PAPER

Electron spin resonance studies of (La$_{0.6}$Ln$_{0.4}$)$_{0.67}$Ca$_{0.33}$MnO$_3$ (Ln = La, Pr, Nd and Sm) nanoparticles at different temperatures

Kai Leng$^1$, Weiren Xia$^1$, Qingkai Tang$^1$, Li Yang$^1$, Zhiwei Wu$^1$, Kang Yi$^1$ and Xinhua Zhu$^1$ $^*$

$^1$ National Laboratory of Solid State Microstructures, School of Physics, Nanjing University, Nanjing 210093, People’s Republic of China
$^2$ Kuang Yaming Honors School, Nanjing University, Nanjing 210093, People’s Republic of China

E-mail: xhzhu@nju.edu.cn

Keywords: perovskite manganite nanoparticles, Ln-doped (La$_{0.6}$Ln$_{0.4}$)$_{0.67}$Ca$_{0.33}$MnO$_3$, sol-gel process, electron spin resonance, microscopic magnetic properties

Abstract

In this work, (La$_{0.6}$Ln$_{0.4}$)$_{0.67}$Ca$_{0.33}$MnO$_3$ (Ln = La, Pr, Nd and Sm) nanoparticles (NPs) synthesized by sol-gel process were investigated by electron spin resonance (ESR) in the temperature range 100–330 K. At the high temperature the ESR signals of La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) NPs only consist of a single peak with Landé g factor of 2.0. This signal is contributed from the paramagnetic (PM) Mn ions in the LCMO NPs. With decreasing the temperature the PM resonance line is split into two resonance lines, one is ferromagnetic (FM) resonance line shifting towards low field while the other is antiferromagnetic (AFM) resonance line moving to a high field. The resonance peak-to-peak spectra linewidth, increases monotonically with decreasing the temperature owing to the strong double exchange interactions below the Curie temperature ($T_c$). Resonance field is almost temperature independent in the PM phase whereas it drops fast at temperature below $T_c$. Consequently, the Landé g factor in the PM region is very close to 2.0 whereas in the range of 2.17–2.47 under FM state due to the strong FM interactions. For the Pr (Nd)-doped LCMO NPs below $T_c$, their g values are in the range of 2.04–2.18 due to the substantial reduction of the FM interactions caused by the Pr (Nd)-doping at La-site. The g values of the Sm-doped LCMO NPs exhibit a slight fluctuation around 1.88 (but smaller than 2.0) within the measured temperature due to the existence of weak magnetic interactions under the PM states.

1. Introduction

Nanoparticles (NPs) have attracted much attention due to their excellent properties as compared to their bulk counterpart [1–3]. Among them, perovskite manganite NPs have been intensively studied in the past decade due to their intriguing physical properties such as colossal magnetoresistance, charge-ordering, orbital-ordering, phase separation and spin glass behaviour [4–9]. These rich physical properties are originally resulted from the strong competition between the spin, charge, orbital and lattice degrees of freedom [4, 5]. At present, La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) NP is one of the well investigated archetypes among the huge family of perovskite manganites [6, 7]. To meet the application requirements in the fields of magnetic sensors, spintronic devices, magnetocaloric refrigeration, magnetic resonance imaging, and drug delivery, the physical properties of LCMO NPs are urgently to be improved. It has been reported that the substitution of La$^{3+}$ ions by smaller and magnetic heavy rare earth elements is an effective route to achieve the above aims [10–14]. In the previous works [15, 16], we have reported the synthesis, structural characterization, magnetic and optical properties of Ln-doped LCMO (Ln = La, Pr, Nd and Sm) NPs. Powder x-ray diffraction patterns and structural Rietveld refinements confirm that these NPs exhibit an orthorhombic crystal structure belonging to the Pnma space group. Their unit cell volumes are found to be reduced in the sequence of La$^{3+}$ > Pr$^{3+}$ > Nd$^{3+}$ > Sm$^{3+}$ due to the steric effect. The LCMO NPs became heavily agglomerated due to the Ln-doping, and the average particle size was decreased from 61 nm to $\sim$30 nm. Their Curie temperature ($T_c$) was reduced in the order of La$^{3+}$ > Pr$^{3+}$ > Nd$^{3+}$ > Sm$^{3+}$. A spin-glass...
behaviour was observed in the LCMO NPs whereas a magnetic cluster-glass behaviour was developed in the Sm-doped LCMO NPs. Long-range ferromagnetic (FM) interactions are weakened in the LCMO system due to the Ln-doping.

