2a and 2b. The evaporation of flux causes an increase in supersaturation near the surfaces. In three dimensional morphology of the crystals, the mechanism of step growth generation is initiated by 2D nucleation followed by subsequent step propagation. The step growth process is dominant when the super saturation level is moderate. The layer pattern depends on different growth conditions such as temperature fluctuation, supersaturation of liquid phase, etc. In some cubic-shaped crystals, the face appeared hollow because the latent dissipation was more rapid at the corners than at the inside of the faces [12]. A high degree of supersaturation can dominate the growth process and this leads to crystals with hollow shape as is shown in figure 2c and 2d.

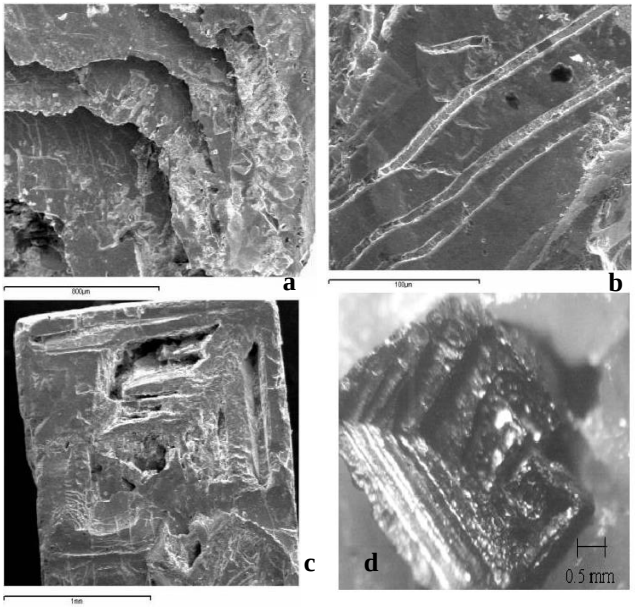

Fig. 2. SEM image of (2a, 2b) 2D layer growth pattern and crystal (2c,2d) optical microscope image of hopper growth pattern of flux grown $La_{0.9}Pb_{0.1}MnO_3$ single

The powder X-ray diffraction pattern indicates that the sample was in trigonal structure with space group $R\bar{3}C$ in which La/Pb are at 6a(0, 0, 1/4) positions, Mn at 6b(0, 0, 1/2) and O at 18e(x, 0,1/4) position. The structural parameters were obtained by refining the XRD pattern using the MAUD program, which combines the Rietveld method and the Fourier transform analysis, well adapted especially in the presence of broadened Bragg peaks [10] L. Lutteroti, MAUD, Materials Analysis using Diffraction, Version: 1.84 (2002) [13]. The refined lattice parameter values were a = b= 5.5285(1) Å, c =13.4180(3) Å. The structural parameters obtained agree with the reported value [15]. The respective residuals were Sig = 1.2, Rw (%) = 10.95, Rnw(%) = 0.10, Rb (%) = 8.62, Rexp (%) = 8. Refinement results shows ≈ 1% of PbO impurity and this may be due to the flux materials deposited on the surface of the grown single crystals after growth. The weight fraction of LPMO and PbO estimated from the refinements were 0.9885 and 0.0115 (Massicot). Figure 3 shows the Rietveld plot of powder XRD data for LPMO single crystals at room temperature. The mark in the picture indicates the position of allowed Bragg reflections of PbO and LPMO. The line curve at the bottom gives the difference between the observed and the calculated powder XRD pattern. The quality of

the grown crystals was confirmed using the Laue back reflection method. The back reflection Laue photograph shows 'ab' plane of trigonal lattice and clear reflection spots with no shadows confirm the good quality of the crystals. Back reflection Laue photograph has shown in the inset of the figure 3.

