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# A variable temperature EPR study of the manganites $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$ ($x=0.0$, 0.1, 0.2, 0.33): Small polaron hopping conductivity and Griffiths phase

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ABSTRACT

Four manganite samples of the series, $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$, with $x=0.0$, 0.1, 0.2 and 0.33, were investigated by X-band (~9.5 GHz) electron paramagnetic resonance (EPR) in the temperature range 4–300 K. The temperature dependences of EPR lines and linewidths of the samples with $x=0.0$, 0.1 and 0.2, containing $Ba^{2+}$ ions, exhibit similar behavior, all characterized by the transition temperatures ($T_C$) to ferromagnetic states in the 110–150 K range. However, the sample with $x=0.33$ (containing no $Ba^{2+}$ ions) is characterized by a much higher $T_C=205$ K. This is due to significant structural changes effected by the substitution of $Ba^{2+}$ ions by $Sr^{2+}$ ions. There is an evidence of exchange narrowing of EPR lines near $T_{min}$, where the linewidth exhibits the minimum. Further, a correlation between the temperature dependence of the EPR linewidth and conductivity is observed in all samples, ascribed to the influence of small-polaron hopping conductivity in the paramagnetic state. The peak-to-peak EPR linewidth was fitted to $\Delta B_{pp}(T)=\Delta B_{pp,min}+A/T\exp(-E_a/k_BT)$, with $E_a=0.09$ eV for $x=0.0$, 0.1 and 0.2 and $E_a=0.25$ eV for $x=0.33$. From the published resistivity data, fitted here to $\sigma(T)\propto 1/T\exp(-E_\sigma/k_BT)$, the value of $E_\sigma$, the activation energy, was found to be $E_\sigma=0.18$ eV for samples with $x=0.0$, 0.1 and 0.2 and $E_\sigma=0.25$ eV for the sample with $x=0.33$. The differences in the values of $E_a$ and $E_\sigma$ in the samples with $x=$ 0.0, 0.1and 0.2 and $x=0.33$ has been ascribed to the differences in the flip-flop and spin-hopping rates. The presence of Griffiths phase for the samples with $x=0.1$ and 0.2 is indicated; it is characterized by coexistence of ferromagnetic nanostructures (ferrons) and paramagnetic phase, attributed to electronic phase separation.



## 1. Introduction

The compounds $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$ have the common formula $A_{1-y}B_yMnO_3$ (where A=La, Sm, Pr, or another rare-earth ion, and B=Ca, Ba, Sr; $y=1/3$). They are members of a large series of rare-earth manganites exhibiting giant magnetoresistance. Their transport, magnetic and structural properties are very sensitive to the substitution of trivalent rare-earth ion ($A^{3+}$), as well as that of divalent ions ($B^{2+}$). These compounds have been the subject of several investigations, including FMR/EPR investigations of Mn ions. (See Refs. [1–25] in the reference section, where the details of particular investigations have been included. Here FMR stands for ferromagnetic resonance.) Special attention was given to the spin dynamics of the Mn ions near the magnetic phase transition, and explanation of the pseudolinear increase in EPR linewidth in the paramagnetic state of these compounds above the Curie temperature. Despite all these efforts, the magnetic behavior of these compounds has not been fully understood as yet.

The effect of substitution of the $Sr^{2+}$ ion, with the ionic radius of 1.12 Å, for the $Ba^{2+}$ ion, with the larger ionic radius of 1.34 Å, has been investigated here on the EPR spectra in the manganites $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$, $x=0.0$, 0.1, 0.2, and 0.33. This substitution affects the structure of these compounds leading to a deviation from the ideal cubic structure, the degree of which is dependent on the ionic radius of the substituting divalent cation. The amount of substitution governs the fractional contents of the $Mn^{3+}$ and $Mn^{4+}$ ions present in these samples. The change in the average size of the cation at the B site of these perovskites results in large changes in their transport and magnetic properties due to modification of the Mn–O–Mn bond angles and Mn–O distances, thereby influencing the $e_g$ electron hopping between the $Mn^{3+}$

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and $Mn^{4+}$ states. Also, such distortion of the bond angles and distances gives rise to competing superexchange and double-exchange interactions, causing electronic phase separation. It is noted here that increasing Ba content leads to increasing disorder in the system, and therefore to a possible appearance of enhanced spin-glass like phase in these samples. Further, in these compounds, diamagnetic La ions are partly substituted by the paramagnetic Kramers $Sm^{3+}$ ions, which strongly affects the magnetic states of these compounds below their phase transitions: where there occurs a competition between the ferro and antiferromagnetic states, which, in turn, affects their magnetoresistance [1–10]. Asthana et al. [9] reported detailed investigations of the magnetic susceptibility and conductivity in the temperature range 4–320 K in these compounds, whereas Huanyin et al. [1] investigated the influence of heavy doping of Sm in $La_{0.67}Sr_{0.33}MnO_3$.

This paper reports a detailed X-band (~9.5 GHz) electron paramagnetic resonance (EPR) study of the manganite compounds $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$ ($x$=0.0, 0.1, 0.2 and 0.33) in the temperature range 4–300 K. Apart from studying the occurrence of Griffiths phase in the samples with $x$=0.1 and 0.2, an important aim of the present work is to understand the behavior of the broadening of EPR lines in the paramagnetic state and to investigate the ferromagnetic nanostructures (ferrons) in these compounds.

