An EPR study of Ba-substituted $(La_{0.33}Sm_{0.67})_{0.67}Sr_{0.33-x}Ba_xMnO_3$

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1. Introduction

The series of compounds $(La_{0.33}Sm_{0.67})_{0.67}Sr_{0.33-x}Ba_xMnO_3$ with Ba (x = 0, 0.13, 0.23, 0.33) exhibit drastic changes in magnetic and electric properties when the Ba content varies from 0 to 0.13 [1]. In particular, an EPR study of this series confirmed drastic changes in the EPR linewidth and revealed phase separation in the vicinity of T_C and the appearance of Griffiths phase in paramagnetic region [2]. The pseudolinear behaviour of EPR linewidth in the paramagnetic region was explained on the basis of small polaron hopping model [3]. However, for the samples with disorder not only in the rare earth ions, but also in the alkaline earth ions system, due to Ba substitution of Sr ions, one has to invoke Mott's variable range hopping (VRH) mechanism [4].

2. Phase separation and Griffiths phase

These ceramic samples were synthesized by citrate sol-gel method based on citrate gel formation with ethylene glycol. The Mn^{2+} EPR spectra of were recorded in the temperature region 110 – 450 K at X-band (9.45 GHz). Phase separation for samples with x = 0.01 and 0.03 was observed at temperature near phase transition. For other samples, the phase transition occurs in a smooth manner. The EPR signals, corresponding to Griffiths phase, were observed in the samples with x = 0.03, 0.06, 0.09. The temperature dependence of the EPR linewidth in the paramagnetic phase was analyzed on the basis of variable range hoping model. It was concluded, that increasing disorder in the compounds $(La_{0.33}Sm_{0.67})_{0.67}Sr_{0.33-x}Ba_xMnO_3$ is consistent with this model. Assuming that the EPR linewidth is proportional to the conductivity in $(La_{1/3}Sm_{2/3})_{2/3}Sr_{1/3-x}Ba_xMnO_3$, which follows variable range hopping model, then the EPR linewidth can be expressed as:

$$\Delta B_{pp}(T) = \Delta B_{pp,min} + C \cdot \exp(-(T_0/T)^{1/4}) \qquad (1)$$

The second term of Eq. (1) provides linear dependence to the EPR linewidth, with the reasonable value of the parameter $T_0 \sim 10^6$ K. Therefore VRH model is valid for $(La_{0.33}Sm_{0.67})_{0.67}Sr_{0.33-x}Ba_xMnO_3$ system.

3. Discussion

The salient features of the EPR study on the manganite samples of $(La_{1/3}Sm_{2/3})_{2/3}Sr_xBa_{0.33-x}MnO_3$ presented here are as follows.

(i) The substitution of Ba^{2+} ions by Sr^{2+} ions has a profound effect on T_c, the magnetic phase transition temperature, and T_{min}, at which the minimum of the EPR linewidth occurs.

(ii) The phase separation near phase transition temperature was observed only for the samples with x =0.01 and 0.03.

(iii) The processes of temperature-independent exchange narrowing and temperature-dependent hopping conductivity affect the EPR linewidth. Variable range hopping mechanism explains linear dependence of EPR linewidth on temperature in the paramagnetic region with reasonable good VRH parameter T_0.

Presence of Griffiths phase, characterized by the coexistence of ferron nanostructures and paramagnetic bulk state was clearly observed in the samples with x = 0.03, 0.06. There is more complicated ferroic behavior with co-existence of paramagnetic and ferromagnetic phase, for the sample with x = 0.09 below 300 K. This behavior is surprising, considering that no such behavior was observed for the sample with x = 0.13, for which the EPR signal was observed from phase transition to about 300 K.

The difference in the electric and magnetic properties between the samples without Ba and with even very light Ba doping (x = 0.01) can be ascribed to the change of T_0 with the structure changes. Since $kT_0 = 18\alpha^3/N(E_p)$, $N(E_p)$ -- electron density, $L = 1/\alpha$ -- localization length, both $N(E_p)$ and L are responsible for sharp change of T_0.

4. Conclusions

Sharp change with Ba doping in the phase transition temperature T_C, as well as in the variable-range hopping parameter T_0 is due to the transition from small polaron hopping model for the samples without Ba to variable range hopping for the samples doped with Ba.

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References

[1] S. Asthana, A. K. Nigam, S. K. Malik, D. Bahadur. – *J. Alloys Compd.* **450**, 136-141 (2008).

[2] S. K. Misra, S. I. Andronenko, S. Asthana and D. Bahadur. – *J. Magn. Magn. Mater.* **322**, 2902-2907 (2010).

[3] A. Shengelaya, Guo-meng Zhao, H. Keller, K. A. Muller, B. I. Kochelaev. – *Phys. Rev. B* **61**, 5888-5890 (2000)

[4] Guo Huanyin, Liu Ning, Yan Guoqing, Tong Wei. – *Journal of rare earths*, **24**, 206 – 213 (2006).