

## EPR studies of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{MnFe}_2\text{O}_4$ superconducting composites

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**Abstract.** Electron paramagnetic resonance (EPR) studies are carried out on composite samples of  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}/(\text{MnFe}_2\text{O}_4)_x$  superconductors with  $0.00 \leq x \leq 0.20$  wt% at different temperatures  $100\text{K} \leq T \leq 295\text{K}$ . An EPR signal of  $\text{Cu}^{2+}$  ions in the orthorhombic local symmetry is observed. Moreover, the EPR signal intensity increases as the temperature decreases from room temperature down to 100 K. The temperature dependence of g-factors indicates the pseudogap onset temperature ( $T^*$ ), corresponding to the peak of the observed curves between 127 K and 162 K. The number of spins ( $N$ ) participating in EPR resonance are calculated as a function of both nanosized  $\text{MnFe}_2\text{O}_4$  addition and temperature. In particular, it is shown that any EPR signal for  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}/(\text{MnFe}_2\text{O}_4)_x$  is probably due to small amount of spurious phases typically present in the samples such as  $\text{BaCuO}_2$ . The presence of  $\text{BaCuO}_2$  is confirmed by magnetization-field (M-H) hysteresis measurements

### 1. Introduction

Electron paramagnetic resonance (EPR) is a powerful tool in high temperature superconductors (HTSCs) for examining their magnetic origin, and clarifying the nature of the superconducting mechanism [1]. However, a large number of investigations on HTSCs of the type  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (RE-123, RE rare-earth ions) using the EPR method have been reported [2]. The majority of these investigations exhibit a characteristic EPR signal of  $\text{Cu}^{2+}$  ions with orthorhombic local symmetry. Up to now, a number of authors have suggested that this spectrum of  $\text{Cu}^{2+}$  ions arises from other phases, e.g. green phase or  $\text{BaCuO}_2$  [3]. However, this only enhances its importance as a tool for the detection of  $\text{Cu}^{2+}$  containing impurities. In the present work, we report on the EPR studies of Sm-123 added with nanosized  $\text{MnFe}_2\text{O}_4$ , with  $0.00 \leq x \leq 0.20$  wt%.

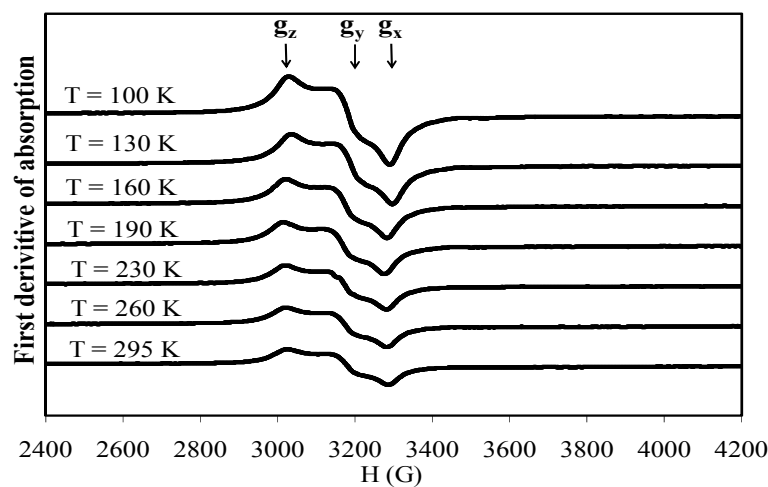
### 2. Experimental Techniques

Nanosized superparamagnetic ( $\text{MnFe}_2\text{O}_4$ ) and  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}/(\text{MnFe}_2\text{O}_4)_x$ ,  $x = 0.0, 0.02, 0.08, 0.15$  and  $0.20$  wt%, superconducting samples were prepared by the co-precipitation method and the conventional solid state reaction respectively, as previously reported [4]. EPR measurements were performed with a Bruker ER 041 X-band spectrometer operating at 9.24 GHz using 100 kHz field modulation in the temperature range 100–295 K. A vibrating sample magnetometer (VSM), Lakeshore 7410, was used to investigate the magnetic properties at 77K.