In the present work, we focus on the electron spin resonance (ESR) studies of the \( (\text{La}_{0.6} \cdot \text{Ln}_{0.4})_{0.67} \text{Ca}_{0.33} \text{MnO}_3 \) (\( \text{Ln} = \text{La}, \text{Pr}, \text{Nd} \) and \( \text{Sm} \)) manganite NPs synthesized by sol-gel process. Their ESR spectra parameters (e.g., resonance field \( (H_r) \), \( g \) factor, resonance peak-to-peak spectra linewidth \( (\Delta H_{pp}) \), and resonance intensity) can provide the microstructural information such as charge states, \( g \) factor, interactions between ions and lattices, magnetic ordering and relaxation processes in the perovskite manganites, helping us to establish the magnetic correlations in these NPs \([17, 18]\). The ESR signals generated in the doped perovskite manganites are originally from the \( \text{Mn}^{4+} \) ions \( (3d^0, S = 3/2) \) whereas the Jahn-Teller \( \text{Mn}^{3+} \) ions \( (3d^5, S = 2) \) are ESR silent, but it could produce an ESR signal due to the polaron hopping process. The \( \text{Mn}^{2+} \) ions \( (3d^5, S = 5/2) \) can be generated via the disproportionation process: \( 2\text{Mn}^{2+} = \text{Mn}^{3+} + \text{Mn}^{4+} \) in doped perovskite manganites, which could contribute to the overall ESR signal \([19]\). However, in the doped perovskite manganites \( \text{Mn}^{2+} \) ions are found to be very few, thus, their contributions to the ESR signals of the doped perovskite manganites can be almost ignored. Up to date, numerous ESR studies have been made to investigate the doped perovskite manganites. Special attention is given to the spin dynamics of the Mn ions near and above \( T_C \) \([20, 21]\), phase separation \([22, 23]\), Jahn-Teller polaron formation \([24, 25]\), and Griffiths phase \([25–27]\). Recently, Misra et al \([28]\) performed the ESR studies of the manganites \( \text{La}_{0.7} \cdot \text{Eu}_{0.3} \text{Sr}_{0.3} \text{MnO}_3 \) \((x = 0.4, 0.5, 0.6, 0.7) \) in temperature range of 175–400 K. They found that the positions and widths of the ESR lines of all the Eu-Sr manganite samples varied with temperature in a similar manner. The ESR data revealed that these Eu-Sr manganites were FM, and their \( T_C \) values decreased gradually as the Eu content \((x) \) increased, specifically from \( T_C \approx 111 \) K \((x = 0.5) \) to \( T_C \approx 57 \) K \((x = 0.7) \). The temperature dependence of the ESR linewidth was found to be linear in the various \( \text{La}_{0.7} \cdot \text{Eu}_{0.3} \text{Sr}_{0.3} \text{MnO}_3 \) samples, which was caused by the presence of conductivity due to the hopping of small polarons. Ning et al \([29]\) reported the ESR study of Fe doping effect in the manganites of \( \text{La}_{0.6} \cdot \text{Ca}_{0.33} \text{Mn}_{1-x} \text{Fe}_x \text{O}_3 \) \((x = 0, 0.0, 0.04) \). The temperature dependence of the ESR spectra revealed the presence of phase separation above and below \( T_C \) in \( x = 0.0 \) and 0.04 samples, respectively. The \( g \)-value increased gradually with decreasing temperature in the paramagnetic (PM) state, which indicated the existence of weak spin correlations above \( T_C \). Vijayan et al \([30]\) also reported ESR studies of the \( \text{Bi}_{0.3} \text{Ca}_{0.3} \text{MnO}_3 \) \((x = 0.0, 0.04) \) samples. The ESR spectra demonstrated a strong interplay between FM and antiferromagnetic (AFM) interactions as a function of temperature and composition of the sample. The coexistence of FM and AFM phases was observed in the temperature range \( T_{CO} \) \((charge\ ordering\ temperature) > T > T_O \) \((long-range\ AFM\ onset\ temperature) \) for all the samples. In the case of \( T > T_{CO} \), all the samples exhibit FM dominated interactions in PM state. Despite of all the above efforts, there have been no ESR studies on the \( \text{La}_{0.6} \cdot \text{Ln}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) manganite NPs. The objective of this work is to study the charge states of manganese ions, the long-range spin-ordering as well as the dynamic magnetic interactions in the \( \text{La}_{0.6} \cdot \text{Ln}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) NPs by ESR spectra, to better understand their microscopic magnetic properties.

