

## Effect of rare-earth doping on the superconducting properties of MgB<sub>2</sub>

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The bulk polycrystalline samples with nominal compositions Mg<sub>1-x</sub>(Eu<sub>2</sub>O<sub>3</sub>)<sub>x/2</sub>B<sub>2</sub> and Mg<sub>1-x</sub>(Pr<sub>6</sub>O<sub>11</sub>)<sub>x/6</sub>B<sub>2</sub> (where  $x=0.0, 0.01, 0.02, 0.03, 0.04,$  and  $0.05$ ) have been prepared via standard solid-state reaction route. The x-ray diffraction (XRD) results of both series of materials reveal the presence of secondary phases MgO and REB<sub>6</sub> (RE=Eu/Pr) besides the main hexagonal phase of MgB<sub>2</sub>. The magnetic and electrical measurements show that transition temperatures ( $T_c$ ) of both Eu<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>-doped MgB<sub>2</sub> samples decrease from 39 to 37 K when values of  $x$  increase from 0.0 to 0.05. Improvement in critical current density ( $J_c$ ) at 10 K has been observed at higher fields ( $>4$  T) for Eu<sub>2</sub>O<sub>3</sub>-doped samples of composition  $x=0.04$  and in entire field range (0–5 T) in the case of Pr<sub>6</sub>O<sub>11</sub>-doped samples of composition  $x=0.03$  as compared to the  $J_c$  values of other compositions. The  $J_c$  values at 5 T field and 10 K of undoped,  $x=0.03$  for Pr<sub>6</sub>O<sub>11</sub>-doped and  $x=0.04$  for Eu<sub>2</sub>O<sub>3</sub>-doped MgB<sub>2</sub> samples are  $2.21 \times 10^3$ ,  $1.15 \times 10^4$ , and  $1.10 \times 10^4$  A/cm<sup>2</sup>, respectively. Improvement in  $H_{c2}$  and  $H_{irr}$  has also been observed in doped samples. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072379]

The MgB<sub>2</sub> superconductor with transition temperature ( $T_c$ ) ~ 39 K has been considered as a promising material for practical applications in a temperature range of 20–30 K.<sup>1</sup> The strong potential for commercial applications of MgB<sub>2</sub> is due to its low cost, low anisotropy, larger coherence lengths, and strong coupling across grain boundaries.<sup>2,3</sup> Pristine MgB<sub>2</sub>, however, does not appear to be very promising for applications because of its low  $H_{c2}$  and  $H_{irr}$  values.  $J_c$  of pure MgB<sub>2</sub> falls rapidly in high fields due to poor grain connectivity and lack of pinning centers. Therefore, to make practical devices using MgB<sub>2</sub>, it is essential to improve its critical current density  $J_c(H)$  in high magnetic fields  $H$ , upper critical field ( $H_{c2}$ ), and irreversibility field ( $H_{irr}$ ). For this a lot of efforts have been made in previous years using various methods, such as irradiation,<sup>4</sup> chemical doping,<sup>5</sup> and increasing grain boundaries through reducing grain size. Several C-containing dopants such as nanodiamond, nanocarbon tubes, SiC, etc.<sup>6–8</sup> have been used to improve the superconducting properties of MgB<sub>2</sub>. Usually it has been seen that the substitutions of magnetic elements with strong magnetic moment such as Fe, Co, etc.<sup>9,10</sup> into MgB<sub>2</sub> degrade superconducting properties. On the other hand, doping of rare-earth (RE) elements which also possess magnetic moment into MgB<sub>2</sub> do not degrade much its superconductivity. Recently, the addition of nano- and submicron particles of RE oxides such as Y<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, and Pr<sub>6</sub>O<sub>11</sub> have been found to increase the flux pinning in MgB<sub>2</sub>.<sup>11–14</sup> In this paper we report the effect of Eu<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> doping on the structural and superconducting properties of MgB<sub>2</sub>. Improvement in  $J_c(H)$ ,  $H_{c2}$ , and  $H_{irr}$  of the doped samples have been observed in the present study.