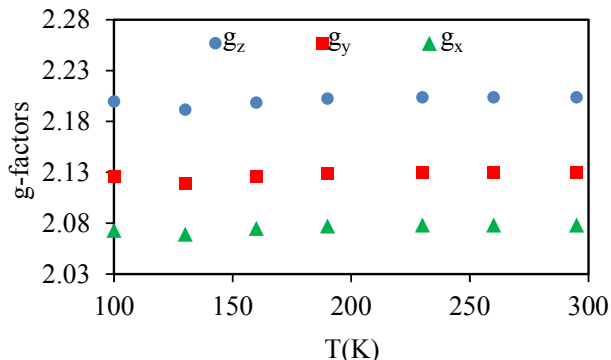
### 3. Results and Discussion

In our previous work [4] effects of nanosized  $\text{MnFe}_2\text{O}_4$  addition on superconducting properties of  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Sm-123) has been investigated in details. The value of  $T_c$  decreases from 91.50 K to 79.01 K as  $x$  increases from 0.00 to 0.20 wt% which consistent with that the magnetic impurities generally suppress superconductivity. Figure 1 shows the first derivative EPR absorption spectra of Sm-123 pure sample at temperatures  $100\text{K} \leq T \leq 295\text{K}$ . In the all temperature range, the EPR spectra consist of a single strongly asymmetric line corresponding to an anisotropic g-factor with three principal g-values  $g_x$ ,  $g_y$  and  $g_z$  characteristic of an orthorhombic symmetry around the  $\text{Cu}^{2+}$  ion [3].

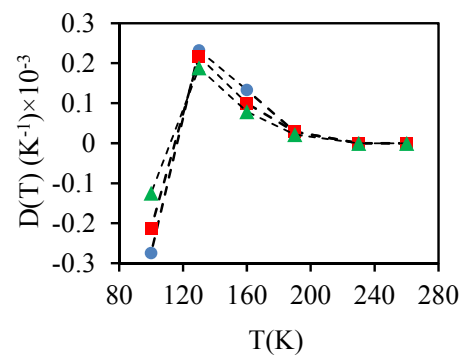


**Figure 1.** First derivative absorption spectra for  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$  at different temperatures.

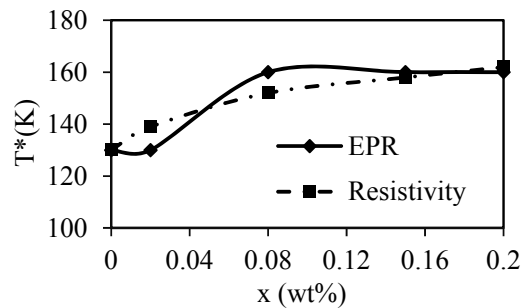
The variation of the anisotropic g-values with  $T$  for Sm-123 pure sample is shown in figure 2. It is observed that  $g_x$ ,  $g_y$  and  $g_z$  decrease with increasing temperature up to 130K then increase slightly again. The observed peak of the anisotropic g-factors variation with  $T$  is corresponding to the opening of pseudo-gap (PG) [5]. PG is defined as the onset of negative deviation for linear temperature dependence in-plane resistivity at high  $T$ . Then, PG onset temperature  $T^*$  is established by the derivative  $D_i(T) = (g_{i,j} - g_{i,k})/(T_j - T_k)$  and plotted as shown in figure 3, where  $T_j > T_k$  for the anisotropic  $g_i$  ( $i = x, y$  and  $z$ ). One can find that  $T^*$  ( $\approx 130$  K) for Sm-123 ( $T_c \approx 91.5$  K) coincides with the phase boundary established by resistivity ( $T^* = 127 \pm 2$  K) [4]. The variation of  $T^*$  determined from resistivity and EPR with nanosized  $\text{MnFe}_2\text{O}_4$  is shown in figure 4. It is observed that  $T^*$  obtained from the both methods are nearly close to each other and exhibiting the same trend,  $T^*$  increases with nanosized  $\text{MnFe}_2\text{O}_4$  addition up to  $x = 0.20$  wt%. This result suggests the existence of orthorhombically elongated octahedral  $\text{Cu}^{2+}$  (1) sites suffering the Jan-Teller effect via the vibration interactions [8].