2. Experimental

In this work, \( \text{La}_{0.6} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) (pristine sample) and Ln-doped \( \text{La}_{0.6} \cdot \text{Ln}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) \((\text{Ln} = \text{Pr}, \text{Nd} \) and \( \text{Sm} \)) NPs were synthesized via a sol-gel processing, details were described elsewhere \([15]\). (\( \text{La}_{0.6} \cdot \text{Pr}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \), \( \text{La}_{0.6} \cdot \text{Nd}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \), and \( \text{La}_{0.6} \cdot \text{Sm}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) NPs are abbreviated as Pr-doped LCMO, Nd-doped LCMO, and Sm-doped LCMO \((\text{hereafter}) \), respectively. The \( T_C \) values for LCMO, Pr-doped LCMO, Nd-doped LCMO, and Sm-doped LCMO NPs were determined to be 254, 178, 149, and 81 K, respectively \([15]\).

ESR spectra were collected from the Ln-doped \( \text{La}_{0.6} \cdot \text{Ln}_{0.4} \cdot \text{Ca}_{0.33} \text{MnO}_3 \) \((\text{Ln} = \text{La}, \text{Pr}, \text{Nd} \) and \( \text{Sm} \)) manganite NPs by using a Bruker EMX-10/12 X-band \((9.49 \text{ GHz}) \) spectrometer across a temperature range of 100–330 K. The applied magnetic field was in the range of 0–7000 Gauss. The first-derivative of the ESR absorption line was monitored as a function of the applied field, and Lorentz fittings of the resonance spectra were made. The resonance peak-to-peak spectra linewidth \( (\Delta H_{pp}) \) was defined by the maxima and minima in the first derivative signal curve \([31]\). The obtained ESR parameters are used to determine the local charges and spin states, and their interactions in these NPs.

\[
g = \frac{\hbar v}{\mu_B H_r}
\]

where \( \hbar \) denotes the Planck’s constant, \( v \) is the irradiating microwave frequency \( (v = 9.49 \text{ GHz}) \), and \( \mu_B \) is the Bohr magneton, and \( H_r \) represents the resonance field determined by the zero-crossing point in the first derivative signal curve \([31]\). The obtained ESR parameters are used to determine the local charges and spin states, and their interactions in these NPs.
3. Results and discussion

Figure 1(a) represents temperature dependence of the ESR spectra of LCMO NPs measured from 110 K to 300 K. It is noticed that in the high temperature region all the ESR signals only consist of a single peak with $g = 2.0$ around the position of 3400 G. This signal is contributed from the PM Mn ions in the LCMO NPs, as marked with a straight line. With reducing the temperature the PM resonance line was found to be broadened and split. At a further lower temperature the ESR signal is broken into two resonance lines, one shifting towards low field whereas the other moving to a high field. The former one is named as a FM resonance line (marked with an arrow, ↑), which is normally observed in the perovskite La_{1-x}A_xMnO_3 compounds [31]. The latter one in the high field region refers to AFM resonance lines (marked with triangles, ▲) [32]. As observed in figure 1(b), when the temperature is decreased the value of $\Delta H_{pp}$ increases continuously, indicating the linewidths of the ESR spectra become wider. Similar phenomenon was also observed in temperature dependence of the ESR spectra of an ordered double perovskite Ba$_2$FeMoO$_6$ [33] and polycrystalline Sr$_2$FeMoO$_6$ samples [34]. Since the width of an ESR line is inversely proportional to the relaxation time of the paramagnetic species having different interactions with their surroundings, thus, the relaxation time of the paramagnetic species (e.g., Mn$^{4+}$ ions) in the LCMO NPs is much shorter as decreasing the temperature below $T_C$. That is in according with the stronger double exchange (DE) interactions via the Mn$^{4+}$-O-Mn$^{4+}$ bonds in the LCMO NPs at low temperatures below $T_C$, and also with the higher magnetizations at low temperatures. Resonance field ($H_r$) is almost temperature independent in the PM phase whereas it drops fast as the temperature decreases below $T_C$. That is attributed to the continuous increase of the effective internal fields resulted from the strong FM interactions in FM phase. The Landé $g$-factor correlates inversely with $H_r$, as described by equation (1), which changes with the