The bulk polycrystalline samples of Eu<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>-doped MgB<sub>2</sub> were synthesized, respectively, with nominal compositions Mg<sub>1-x</sub>(Eu<sub>2</sub>O<sub>3</sub>)<sub>x/2</sub>B<sub>2</sub> and Mg<sub>1-x</sub>(Pr<sub>6</sub>O<sub>11</sub>)<sub>x/6</sub>B<sub>2</sub> (where  $x=0.0, 0.01, 0.02, 0.03, 0.04,$  and  $0.05$ ) via standard solid-state reaction route by sintering at 850 °C for 3 h in Ar atmosphere. The structural and phase analyses of the samples were performed using x-ray diffractometer. The variation in resistance with temperature was studied with increasing magnetic field up to 8 T using Quantum Design physical property measurement system. The magnetic measurements were performed by using superconducting quantum interference device magnetometer.

Figure 1 shows the x-ray diffraction (XRD) patterns of Eu<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub>-doped MgB<sub>2</sub> samples synthesized in the present work. The XRD patterns reveal the presence of secondary phases MgO and EuB<sub>6</sub>/PrB<sub>6</sub> besides the main MgB<sub>2</sub> phase. In the XRD patterns of Pr<sub>6</sub>O<sub>11</sub>-doped samples of compositions  $x \geq 0.03$  there is one weak peak corresponding to PrB<sub>4</sub> phase. All the impurity peaks are marked in Fig. 1. The peak intensities of EuB<sub>6</sub>/PrB<sub>6</sub> peaks increase with increase in Eu<sub>2</sub>O<sub>3</sub>/Pr<sub>6</sub>O<sub>11</sub> content in the samples. This indicates that Eu<sub>2</sub>O<sub>3</sub>/Pr<sub>6</sub>O<sub>11</sub> decomposed at reaction temperature and reacted with B to form EuB<sub>6</sub>/PrB<sub>6</sub>. We have estimated the volume fraction of EuB<sub>6</sub>/PrB<sub>6</sub> in the samples from the x-ray peak intensities using the relation: volume fraction of EuB<sub>6</sub> or PrB<sub>6</sub> phase =  $\sum$  integrated peak intensities of EuB<sub>6</sub> or PrB<sub>6</sub> phase /  $\sum$  integrated intensities of all phases. In Eu<sub>2</sub>O<sub>3</sub>-doped samples the volume fractions of EuB<sub>6</sub> are 0.200, 0.266, 0.355, 0.423, and 0.417 for  $x=0.01, 0.02, 0.03, 0.04,$  and  $0.05$ , respectively. Similarly in Pr<sub>6</sub>O<sub>11</sub>-doped samples the volume fractions of PrB<sub>6</sub> are 0.081, 0.244, 0.451, 0.458, and 0.467 for  $x=0.01, 0.02, 0.03, 0.04,$  and  $0.05$ , respectively. Thus volume fraction of EuB<sub>6</sub>/PrB<sub>6</sub> phase in the samples increases with the increase in doping concentration of Eu/Pr.

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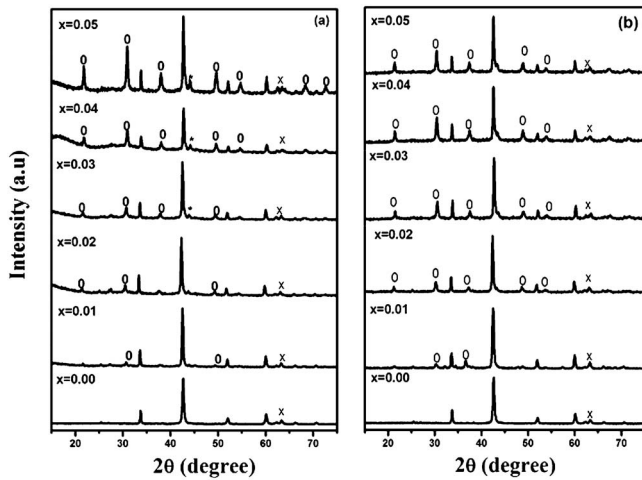


FIG. 1. XRD patterns of the sample synthesized with nominal compositions  $Mg_{1-x}(Pr_6O_{11})_{x/6}B_2$  (a) and  $Mg_{1-x}(Eu_2O_3)_{x/2}B_2$  (b). X, 0, and \* represent peaks of  $MgO$ ,  $REB_6$ , and  $PrB_4$ , respectively.