**Figure 2.** Variation of g-factors with  $T$  for Sm-123.

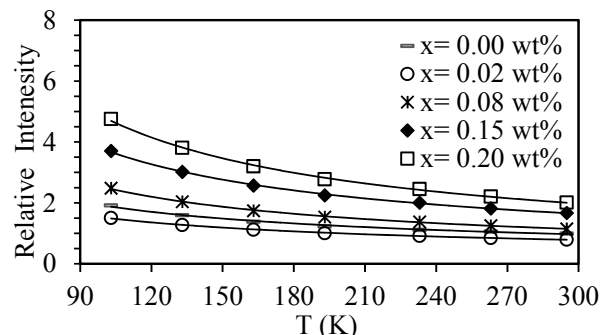


**Figure 3.** Derivatives of  $g_i$  ( $i = x, y$  and  $z$ ).



**Figure 4.** Variation of  $T^*$  as a function of nanosized  $\text{MnFe}_2\text{O}_4$  content.

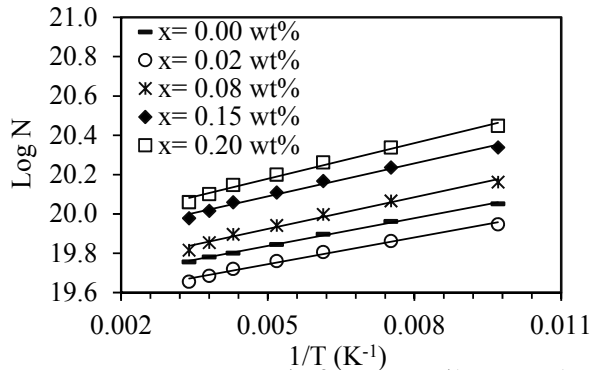
However, the EPR relative intensity decreases as the nanosized  $\text{MnFe}_2\text{O}_4$  addition increases up to 0.02 wt% and then increases with further addition  $x > 0.02$  wt% as shown in figure 5. This is proportional to the amount of  $\text{BaCuO}_2$  typically present in the samples as supported by our X-ray diffraction (XRD) results [4]. Based on this observation, we assume that this EPR spectrum originates mainly from delocalized d electrons of  $\text{Cu}^{2+}$  ions of the  $\text{BaCuO}_2$  compound [7]. However, the relative EPR line intensity for  $\text{Sm-123}/(\text{MnFe}_2\text{O}_4)_x$  composites increases as the temperature decreases from 295K down to 100 K as approximately Curie-Weiss law at  $T > T_c$  [8].



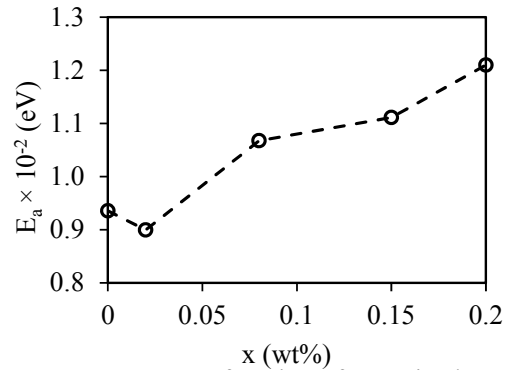
**Figure 5.** Variation of EPR relative intensity with  $T$  for  $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}/(\text{MnFe}_2\text{O}_4)_x$ .