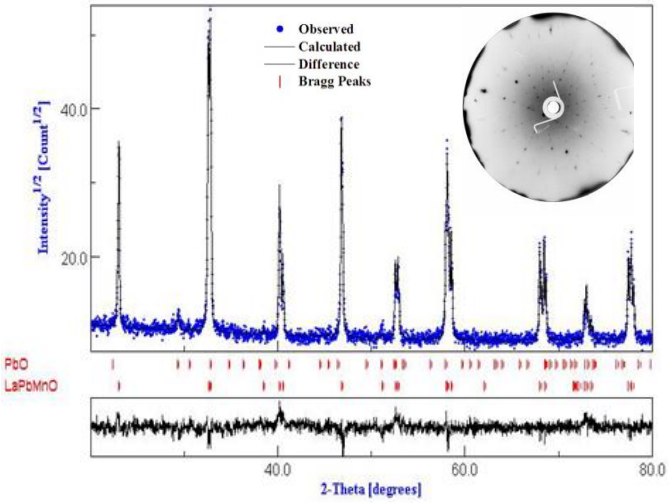

Fig. 3. Rietveld plot of powder XRD data for La0.9Pb0.1MnO3 single crystals. Inset shows X-ray back reflected Laue pattern.

The transport properties of $La_{0.9}Pb_{0.1}MnO_3$ single crystals were measured in the temperature ranges of 30K to 300K. The sample shows broad peaks around insulator-metal transitions temperature (T_{im}) which was 247K. It was observed that the resistivity increased with decreasing temperature up to T_{im}, and the resistivity decreased with a further decrease in temperature below T_{im}. It is well known that the transport properties of these materials exhibit a transition from a paramagnetic insulating state to a ferromagnetic metallic state as the temperature is lowered and that the Curie temperature T_C is very close to T_{im}. The collapse of electrical resistivity below T_C is evidence that there is a strong interaction between charge carrier and magnetic moment. In the absence of a magnetic field, the resistivity (ρ) has a peak around T_C (252K). The temperature dependence of resistivity was studied with 6T field. The applied field of 6T raises the Tim from 247K to 306 K and suppresses the resistivity peak thus yielding a large magneto-resistance near the Curie temperatures. Figure 4 shows that the temperature-dependent resistivity was measured in the 0T and 6T field for the LPMO single crystal. An applied magnetic field (H) suppresses the resistivity and thus leads to a negative CMR, where CMR is defined as [[ρ (T, H) - ρ(T, 0)] / ρ (T, 0)]x100. A maximal CMR occurs around T_C under a magnetic field of H = 6T as is shown in inset of figure 4. The ferromagnetic metallic (FMM) state suppresses the paramagnetic insulating (PMI) state, and hence, the peak temperature (TP) shifts to the high temperature regime with the application of the magnetic field. The resistivity at 250K drops by 10^{-4}Ω.cm under the application of the 6T field. We observed that the CMR value is 99% and was larger than the reported value for this LPMO system [15].

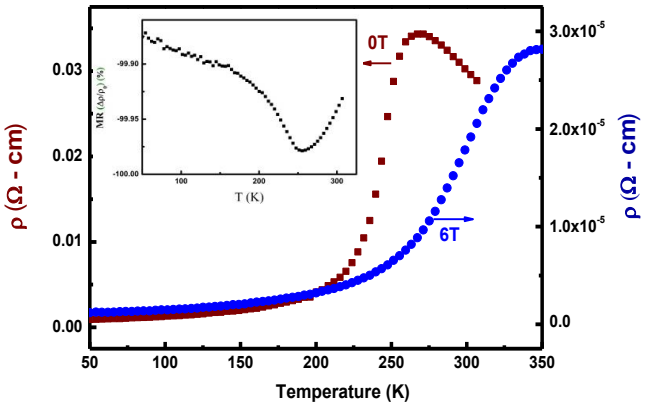

Fig. 4. Temperature dependent resistivity of $La_{0.9}Pb_{0.1}MnO_3$ single crystal with applied field of 0T and 6T field. Inset shows temperature dependent colossal magnetoresistance.