---

**Figure 1.** (a) Temperature dependent ESR spectra of the LCMO NPs measured from 110 K to 300 K. $\Delta H_{pp}$ and $H_r$ represent the peak-to-peak linewidth and resonant field, respectively. PM, FM, and AFM peaks are marked with straight line, ↑, and ▲, respectively. (b) The obtained ESR parameters ($\Delta H_{pp}$ and $H_r$) as a function of the temperature. Inset is the corresponding $g$ factor as a function of temperature.
temperature, as depicted in the inset of figure 1(b). Despite the $g$ parameter is not included in the spin Hamiltonian, it reflects the influence of crystal field environment on the spin–orbit coupling of the Mn$^{3+}$ ions in the LCMO NPs. At the temperature above $T_c$, the LCMO NPs exhibit PM behavior, the DE interactions between Mn$^{3+}$ and Mn$^{4+}$ ions are much weak. Due to the thermal energy high enough, the local (or internal) magnetic field formed by the small magnets around paramagnetic ions, is submerged. Thus, free interactions between the Mn site spins and the applied field and the microwave field take place. As a consequence, the magnetic field required to satisfy the resonance condition is fully contributed by the external field. Therefore, the calculated $g$ value in the PM region is very close to 2.0, approaching to the Landé $g$-factor value of free electrons ($g_e = 2.023$). Below $T_c$, the LCMO NPs are in FM state, where long-range spin orders are formed due to the strong DE interactions via the Mn$^{3+}$–O–Mn$^{4+}$ bonds. An intense local (or internal) exchange magnetic field (estimated to be in the order of $10^3$ G) is generated, thus, only a lower external magnetic field applied on the Mn site spins is required to achieve the resonance condition [35]. That accounts for why the $g$ value continuously increases with decreasing the temperature below $T_c$, which reflects the strong interactions between the Mn site spins in the LCMO NPs. Previously, in the ESR spectra of LCMO powders grinded from the corresponding single crystal, besides the FM resonance line a FM resonance line was also observed at the low-field side between the temperature of 220 K and 250 K, and it shifted towards lower fields with further reducing the temperature [29]. The coexistence of the PM and FM resonance lines is attributed to a phase separation around $T_c (\approx 220$ K), where the FM and PM phases coexist. The observed weak AFM resonance lines are ascribed to the AFM superexchange coupling in the LCMO NPs, which is resulted from the interactions between the Mn$^{3+}$ and Mn$^{4+}$ (or Mn$^{3+}$ and Mn$^{4+}$) ions.