The number of spins  $N$  participating in the resonance can be calculated at different temperatures by comparing the area under the absorption curve with that of a standard  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  [1]. As expected from Boltzmann's law, a linear relationship between  $\log(N)$  and  $1/T$  for  $\text{Sm-123}/(\text{MnFe}_2\text{O}_4)_x$  composites is shown in figure 6. It is found that  $N$  decreases as the nanosized  $\text{MnFe}_2\text{O}_4$  addition increases up to 0.02 wt% then increases for  $x > 0.02$  wt%. Furthermore, it increases with temperature decreasing from 295K down to 100K. The activation energy  $E_a$  as a function of nanosized  $\text{MnFe}_2\text{O}_4$  addition are calculated from the slope of lines as shown in figure 7. The enhancement in  $E_a$  for  $x > 0.02$  wt%, is consequently the result of increasing  $N$  with nanosized  $\text{MnFe}_2\text{O}_4$  addition for  $x > 0.02$  wt%. Figure 8 shows the  $M-H$  curves of  $\text{Sm-123}/(\text{MnFe}_2\text{O}_4)_x$  at 77 K. As it is seen all the samples show a paramagnetic character. Magnetization increases linearly with the magnetic field and does not saturate even at 20kG. However, in this case, superconductivity seems to be dominant, especially at low fields. The  $M-H$  curves show small hysteresis at 77 K. Such a hysteresis, which is proportional with the critical current density  $J_c$ , is commonly encountered at the  $M-H$  curves of typical ceramic superconductors. The possible reason of paramagnetism like behavior may be accounted for  $\text{BaCuO}_2$  impurity phase present in the samples. Similar paramagnetism like behavior observed by Tobal [9] for Y-123 superconductor. These results confirmed that our EPR measurements are mainly due to small amounts of  $\text{BaCuO}_2$  present in the samples. The sample with 0.02 wt%  $\text{MnFe}_2\text{O}_4$  addition has the largest  $\Delta M$  and the weaker  $\text{Cu}^{2+}$  EPR signal. Therefore, It is suggested that an amount ( $\sim 0.02$ wt %) of  $\text{MnFe}_2\text{O}_4$  addition in the Sm-123

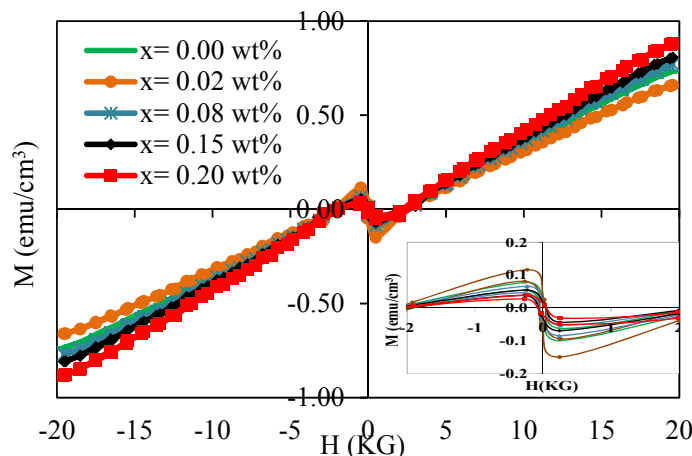
superconductor can increase  $J_c$  due to enhancement of flux pinning properties and phase purity. Beyond  $x > 0.02$  wt% the hysteresis width and consequently, the flux pinning and  $J_c$  decreased.



**Figure 6.** Log N vs.  $1/T$  for Sm-123/(MnFe<sub>2</sub>O<sub>4</sub>)<sub>x</sub>.



**Figure 7.**  $E_a$  as a function of nanosized MnFe<sub>2</sub>O<sub>4</sub>.



**Figure 8.** M-H hysteresis loop for Sm-123/(MnFe<sub>2</sub>O<sub>4</sub>)<sub>x</sub> (The inset shows magnified M-H curves).

#### 4. Conclusion

The EPR signal of Sm-123/(MnFe<sub>2</sub>O<sub>4</sub>)<sub>x</sub> composites comprises a dominant Cu<sup>2+</sup> anisotropic pattern, which is mainly due to the impurity phase BaCuO<sub>2</sub>. However, the addition of nanosized MnFe<sub>2</sub>O<sub>4</sub> up to  $x = 0.02$  wt% improved the flux pinning and  $J_c$ .

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