To study the ferromagnetic state of the samples, the hysteresis was measured at 10K with a field of 10KOe parallel and perpendicular to the ab plane as shown in figure 5. The magnetic field parallel to the ab plane showed easy axis of magnetization and saturated around 3KOe. While the magnetic field perpendicular to the ab plane showed hard axis of magnetization and saturated around 6KOe field. The difference in saturation magnetization is due to magneto crystalline anisotropy. While increasing the temperature, the hysteresis follows the nature of the regular soft magnetic material and the coercivity of the compound depends on the temperature. The temperature dependence of DC magnetization (M) of $La_{0.9}Pb_{0.1}MnO_3$ single crystal was studied with the applied field of 500Oe. Magnetization rose sharply up to T_C (252 K) and showed saturation in the low temperature region due to the ferromagnetic ordering as shown in Figure 4. This showed that the samples exhibit sharp paramagnetic to ferromagnetic (PM-FM) transition (Curie temperature)

calculated from the peak of dM/dT in the M vs T curve.

In ZFC measurements, the magnetization from low temperature decreased continuously near T_C and approaches to zero above T_C. In order to study the evolution of the magnetic properties as a function of the low magnetic field magnetic measurements were carried out. The magnetization of the sample was measured at Zero field cooled (ZFC) and at Field cooled (FC) conditions with field H= 20Oe and 500Oe. The data obtained in the heating process was in the temperature range of 10-300K as shown in the figure 6.

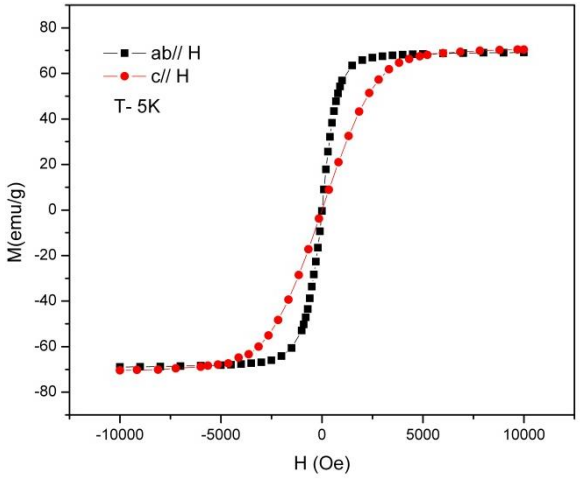

Fig.5. Field dependent magnetization(half cycle) measurement at 10K along ab plane and perpendicular to ab plane.

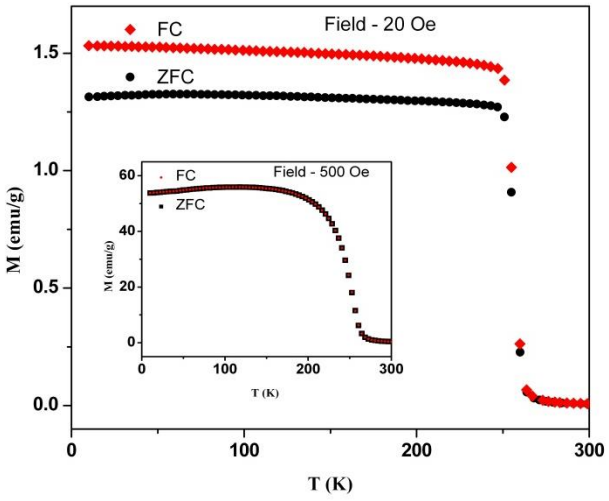

Fig. 6. Temperature dependent of magnetization with applied field of 20Oe. Inset show the temperature dependent of magnetization with applied field of 500Oe.

The measurement of low field ZFC–FC measurement is generally used to characterize spin-glass behavior. Paramagnetic to ferromagnetic transition occurred at 252K in both cases and showed monotonic increase in magnetization below T_C. Magnetization at 20Oe field was identical up to T_r (irreversible temperature) and below this ZFC and FC curves started to deviate from each other. The irreversibility of the curve is due to the cluster glass (CG). ZFC results show that the MZFC increases to a maximum value at T_r then deviates from MFC with decreasing temperature. The ZFC and FC magnetization irreversibility suggestes that the spontaneous magnetic state at low temperature is a magnetic cluster glass –like state. The position of maximum T_r of MZFC marks the defreezing temperature of the cluster glass [16] and above T_r the system gradually approaches the paramagnetic state after T_C. Fundamentally, a cluster glass is a type of spin glass. The magnitude of splitting and the T_r depend on the magnetic field. The field of 500Oe was applied to study the magnetic field dependence behavior. Irreversibility was not observed between ZFC and FC measurement for this field as shown in the figure 7.