Temperature dependent ESR spectra of the (La$_{0.6}$Ln$_{0.4}$)$_2$Ca$_{0.5}$Mn$_3$O$_{12}$ NPs ($Ln = Pr, Nd$ and Sm) are shown in figures 2–4, respectively. Figure 2(a) shows the ESR spectra of Pr-doped LCMO NPs measured from 110 K to 210 K. At high temperature above 180 K, all the ESR signals exhibit only single peak around 3405 G, corresponding to $g = 2.0$. That is contributed from the PM Mn ions, which are freely to interact with the applied field and the microwave field. However, at the temperature below 180 K (e.g., 160 K and 110 K), the ESR spectra are split into two lines, which are named as low-field (LF) and high-field (HF) resonance lines, respectively, similar to the case of LCMO NPs. A similar split of ESR spectra was also reported in the half-doped Nd$_{0.5}$Sr$_{0.5}$Ca$_{0.5}$Mn$_3$O$_{12}$ (0.0 $\leq x \leq 0.50$) manganite ceramics [36] and La$_{0.9}$Ca$_{0.1}$Mn$_3$O$_{12}$ ceramics [37]. The observed AFM resonance line indicates the appearance of AFM and FM states in the (La$_{0.6}$Pr$_{0.4}$)$_2$Ca$_{0.5}$Mn$_3$O$_{12}$ NPs although the FM state is predominant one. The intensity of the $dP/dH$ spectra reaches a maximum at 160 K, suggesting a variation of the magnetization state. The $\Delta H_{ip}$ increases with decreasing temperature, which is ascribed to the existence of AFM ordering. $H_i$ has a general reduction tendency as decreasing the temperature whereas two inflection points appear at 170 and 190 K, respectively. The possible physical origins can be explained as followings. Based on the magnetic field and temperature dependence of dc magnetizations of the Pr-doped LCMO NPs recorded in ZFC and FC modes and under the magnetic field of 0.05 T, the freezing temperature ($T_f$) of the Pr-doped LCMO NPs was determined to be 156 K (the temperature at which the ZFC curve reaches the maximum value) [15], and around this temperature the FM clusters were frozen. These frozen FM clusters could make large contribution to the internal exchange magnetic field, enabling a lowest external field applied on the Mn site spins to achieve the resonance conditions. Thus, the $g$ value exhibits an extreme large value (or $H_i$ has an extreme low value) at 170 K. The $T_c$ value of the Pr-doped LCMO NPs was determined to be about 180 K, therefore, at 190 K the Pr-doped LCMO NPs exhibited the PM behavior, where weak spin correlations exist in the Pr-doped LCMO NPs. Thus, the $g$ value is much small (or $H_i$ has an extreme large value). The corresponding $g$ factor variation is shown as an inset in figure 2(b). Below $T_c (= 178$ K) the calculated $g$ values are substantially larger than 2.0, exhibiting a significant increment with decreasing the temperature. That is attributed to a lower external field required to apply on the Mn site spins to achieve the resonance conditions because intense internal fields are added to the applied field.

Similar ESR spectra are observed in the Nd-doped LCMO NPs, as shown in figure 3. As the temperature decreases from 160 K to 110 K the shapes of ESR spectra profiles change gradually from a broad line to an asymmetric Lorentzian line (see figure 3(a)). The intensity of the $dP/dH$ spectra reaches a maximum at 130 K. $\Delta H_{ip}$ increases with decreasing temperature, and sharp increase appears around 150 K, just near the $T_c (= 149$ K). That can be ascribed to the appearance of spontaneous magnetization due to the PM–FM transition. It is noticed that $H_i$ has a general reduction tendency as decreasing the temperature, however, two inflection points appear at 120 K and 150 K, respectively. The possible physical origins are the same as the case of the Pr-doped LCMO NPs, as described above. The temperature dependent $g$ value is shown as an inset in figure 3(b), where the $g$ value is close to 2.0 in the PM phase region and exhibits an increasing trend above 2.0. The highest $g$ value ($g = 2.207$) appeared at 120 K, close to the freezing temperature, $T_f (= 115$ K), where the FM clusters were frozen. These frozen FM clusters offer large contributions to the internal exchange magnetic field, making a small external field applied on the Mn site spins achieve the resonance conditions. Thus, the $g$ value exhibits a maximum value at 120 K.
Figure 4 displays the ESR spectra of the Sm-doped LCMO NPs (with $T_c = 81$ K) measured from 110 K to 300 K (within the PM region). As shown in figure 4(a), with decreasing the temperature the profiles of the ESR spectra change gradually from a much broad line to a symmetric Lorentzian line at 110 K. The intensity of the $dP/dH$ also reaches a maximum at 110 K within the measured temperature range. That is attributed to the Sm-doped LCMO NPs close to $T_c (= 81$ K) from high temperature side, approaching to the PM-FM transition. Due to their much low Curie temperature, the Sm-doped LCMO NPs are under the PM states with much small magnetizations within the measured temperature range, so the magnetic interactions (e.g. spin-lattice interaction, spin-spin interaction) in the Sm-doped LCMO NPs are much weak. Thus, the spin lifetime ($\delta t$) of the electron from the PM Mn ions in the Sm-doped LCMO NPs becomes longer due to the weaker magnetic interactions. Based on the uncertainty principle, $\delta E \cdot \delta t \sim \hbar/2\pi$, or expressed in another equivalent form, $\delta H \cdot \delta t \sim \hbar/(2\pi \gamma_e)$, where $\gamma_e$ is electronic magnetogyric ratio. Obviously, the longer $\delta t$ is, the smaller $\delta H$ is, that means a narrower width of an ESR line. That is the reason why the $\Delta H_{PP}$ exhibits a general reduction tendency as decreasing the temperature under the PM states. It is found that the $g$ values exhibit a slight fluctuation around $g = 1.88$ (but smaller than 2.0), as illustrated in the inset of figure 4(b). That is ascribed to the weak magnetic interactions in the Sm-doped LCMO NPs under PM states. Our ESR spectra do not exhibit the hyperfine lines contributed from the Mn$^{2+}$ ions, which was reported previously in the LaAlO$_3$-(La$_{0.67}$Sr$_{0.33}$)MnO$_3$ system [19]. Therefore, the absence of Mn$^{2+}$ ion in the present NPs is revealed by ESR spectra, which is consistent with our previous XPS spectra [15, 16], where the dual chemical states of Mn$^{3+}$ and Mn$^{4+}$ ions in the NPs are confirmed.
4. Conclusions

