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ORIGINAL PAPER

Improving the Critical Temperature of MgB_2 Superconducting Metamaterials Induced by Electroluminescence

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Abstract The MgB_2 superconductor was doped with electroluminescent Y_2O_3:Eu, to synthesise a superconducting metamaterial. The temperature dependence of the resistivity of the superconductor indicates that the critical temperature (T_C) of samples decreases when increasing the amount of doped Y_2O_3 nanorods, due to impurity (Y_2O_3, MgO and YB_4). However, the T_C of the samples increase with increasing amount of doped Y_2O_3:Eu^{3+} nanorods, which are opposite to doped Y_2O_3 nanorods. Moreover, the transition temperature of the sample doped with 8 wt % Y_2O_3:Eu^{3+}nanorods is higher than those of doped and pure MgB_2. The T_C of the sample doped with 8 wt % Y_2O_3:Eu^{3+} nanorods is 1.15 K higher than that of the sample doped with 8 wt % Y_2O_3. The T_C of sample doped with 8 wt% Y_2O_3:Eu^{3+} is 0.4 K higher than that of pure MgB_2. Results indicate that doping electroluminescent materials into MgB_2 increases the transition temperature; this novel strategy may also be applicable to other superconductors.

Keywords Y_2O_3:Eu^{3+} nanorods · MgB_2 superconductor · Solid-state method · T_C

1 Introduction

The binary metal boride superconductor MgB_2 has attracted considerable attention in theoretical studies and applications [1–6]. MgB_2 presents a great potential in superconductive device applications because of its advantages, namely, relatively high critical temperature (T_C nearly 40 K) [1], large superconducting correlation length [7], high critical current density, wide energy gap [8] and facile preparation.

MgB_2 is an inexpensive type II superconductor with a simple structure and can be easily synthesised [3]. However, the application of MgB_2 is restricted by its lower T_C compared with those of high-temperature superconductors. Several studies attempted to increase T_C by using doping agents. Results indicated that dopants decrease the T_C of the MgB_2 superconductor [9] and affect its physical properties, such as carrier concentration, lattice constant and crystallinity [10]. For example, doping aluminium (or carbon) in place of Mg (or B) in MgB_2 significantly decreases the T_C of MgB_2 [11]. Recently, Ma et al. increased the T_C of commercial MgB_2 from 33.0 to 37.8 K through nonsubstitutional hole-doping of the MgB_2 structure with small, single-wall carbon nanotube inclusions [12].

Metamaterials have gained increased attention because of their special properties and application potential [13–17]. In 2007, our group proposed that combining inorganic electroluminescent (EL) materials with metamaterials can induce a substantial change in superconducting materials, left-handed materials, photonic crystals and so on [18]. In the same year, Jang et al. studied the effects of ZnO doping on the superconductivity and crystal structure of the (Bi, Pb)-2233 superconductor [19]. Light-induced superconductivity has recently been considered as a research hotspot. In 2011, Cavalleri et al. used mid-infrared femtosecond pulses to transform a stripe-ordered compound, namely, nonsuperconducting $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$, into a transient three-dimensional superconductor [20]. In 2013, Cavalleri et al. experimentally demonstrated the excitation of Josephson plasma in $La_{1.84}Sr_{0.16}CuO_4$, by using intense

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narrowband radiation from infrared free-electron laser tuned to the 2-THz Josephson plasma resonance [21]. The group believed that laser pulse led to deformed crystal structures and induced superconductivity [22].

Y_2O_3:Eu^{3+} phosphor is a well-known red phosphor used in fluorescent light, field emission displays and cathode ray tubes, because of its excellent luminescence efficiency, narrow spectra, high brightness and environmental and chemical stability [23, 24]. In this paper, we examined the effect of electroluminescence on T_C by doping Y_2O_3, Y_2O_3:Sm^{3+} and Y_2O_3:Eu^{3+} nanorods into the MgB_2 superconductor to produce a superconducting metamaterial. The appropriate doping content for increasing the T_C of the MgB_2 superconducting metamaterial was demonstrated by controlling the concentration of Y_2O_3:Eu^{3+} nanorods.