In addition, from the XRD results we have not seen appreciable change in the lattice parameters with doping concentration of  $Pr_6O_{11}$  and  $Eu_2O_3$ . This indicates that possibly Pr and Eu are not doped into the  $MgB_2$  lattice. It is also seen that the broadening of diffraction peaks of  $MgB_2$  phase increases in both series of compounds with doping concentration except for  $Pr_6O_{11}$ -doped sample of composition  $x = 0.01$ . From this result it is concluded that particle size of the samples decreases with the increase in doping concentration. This is possibly due to strain produced by the secondary phases which concentration increases on increasing doping concentration.

The transition temperatures ( $T_c$ ) of  $Eu_2O_3$ - and  $Pr_6O_{11}$ -doped  $MgB_2$  samples have been determined from the resistance versus temperature ( $R$ - $T$ ) measurements. From the  $R$ - $T$  measurements (figure not shown here) it has been found that the  $T_c$  decreases only from 39 to 37 K when values of  $x$  increases from 0.0 to 0.05 for both  $Eu_2O_3$ - and  $Pr_6O_{11}$ -doped samples. Only marginal decrease in  $T_c$  with the increase in doping level may be due to small solubility of Eu/Pr in  $MgB_2$ . This is also clear from the XRD patterns that the intensity of peaks of  $EuB_6/PrB_6$  phase increases rapidly with the increase in doping level (see Fig. 1). Therefore, doped Eu/Pr does not directly affect the boron sheet which is responsible for superconductivity in  $MgB_2$ . From the present result it is also concluded that the pair-breaking effect of the magnetic moment of the RE elements is not striking in  $MgB_2$ . Further, from the  $R$ - $T$  measurements it has been found that the residual resistivity ratio ( $RRR = R_{300}/R_{onset}$ ) values continuously decreases with  $x$  (from 3.38 to 2.81 in  $Pr_6O_{11}$ -doped  $MgB_2$  and from 3.38 to 2.54 in  $Eu_2O_3$ -doped  $MgB_2$ ). This is due to the increase in the amount of impurity phases as doping concentration increases in the samples. These impurity phases can enhance the electron scattering, and hence the decreased RRR value.<sup>15</sup> The insets of Fig. 2(a) and 2(b) show, respectively, the  $R$ - $T$  plots of  $Pr_6O_{11}$  and  $Eu_2O_3$ -doped samples ( $x = 0.01$ ) measured at different fields (0–8 T). Similar plots have been obtained for other compositions. The transition temperatures of both doped and un-