In summary, the microscopic magnetic properties of the Ln-doped \((\text{La}_{0.6}\text{Ln}_{0.4})_{0.67}\text{Ca}_{0.33}\text{MnO}_3 (\text{Ln} = \text{La}, \text{Pr}, \text{Nd} \text{and Sm})\) NPs were systematically investigated by the ESR spectra. The ESR spectra of LCMO NPs reveal that \(H_r\) exhibits almost temperature independent in the PM phase region whereas it decreases quickly as the temperature further decreases below \(T_C\). That is ascribed to an increase of the effective internal fields due to the strong DE interactions between the \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\) ions, which reduces the applied external field required to achieve the resonance condition. The corresponding \(g\) factor was in the range of 2.17–2.47, much higher than that of free electrons \((g_e = 2.023)\). In contrast, the \(g\) values of the Pr (Nd)-doped LCMO NPs below \(T_C\) are in the range of 2.04–2.18, smaller than that of LCMO NPs. That is resulted from the reduced DE interactions caused by the doping Pr (Nd) at La-site. The \(g\) values of the Sm-doped LCMO NPs (with \(T_C = 81\text{ K}\)) exhibit a slight fluctuation around 1.88 (smaller than 2.0) across temperatures of 100–330 K owing to the weak magnetic interactions under PM states. Hyperfine lines contributed from \(\text{Mn}^{2+}\) ions were not observed in the present ESR spectra, indicating the absence of \(\text{Mn}^{2+}\) ions in the present NPs, which was consistent with our previous XPS data.

Acknowledgments

The authors acknowledge financial supports from National Natural Science Foundation of China under grant Nos. 11974170 and 11674161, Natural Science Foundation of Jiangsu Province under grant No. BK20181250,
and undergraduate teaching reform projects from Nanjing University under grant Nos. X20191028402 and 202010284036X.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Xinhua Zhu @ https://orcid.org/0000-0003-1508-1563

References

[1] Kurban H, Dalkılıç M, Temiz S and Kurban M 2020 Tailoring the structural properties and electronic structure of anatase, brookite and rutile phase TiO$_2$ nanoparticles: DFTB calculations *Comput. Mater. Sci.* **183** 109843
[2] Kurban H, Kurban M and Dalkılıç M 2019 Density-functional tight-binding approach for the structural analysis and electronic structure of copper hydride metallic nanoparticles Mater. Today Commun. 21 100648

[3] Kurban H, Alaei S and Kurban M 2021 Effect of Mg content on electronic structure, optical and structural properties of amorphous ZnO nanoparticles: a DFTB study J. Non-Cryst. Solids 560 120726

[4] Tokura Y 2006 Critical features of colossal magnetoresistive manganites Rep. Prog. Phys. 69 797–851

[5] Dagotto E, Hotta T and Moreo A 2001 Colossal magnetoresistive materials: the key role of phase separation Phys. Rep. 344 1–153