2 Experimental Section

Bulk MgB_2 sample was synthesised with Y_2O_3:Eu^{3+} nanorods by traditional solid-state sintering [25]. Briefly, 0.22 g of magnesium (Mg, 97 % purity, 10 μm in size), 0.18 g of boron (B, 99.99 % purity, 1 μm in size) and Y_2O_3:Eu^{3+} (nanorods, 1–2 μm in length, 150–200 nm in diameter) were uniformly mixed at different mass ratios and ground for 20 min in an agate mortar. The mixture was transferred into a mould and pressed into cylindrical tablets at 20 MPa for 30 min. The samples were then sintered at 850 ° C for 2 h under flowing high-purity Ar gas (99.99 % purity) at a heating rate of 5 ° C min^{-1}. These procedures were also used to prepare MgB_2 doped with Y_2O_3 or Y_2O_3:Sm nanorods. Afterwards, the crystal structure was investigated through X-ray diffraction (XRD) by using a BRUKER D8 Advanced X-ray diffractometer with Cu Kα irradiation. Resistivity was measured using the four-probe technique. Electric field was imported through the electrodes. The measuring current was 100 mA.

3 Results and Discussion

The image in Fig. 1 shows the X-ray diffraction patterns of the series of MgB_2 doped with different amounts of Y_2O_3 and Y_2O_3: Eu^{3+} nanorods. Similar with other reports, the XRD results of pure MgB_2 indicate that the MgO phase exists in MgB_2. In comparison, the XRD results of the doping samples show that YB_4 phase, which is generated from the reaction of B and Y_2O_3, appears in the other samples. Surplus Y_2O_3 presents in XRD patterns with increasing amount of doping material. The XRD patterns also indicate that samples doped with Y_2O_3 nanorods are similar to those doped with Y_2O_3:Eu nanorods, because of the effective incorporation of Eu into the lattice of Y_2O_3.

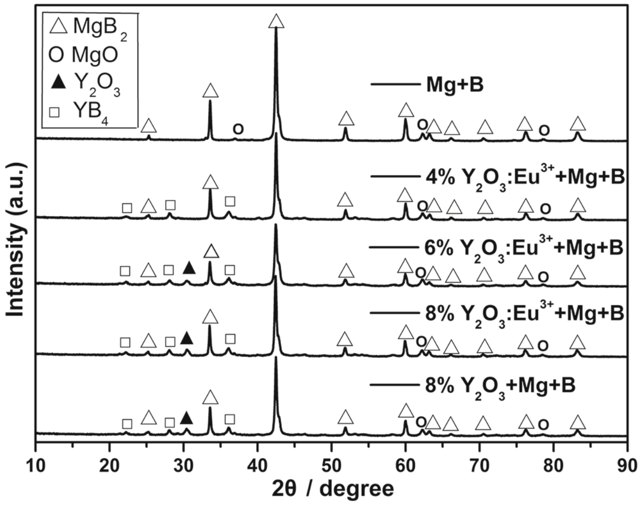

Fig. 1 X-ray diffraction patterns of Y_2O_3- and Y_2O_3:Eu^{3+}-doped MgB_2 samples after sintering

This study aims to prepare a composite superconducting metamaterial consisting of MgB_2 superconductor and Y_2O_3:Eu electroluminescent material. Firstly, we synthesised Y_2O_3:Eu nanorods on the basis of relevant research about Y_2O_3:Eu powders [26]. Figure 2 shows the EL spectrum of Y_2O_3:Eu nanorods. The spectrum indicates that the strongest peak centred at 613 nm corresponds to Eu^{3+} ions typical of transition from $^5D_0$ to $^7F_2$. Moreover, the full width at half maximum of the main emission peak is only 7 nm, suggesting superior monochromaticity, which is