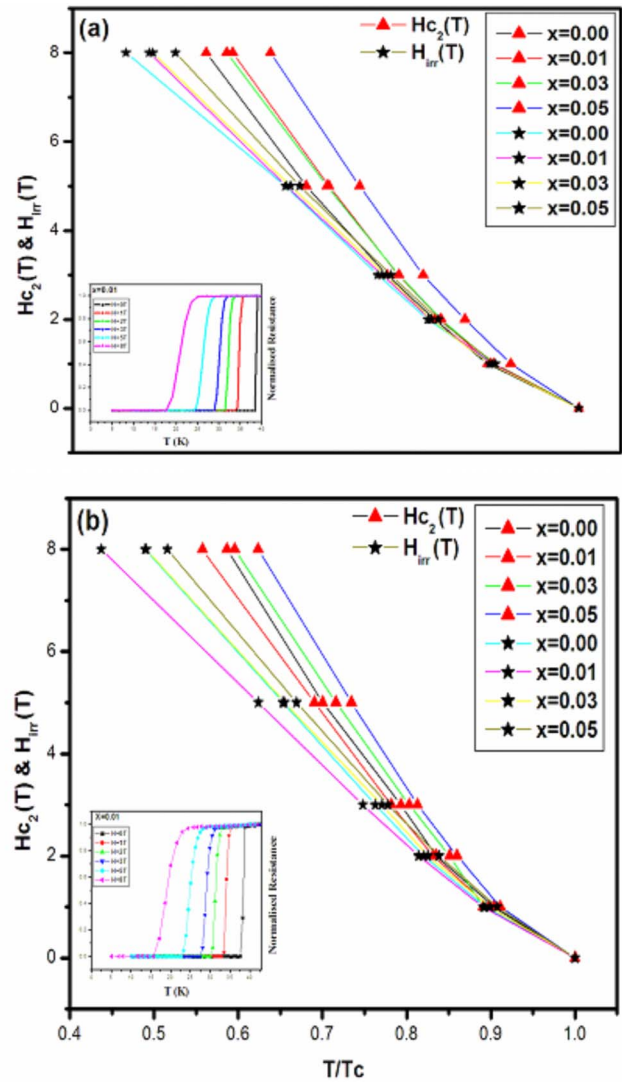


FIG. 2. (Color online)  $H_{c_2}(T)$  and  $H_{irr}(T)$  vs normalized temperature plots of the samples synthesized with nominal compositions  $Mg_{1-x}(Pr_6O_{11})_{x/6}B_2$  (a) and  $Mg_{1-x}(Eu_2O_3)_{x/2}B_2$  (b). Insets of (a) and (b) show, respectively, the  $R$ - $T$  plots of  $Mg_{1-x}(Pr_6O_{11})_{x/6}B_2$  and  $Mg_{1-x}(Eu_2O_3)_{x/2}B_2$  samples ( $x = 0.01$ ) measured in applied fields.

doped samples as usual decrease with the increase in the applied field. However, it has been seen that the reduction in  $T_c$  due to applied field decreases as doping concentration in the sample increases.

The irreversibility field [ $H_{irr}(T)$ ] and the upper critical fields [ $H_{c_2}(T)$ ] at various temperatures of doped and undoped  $MgB_2$  samples have been calculated from the resistive transitions using the criteria of 0.1 and 0.9 of  $R(H, T_c)$ , respectively. The variation in  $H_{c_2}(T)$  and  $H_{irr}(T)$  with respect to reduced temperature for each composition is shown in Fig. 2. From the plots it is clear that the  $H_{c_2}(T)$  values of doped samples are higher than that of undoped one at all temperatures except  $x = 0.01$  for  $Eu_2O_3$ -doped sample. It has been reported that the enhancement in upper critical field occurs from the reduction of the mean free path of the charge carriers and the corresponding reduction of the coherence length.<sup>16</sup> Therefore, in the present case also the enhancement in  $H_{c_2}$  of doped samples is possibly due to lattice distortion created through  $Eu_2O_3$  and  $Pr_6O_{11}$  dopings leading to en-

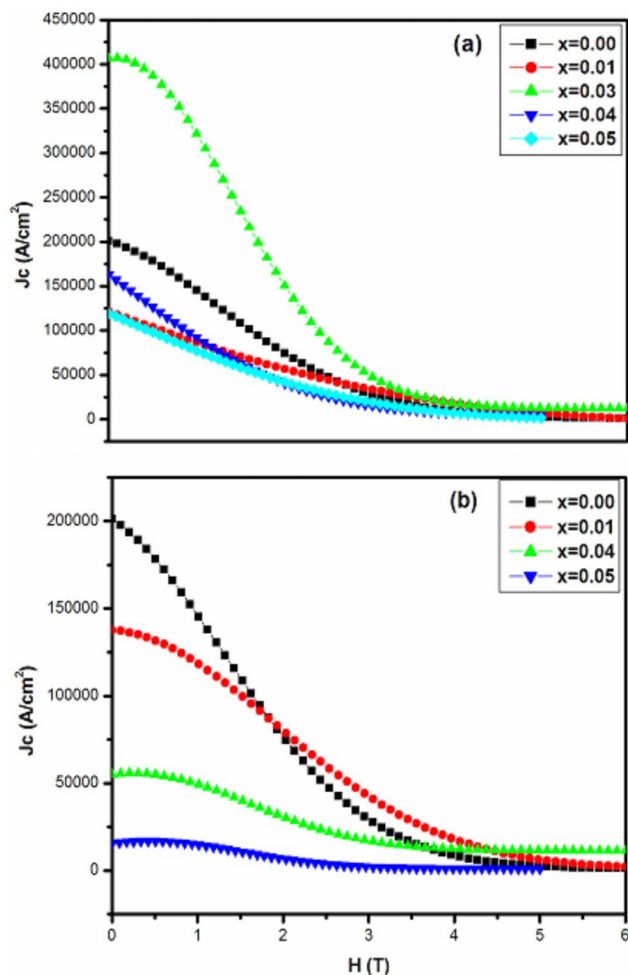


FIG. 3. (Color online)  $J_c$  vs  $H(t)$  plots of the samples synthesized with nominal compositions  $\text{Mg}_{1-x}(\text{Pr}_6\text{O}_{11})_{x/6}\text{B}_2$  (a) and  $\text{Mg}_{1-x}(\text{Eu}_2\text{O}_3)_{x/2}\text{B}_2$  (b).