[6] Coey J M D, Viret M and von Molnar’s 1999 Mixed-valence manganites Adv. Phys. 48 167–293

[7] Ramirez A P 1997 Colossal magnetoresistance J. Phys. Condens. Matter 9 8171–99

[8] Xia W, Pei Z, Leng K and Zhu X H 2020 Research progress in rare-earth–doped perovskite manganite oxide nanostructures Nanoscale Res. Lett. 15 9

[9] Zhang T, Wang X P, Fang Q F and Li X G 2014 Magnetic and ordering in nanosized manganites Appl. Phys. Rev. 1 031302

[10] Barik S K, Aparnadevi M, Rebello A, Naik V B and Mahendiran R 2012 Magnetic and calorimetric studies of manganolycaloric effect in La_{0.5-x}Pr_{x}Ca_{0.5}MnO_{3} J. Appl. Phys. 111 07D726

[11] Pal A, Nagaraja B S, Rachana K J, Supriya K V, Kekuda D, Rao A, Li C R and Kuo Y K 2020 Enhancement of temperature coefficient of resistance (TCR) and magnetoresistance (MR) of La_{0.67–x}RE_{x}Ca_{0.33}MnO_{3} (x = 0, 0.1, 0.2, 0.3) Gd, Nd, Sm system via rare-earth substitution Mater. Res. Express 7 036102

[12] Liu N, Tong W and Zhang Y H 2004 Phase separation and abnormal transport behaviors in La_{0.7–x}Gd_{x}Sr_{0.3}MnO_{3} system Chin. Phys. 13 958–67

[13] Krichene A, Solanki P S, Venkateshwari D, Rayaprol S, Ganesan V, Boujellben W and Kuberkar D G 2015 Magnetic and electrical studies on La_{0.4}Sm_{0.3}Ca_{0.3}MnO_{3} charge-ordered manganite J. Magn. Magn. Mater. 381 470–7

[14] Sudheendra I and Rao C N R 2003 Electronic phase separation in the rare-earth manganites (La_{1−x}Ln_{x})_{0.33}Ca_{0.33}MnO_{3} (Ln = Nd, Gd, and Y) Phys. Condens. Matter 15 3020–40

[15] Xia W R, Leng K, Tang Q K, Yang L, Xie Y T, Wu Z W and Zhu X H 2021 Comparative studies on the structural, magnetic, and optical properties of perovskite Ln_{0.67}Ca_{0.33}MnO_{3} (Ln = La, Pr, Nd, and Sm) manganite nanoparticles synthesized by sol–gel method Appl. Surf. Sci. 43 9580731

[16] Xia W R, Leng K, Tang Q K, Yang L, Xie Y T, Wu Z W, Yi K and Zhu X H 2021 Structural characterization, magnetic and optical properties of perovskite (La_{1−x}Ln_{x})_{0.33}Ca_{0.33}MnO_{3} (Ln = Nd and Sm; x = 0.0–0.5) nanoparticles synthesized via the sol–gel process J. Alloy. Compd. 867 158808

[17] Causa M T et al 1998 High-temperature spin dynamics in CMR manganites: ESR and magnetization Phys. Rev. B 58 3233–9

[18] Eichel R A 2008 Piezolectric ceramics by multifrequency and multipulse electron paramagnetic resonance spectroscopy J. Am. Ceram. Soc. 91 691–701

[19] Andronenko S I, Andronenko R R, Zagrebel’nyi O A and Chezhina N V 2009 EPR Study of compounds in the La_{0.7–x}Gd_{x}Sr_{0.3}MnO_{3} system Phys. Chem. Chem. Phys. 11 6552–9

[20] Gudenko S V, Yu A, Yakubovski O, Gorbenko Y and Kaul A R 2004 EPR study of the spin dynamics of the (La_{1−x}Pr_{x})_{0.3}Ca_{0.3}MnO_{3} system Phys. Solid State 46 2094–102

[21] Kochelaev B I, Shilova E, Deisenhofer J, Krug von Nidda H A, Loidl A, Mukhin A A and Babalsov A M 2003 Phase transitions and spin-relaxation in La_{0.95}Sr_{0.05}MnO_{3} Mod. Phys. Lett. B 17 459–67