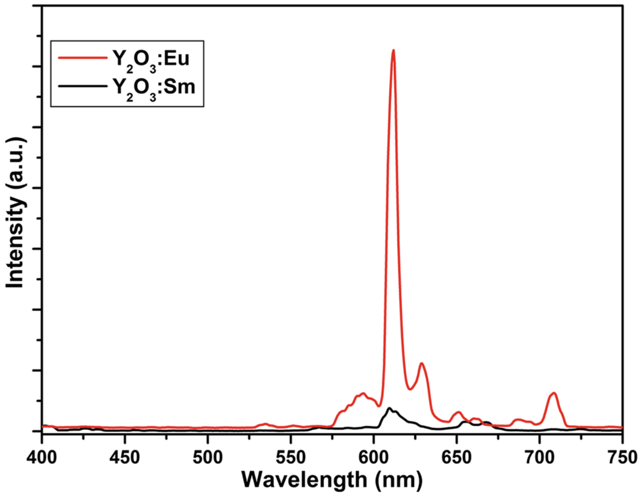

Fig. 2 Electroluminescence spectrum of Y_2O_3:Eu nanorods and Y_2O_3:Sm nanorods

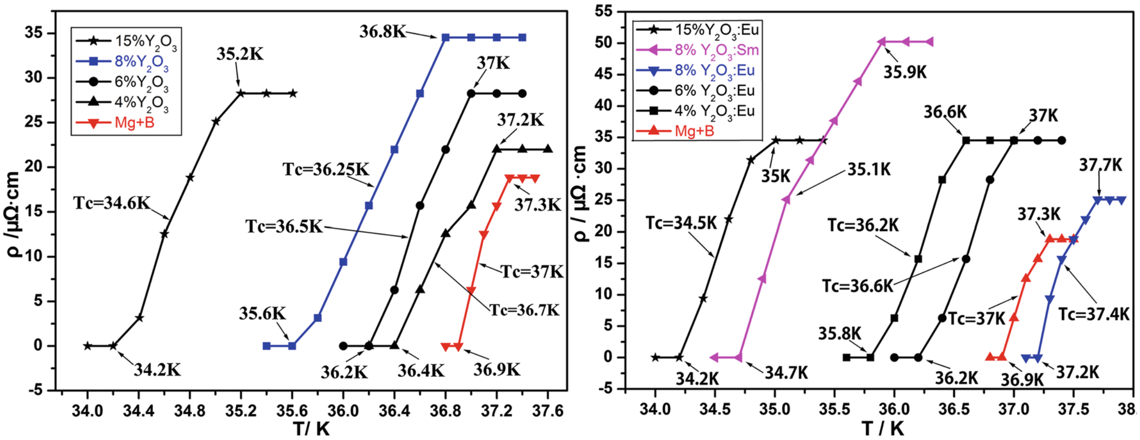

Fig. 3 Temperature dependence of resistivity of the undoped and 4, 6, and 8 wt% doped MgB_2 samples. **a** Doped Y_2O_3 nanorods; **b** doped Y_2O_3:Eu^{3+} nanorods

consistent with other reports. Secondly, the superconducting metamaterials were prepared by doping Y_2O_3:Eu nanorods into MgB_2. Electric field in bulk MgB_2 stimulates the electroluminescence of Y_2O_3:Eu. To further demonstrate the effect of electroluminescence in MgB_2, we synthesised Y_2O_3:Sm nanorods whose electroluminescence intensity is much lower than that of Y_2O_3:Eu (Fig. 2).

Figure 3 presents the temperature dependence of the resistivity of the series of MgB_2 samples doped with different amounts of Y_2O_3 or Y_2O_3:Eu^{3+} nanorods. As is observed in Fig. 3a, the superconducting T_C of pure MgB_2 is 37 K, which is higher than those of other doped samples. The transition width of pure MgB_2 is only 0.4 K, which is also the minimum value in all samples. The superconducting T_C decreases, whereas the width of transition increases with increasing doping amount. For instance, the T_C of the sample doped with 8 wt% Y_2O_3 is 36.25 K, which is lower than that of pure samples. The presence of impurities, such as Y_2O_3, MgO and YB_4, induced the deterioration of intercrystalline connectivity [27, 28].