hanced impurity scattering. The effect of  $\text{Eu}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  dopings on  $H_{c2}$  in the present case is quite different from the earlier results of RE-doped samples. For example, in the case of  $\text{Ho}_2\text{O}_3$ -doped  $\text{MgB}_2$  no change in  $H_{c2}$  has been observed<sup>13</sup> with doping concentration. From Fig. 2 it is clear that the value of  $H_{\text{irr}}$  first decreases up to  $x=0.01$  then increases with  $x$  in  $\text{Eu}_2\text{O}_3$ -doped  $\text{MgB}_2$ . But in the case of  $\text{Pr}_6\text{O}_{11}$ -doped  $\text{MgB}_2$  the value  $H_{\text{irr}}$  increases with  $x$ . Similar results have been obtained earlier on  $\text{Ho}_2\text{O}_3$ - and  $\text{Pr}_6\text{O}_{11}$ -doped  $\text{MgB}_2$  samples.<sup>14</sup>

The field dependence of the critical current density  $J_c(H)$  of the doped and undoped samples, estimated by using beans critical model<sup>17</sup> from the  $M$ - $H$  loops measured at 10 K, is shown in Fig. 3. From Fig. 3(a) it can be seen that in the case of  $\text{Pr}_6\text{O}_{11}$ -doped samples the critical current density of  $x=0.03$  sample has higher value as compared to other samples in the entire field range (0–5 T). For example, at 5 T  $J_c$  values of undoped sample and  $x=0.03$  sample are  $2.21 \times 10^3$  and  $1.15 \times 10^4$  A/cm<sup>2</sup>, respectively. Thus our result on  $J_c(H)$  is different from the result of Pan *et al.*<sup>14</sup> reported earlier. They found that 3%  $\text{Pr}_6\text{O}_{11}$ -doped sample has higher  $J_c$  than undoped one in the low field region and opposite behavior in high field region. But in our case except for  $x=0.03$  all other samples have lower values of  $J_c$  as compared

to undoped sample in whole magnetic field range. From Fig. 3(b) it is clear that in the low field region ( $< 2$  T),  $J_c$  of  $\text{MgB}_2$  decreases as doping concentration of  $\text{Eu}_2\text{O}_3$ -increases. However, when field values exceed 2 T,  $J_c$  of  $x=0.01$  sample becomes greater than that of undoped sample and finally in the fields  $> 4$  T  $J_c$  of  $x=0.04$  sample has higher value as compared to undoped one. Here the values of  $J_c$  at 5 T of undoped sample and  $x=0.04$  sample are  $2.21 \times 10^3$  and  $1.10 \times 10^4$  A/cm<sup>2</sup>, respectively. It is further noted that the rate of decrease in  $J_c$  with field is less for the doped samples as compared to the undoped one. We have studied the magnetic property of  $\text{PrB}_6$  and  $\text{EuB}_6$  impurity phases by measuring the  $M$ - $H$  curves at room temperature (figure not shown) with vibrating sample magnetometer. From the  $M$ - $H$  measurements we have seen that the secondary phases  $\text{PrB}_6$  and  $\text{EuB}_6$  show paramagnetic behavior at room temperature. Thus the presence of magnetic impurities at the grain boundaries may provide stronger attraction force to flux lines than the nonmagnetic impurities and hence enhance the flux pinning effect in  $\text{MgB}_2$  without affecting much its  $T_c$  leading to improvement in  $J_c(H)$  and  $H_{\text{irr}}$  of doped samples.

In summary we have seen improvement in  $J_c(H)$ ,  $H_{c2}$ , and  $H_{\text{irr}}$  of  $\text{MgB}_2$  through doping of RE oxides:  $\text{Pr}_6\text{O}_{11}$  and  $\text{Eu}_2\text{O}_3$ . It is argued that impurity phase  $\text{EuB}_6/\text{PrB}_6$  provide strong flux pinning leading to improvement in  $J_c(H)$  and  $H_{\text{irr}}$ .

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