[22] Eremina R M et al 2011 Phase separation in paramagnetic Eu_{1−x}Sr_{x}MnO_{3} Phys. Rev. B 84 064410

[23] Zhang L, Xu J, Li P and Zhang Y H 2000 Observation of electron phase separation in La_{0.65}Sr_{0.15}Mn_{1−x}Cu_{x}O_{4} perovskites Phys. Rev. B 62 1193–6

[24] Misra S K, Andronenko S L, Asthana S and Babadur D 2010 A variable temperature EPR study of the manganites (La_{1−y}Sm_{y/3})_{0.33}Sr_{0.33}MnO_{3} (x = 0.0, 0.1, 0.2, 0.3) small-polaron hopping conductivity and Griffiths phase J. Magn. Magn. Mater. 322 2902–7

[25] Irvashin V A, Deisenhofer J, von Nidda H A K and Loidl A 2007 Griffiths phases vs magnetic polarons in the lightly doped La_{1−x}Sr_{x}MnO_{3} J. Magn. Magn. Mater. 310 1966–8

[26] Andronenko S I, Rodionov A A, Fedorova A V and Misra S K 2013 Electron paramagnetic resonance study of La_{0.7}Ca_{0.3}Sr_{0.3}MnO_{3} (~x = 0.1) Griffiths phase J. Magn. Magn. Mater. 326 131–46

[27] Deisenhofer J et al 2005 Observation of a Griffiths phase in paramagnetic La_{1−x}Sr_{x}MnO_{3} Phys. Rev. Lett. 95 357202

[28] Misra S, Andronenko S I, Padia P, Vadnal S and Asthana S 2021 EP and magnetization studies of the manganites La_{0.7}–xEu_{x}Sr_{0.3}MnO_{3} (x = 0.4, 0.5, 0.6, 0.7) and La_{0.7}Nd_{0.3}Sr_{0.3}MnO_{3} at different temperatures: conductivity due to hopping of small polaron J. Magn. Magn. Mater. 319 674501

[29] Ning W, Zhang X Q, Cheng Z H and Sun Y 2009 Electron spin resonance study of Fe doping effect in La_{0.67}Ca_{0.33}MnO_{3} J. Magn. Magn. Mater. 321 1159–62

[30] Vijayan D, Kurian J and Singh R 2011 ESR studies on Ba_{0.5}Ca_{0.5}MnO_{3+x} (TE = V, Cu, and Zn) IEEE Trans. Magn. 47 2701–4

[31] Oseroff S B, Torikakhvili M, Singley J, Ali S, Cheong S-W and Schultz S 1996 Evidence for collective spin dynamics above the ordering temperature in La_{1−x}Ca_{x}MnO_{3} Phys. Rev. B 53 6521–5

[32] Fan J, Xie J, Ying Y, Pi L and Zhang Y 2006 Charge order melting and magnetic transition in Nd_{0.5}La_{0.5}MnO_{3} system J. Appl. Phys. 104 07D726

[33] Yoshida K, Kihara S and Haimre Shimizu H 2003 Broadening of ferromagnetic resonance linewidth in Ba_{0.5}Fe_{0.5}MnO_{3} Physica B 359–361 1330–2

[34] Das R, Chaudhuri U, Chanda A and Mahendiran R 2020 Broadband electron spin resonance study in Sr_{0.5}Fe_{0.5}MnO_{3} double perovskite ACS Omega 5 17611–6

[35] Montiel H, Alvarez G, Conde-gallardo A and Zamorano R 2015 Microwave absorption behavior in Cr_{2}O_{3} nanoparticles J. Alloys Compd. 628 272-6

[36] Fan J Y, Hong B, Ying Y, Ling L S, Pi L and Zhang Y H 2008 Strain-driven inverse thermal hysteresis behaviour in half-doped manganites J. Phys. D: Appl. Phys. 41 105013

[37] Rivadulla F, Freita-Alvite M, López-Quintela M A, Hueso L E, Miguéns D R, Sande P and Rivas J 2002 Coexistence of paramagnetic-ordered and ferromagnetic-metallic phases in La_{0.6}Sr_{0.3}MnO_{3} evidenced by electron spin resonance J. Appl. Phys. 91 785–8