The image in Fig. 3b shows that the T_C of samples doped with 4 or 6 wt % Y_2O_3:Eu^{3+} nanorods is lower than that of pure MgB_2, which is consistent with those of samples doped with Y_2O_3. However, theT_C of sample doped with 8 wt % Y_2O_3:Eu^{3+} nanorods is the highest among all samples, including pure MgB_2. The T_C of sample doped with 8 wt % Y_2O_3:Eu^{3+} nanorods is 1.15 K higher than that of the sample doped with 8 wt % Y_2O_3nanorods. It is peculiar that the T_C of sample doped with 8 wt % Y_2O_3:Eu^{3+} nanorods is 0.4 K higher than that of pure MgB_2. The curve of MgB_2 doped with 8 wt % Y_2O_3:Sm is also shown in Fig. 3b to confirm whether electroluminescence or rare earth element affects the transition temperature. The transition temperature of MgB_2 doped with 8 wt % Y_2O_3:Sm is 0.9 K lower than that of MgB_2 doped with 8 wt % Y_2O_3:Eu (Fig. 3b). Europium, which results in bright red light, is critical for T_C.

The images in Fig. 4 presents the T_C of the series of MgB_2 samples doped with different amounts of Y_2O_3 or Y_2O_3:Eu^{3+} nanorods. The T_C values of samples decrease with increasing amount of doped Y_2O_3 nanorods, which is consistent with previous reports. However, it is fantastic that the T_C values of samples increase with the amount of doped Y_2O_3:Eu^{3+} nanorods. Additionally, the T_C of sample doped with 8 wt% Y_2O_3:Eu^{3+} nanorods is 0.4 K higher than that of pure MgB_2. However, the transition temperature decreases rapidly when the doping percentage of Y_2O_3:Eu is larger than 8. The phenomenon cannot be explained by existing theories. The mechanism of increasing superconducting T_C still needs further studies. The transition temperature is one of the most crucial factors that limits

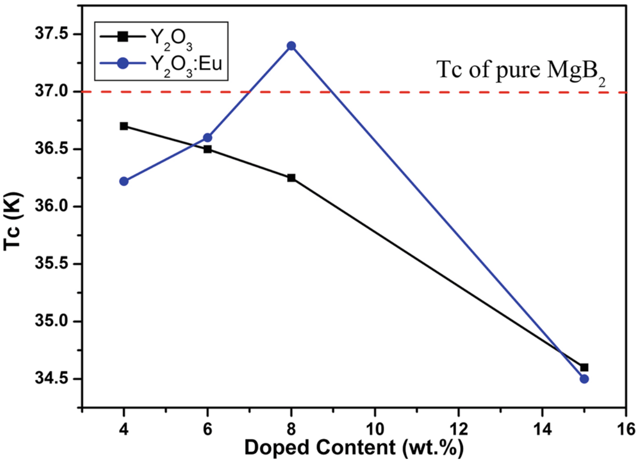

Fig. 4 The T_C of the series MgB_2 samples doped different contents of Y_2O_3 or Y_2O_3:Eu^{3+} nanorods

the application of superconductors. As such, increasing the transition temperature of superconductors is of great interest. Hence, doping EL materials in MgB_2 is a novel strategy for increasing the transition temperature and may also be applicable to other superconductors.

4 Conclusion

We synthesised a composite material, MgB_2 superconductor doped with the EL materials Y_2O_3:Eu, which is called a superconducting metamaterial. The XRD results indicate that the crystallinity and the purity of MgB_2 decrease with increasing the doping content. However, more Y_2O_3:Eu^{3+} would remain in the samples at a high doping content. The temperature dependence of resistivity indicates that the T_C values of samples decrease with increasing amount of doped Y_2O_3 nanorods; this finding is consistent with previous reports. However, it is remarkable that the T_C values of samples increase with increasing amount of doped Y_2O_3:Eu^{3+} nanorods. The T_C of the sample doped with 8 wt% Y_2O_3:$Eu^{3+}$is 1.15 K higher than that of sample doped with 8 wt% Y_2O_3. It is remarkable that the T_C of the sample doped with 8 wt% Y_2O_3:Eu^{3+} is 0.4 K higher than that of pure MgB_2. However, the transition temperature of the sample doped with 8 wt% Y_2O_3:Sm nanorods is 0.9 K lower than that of the sample doped with 8 wt% Y_2O_3:Eu nanorods. Transition temperature is one of the most crucial factors that limits the application of superconductors. Doping EL materials in MgB_2 is a novel strategy for increasing the transition temperature and may also be applicable to other superconductors.

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