## 2. Experimental arrangement

A Bruker ER-200D SRC EPR X-band spectrometer, equipped with an Oxford helium-flow cryostat for temperature variation in the liquid-helium temperature range for 4–150 K, as well as a Bruker temperature controller for variation in the liquid–nitrogen temperature range 120–300 K, was used to investigate the manganite samples $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$. It is noted here that with the Oxford cryostat, one goes to the lowest temperature (4 K) first, and then all measurements are carried out with increasing temperature, whereas with the Bruker cryostat the measurements are made for temperatures decreasing from room temperature. The difference in the direction of temperature change does lead to some hysteresis in the EPR linewidth and line positions. This is similar to that observed in $YBaMn_2O_6$, where the structural phase-transition temperature $T_t$ determined during cooling was found to be less than the phase transition temperature determined during heating. [4]

## 3. EPR spectra

### 3.1. Phase transitions from paramagnetic to magnetically ordered phase

The variation of the first-derivative EPR spectra with temperature for these samples is shown in Figs. 1, 2, 3 and 4 for the samples with $x$=0.0, 0.1, 0.2 and 0.33, respectively. They exhibit essentially the same behavior of the main, intense line as the temperature is lowered. The phase-transition temperatures from the magnetically ordered states to the paramagnetic state, at which spontaneous magnetization drops to zero, as determined from magnetization data [9], are 96, 112, 127 and 203 K, for $x$=0.0, 0.1, 0.2 and 0.33, respectively. For all these samples, $g$~2.0 for the EPR line in the paramagnetic phase. For the sample with $x$=0.33, two lines,—the narrow one situated in the 2200–2800 G range and the broader one centered around 3500 G, were observed clearly below 210 K, as seen in Fig. 4. The broader line disappears below 190 K, at which the sample becomes fully

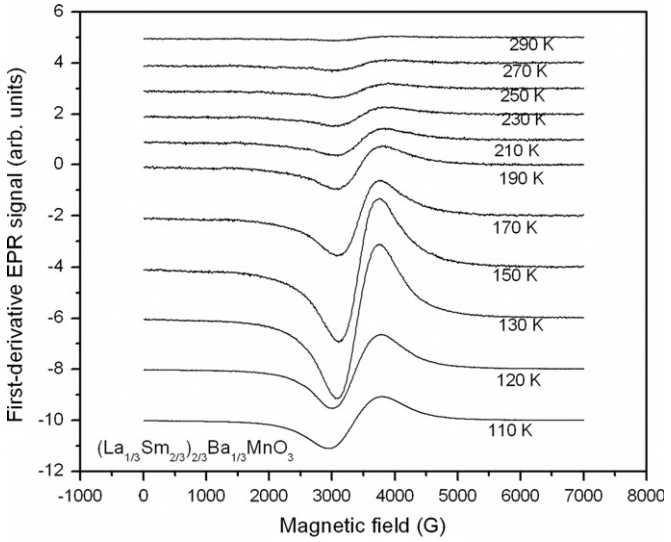


**Fig. 1.** Variation of EPR spectra of $(La_{1/3}Sm_{2/3})_{2/3}Ba_{1/3}MnO_3$ sample ($x$=0.0) versus temperature from 4 to 290 K. EPR lines below and above 110 K were recorded using the Oxford and Bruker temperature controllers, respectively.

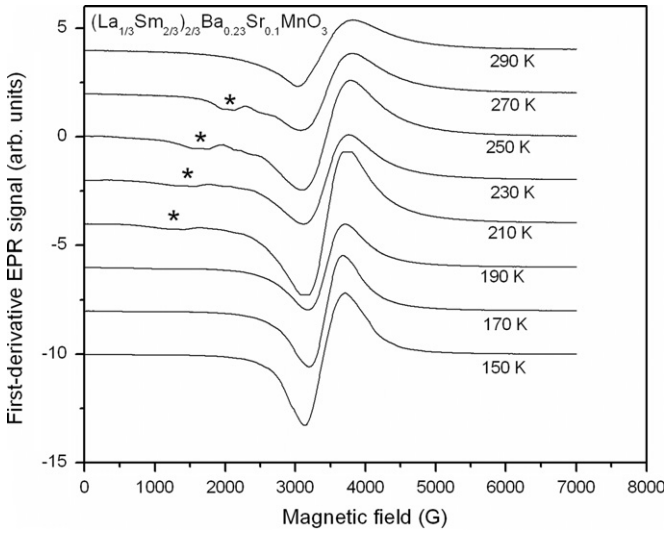


**Fig. 2.** Variation of EPR spectra of $(La_{1/3}Sm_{2/3})_{2/3}Ba_{0.23}Sr_{0.10}MnO_3$ sample ($x$=0.1) versus temperature from 4 to 290 K. The second signal in the region 230–270 K is clearly seen, and indicated by a star. EPR lines below and above 150 K were recorded using the Oxford and Bruker temperature controllers, respectively.

ferromagnetic. The narrower EPR line starts to move to lower magnetic fields with decreasing temperature below 205 K in the ferromagnetic region. In Fig. 5, the overlap of broad and narrow EPR lines is successfully simulated as a weighed sum of two EPR lines, one of these is situated at $g$=2.04 (paramagnetic), whereas the second one (ferromagnetic phase) is situated at a higher $g$ value, varying from 2.5 at 210 K to 2.9 at 200 K as the temperature decreases. The second line has the Lorentzian shape. As revealed by this simulation, the relative contribution of the first line decreases in this temperature region, accompanied by the contribution of the second line increasing sharply, from 13% at 210 K to 60% at 200 K. The presence of two lines at the same temperature, one paramagnetic and the other ferromagnetic, representing two different magnetic phases, is a clear evidence of phase separation in this compound near the magnetic phase transition. This is due to the varying distribution of $Sr^{2+}$ ions over the sample, which, in turn, leads to fluctuations of $Mn^{3+}/Mn^{4+}$