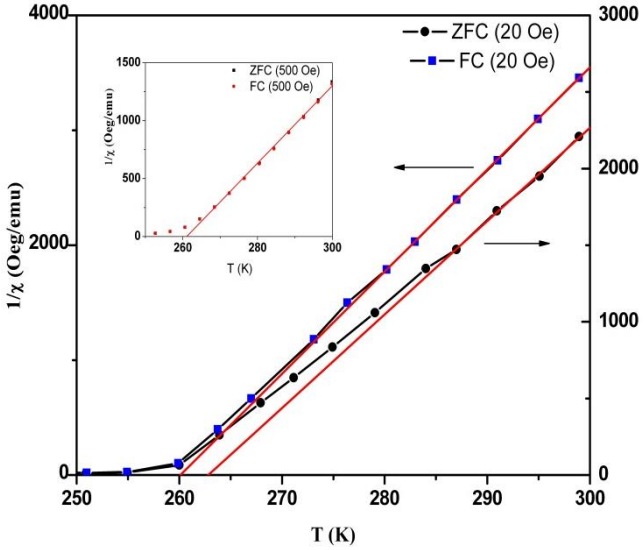

Fig. 7. Temperature dependent inverse susceptibility of LPMO crystals with applied field of 20Oe. Inset shows temperature dependent inverse susceptibility of LPMO crystals with 500Oe magnetic field.

The field dependence in the irreversible region may be due to lack of complete saturation as it is completely saturated in the higher field (500Oe). This may be due to the existence of misalignment of spin in the low applied magnetic field [17]. At lower fields, the magnetization followed mean-field-like fluctuations and the field was not sufficient to destroy the spin misalignment between adjacent

$Mn^{+3/+4}$ ions [18]. The short range behaviour is common in the double exchange ferromagnet because of the negligible interaction between well separated FM islands but these islands are believed to interact with each other when the magnetic field is applied [19]. Above T_C the magnetic susceptibility can be fitted well using Curie-Weiss law. The fitting parameter, Curie-Weiss temperatures (Θ) were 261 K and 263 K for 20Oe and 500Oe which were applied field respectively. The deviation of Θ from the Curie-Weiss law, that generally associates with the ferromagnetic spin clustering effect in the paramagnetic region [20] started at the temperature near to 1.03 Tc and 1.04Tc, these values are lower than the reported values [21]. The inverse susceptibility of the 20 Oe applied field shows splitting between ZFC and FC condition in the inverse paramagnetic susceptibility region as is shown in figure 8. In the case of 500Oe field, the inverse susceptibility did not show any difference between ZFC and FC in the paramagnetic region as shown in the inset of figure 8. The application of low field is not enough to destroy the cluster glass property of the sample as confirmed by ZFC and FC measurements and the moderate field of 20Oe.

Conclusions

Single crystals of $La_{0.9}Pb_{0.1}MnO_{3-\delta}$ have been successfully grown using the flux growth technique. The size of the single crystals from slow cooling technique is restricted due to the large evaporation of flux. The composition could be observed quantitatively by EDX studies. Surface morphology of the grown crystals showed signs of two dimensional layer growth pattern and Hopper growth pattern due to changes in supersaturation. LPMO single crystals showed metal insulator transition (T_{im}) around 247K and this is lower than T_C (252K). The colossal magneto-resistance ratio observed about 99% at the Curie temperature. The hysteresis measurement showed the easy axis of magnetization along the ab plane; and the difference in magnetization is due to magneto crystalline anisotropy. Paramagnetic to ferromagnetic transition occurs at 252K for the application of different field value. Low field ZFC and FC magnetic measurements show that the irreversibility may be due to glassy magnetism and magnetic inhomogeneity. In particular, a cluster glass magnetic state was observed in low magnetic field below the Curie temperature and destroyed in higher applied field values. Inverse susceptibility results clearly indicate the presence of ferromagnetic cluster in the paramagnetic region above the Curie temperature.

Conflict of interest

Authors declare there are no conflicts of interest.

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