Critical Temperature of Smart Meta-superconducting MgB$_2$

Shuo Tao$^1$ · Yongbo Li$^1$ · Guowei Chen$^1$ · Xiaopeng Zhao$^1$

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Abstract Enhancing the critical temperature ($T_C$) is important not only to widen the practical applications but also to expand the theories of superconductivity. Inspired by the meta-material structure, we designed a smart meta-superconductor consisting of MgB$_2$ microparticles and Y$_2$O$_3$/Eu$^{3+}$ nanorods. In the local electric field, Y$_2$O$_3$/Eu$^{3+}$ nanorods generate an electroluminescence (EL) that can excite MgB$_2$ particles, thereby improving the $T_C$ by strengthening the electron–phonon interaction. An MgB$_2$-based superconductor doped with one of four dopants of different EL intensities was prepared by an ex situ process. Results showed that the $T_C$ of MgB$_2$ doped with 2 wt% Y$_2$O$_3$, which is not an EL material, is 33.1 K. However, replacing Y$_2$O$_3$ with Y$_2$O$_3$/Eu$^{3+}$II, which displays a strong EL intensity, can improve the $T_C$ by 2.8 to 35.9 K, which is even higher than that of pure MgB$_2$. The significant increment in $T_C$ results from the EL exciting effect. Apart from EL intensity, the micromorphology and degree of dispersion of the dopants also affected the $T_C$. This smart meta-superconductor provides a new method to increase $T_C$.

Keywords MgB$_2$ · Smart meta-superconductor · Y$_2$O$_3$/Eu$^{3+}$ nanorods · Ex situ · $T_C$

1 Introduction

Since the discovery of superconductivity in Hg at approximately 4.2 K in 1911 [1] the research on superconductivity has continued for over a century. In recent years, a number of new superconductors have been reported. In 2008, Hosono’s group discovered superconductivity in F-doped LaOFeAs [2], which paved the way for a wide-scale research on iron-based superconductors. In 2011, Cavalleri et al. used mid-infrared laser pulses to transform La$_{1.67}$Eu$_{0.2}$Sr$_{0.125}$CuO$_4$ into a transient superconductor [3]. Afterwards, the same group investigated La$_{1.84}$Sr$_{0.16}$CuO$_4$ [4], YBa$_2$Cu$_3$O$_{6.5}$ [5], and K$_3$C$_6$0 [6] using the similar method and observed the behavior of superconducting transition. The said researchers reported that laser pulse deforms the crystal structures and induces superconductivity [7]. Optical methods have been gradually applied to investigate superconductivity. Although some novel superconductors have been discovered and the achievable maximum critical temperature ($T_C$) continues to increase, most superconducting materials of practical value are low-temperature superconductors, especially type II superconductors. However, the $T_C$ of type II superconductors does not exceed the McMillan limit [8, 9].

In 2001, Japanese scientists discovered superconductivity in MgB$_2$ [10]. The $T_C$ of MgB$_2$ is 39 K, which is close to the McMillan limit. The high $T_C$, simple crystal structure, large coherence lengths, high critical current densities and fields, and transparency of grain boundaries of MgB$_2$ indicate the potential of this compound as a good material for both large-scale applications and electronic devices. Improving the $T_C$ of MgB$_2$ is important not only to its practical applications but also to the theories of superconductivity. Many methods have been proposed to improve the $T_C$ of MgB$_2$ [11–17], but the results were unsatisfactory.
Improving the superconducting critical temperature of MgB$_2$ is significant but challenging.

Meta-material is a type of composite material with an artificial structure. The properties of meta-materials are not primarily determined by the matrix material but by artificial structures, such as arrangement and scale [18–20]. This special structure induces a great change in certain properties. Qiao et al. proposed an intelligent fluid dielectric particle structure model based on the structure of a biological cell. These intelligent particles contain multiple rare earth-doped titania particles embedded into the amorphous carbon matrix, which possess a hierarchical porous structure. The efficiency of mechanical/electrical energy transformation for electrorheological fluids based on these intelligent particles is considerably improved by up to eight times [21]. Cargnello et al. studied that the conductivity of lead selenide particles is considerably improved by up to eight times [21].

With the meta-material structure as motivation, our group has long been attempting to improve the superconducting transition temperature. In 2007, our group studied the effects of ZnO electroluminescent material doping on the superconductivity and crystal structure of the (Bi, Pb) –2233 superconductor. Uniformly distributed ZnO nanodetectors were introduced into bismuth strontium calcium copper oxide superconductors by using the nanocomposite method. The effects of different doping methods on the performance of superconductors and distribution of ZnO in superconductors were examined. The results of the standard four-probe method indicated that samples fabricated by different doping methods demonstrate an obvious performance belonging to high-temperature superconductor. High-resolution scanning electron microscopic images show that nano-ZnO (about 100 nm) defects are linearly distributed on the surface of samples fabricated by nanocomposite doping [23]. In the same year, our group proposed that combining inorganic electroluminescence (EL) materials with meta-materials can induce substantial changes in superconducting materials, left-handed materials, photonic crystals, and so on. For example, inorganic EL material quantum dots used as magnetic flux pinning centers, which are orderly arrayed in superconducting materials, may greatly improve the $T_C$ even to room temperature [24]. In addition, based on the fact that the superconducting properties of a material, such as electron–electron pairing interaction and superconducting $T_C$ may be expressed via the effective dielectric response function of the material [25], Smolyaninov et al., has recently proposed a theoretical work for artificial metamaterial superconductors [26]. Subsequently, this metamaterial approach had been applied to increases the $T_C$ of epsilon near zero Al–Al$_2$O$_3$ core–shell metamaterial superconductors [27]. Very recently, our group has prepared an MgB$_2$-based superconducting meta-material doped with Y$_2$O$_3$/Eu$^{3+}$ by an in situ process [28]. Results showed that EL contributes to the improvement of $T_C$ [29]. However, the dopant can react with boron to form YB$_4$ during the in situ process. The amount of residual Y$_2$O$_3$/Eu$^{3+}$ is small, thus leading to a great reduction in EL function.

To avoid such reaction and to further understand the influence of EL on $T_C$, a smart meta-superconductor with a sandwich structure consisting of MgB$_2$ microparticles and Y$_2$O$_3$/Eu$^{3+}$ nanorods was designed in the present study. The nanorods dispersed uniformly around the microparticles. The Y$_2$O$_3$/Eu$^{3+}$ nanorods generate an EL that can improve the $T_C$ under a local electric field. Four types of dopant (Y$_2$O$_3$, Y$_2$O$_3$/Eu$^{3+}$I, Y$_2$O$_3$/Eu$^{3+}$II, and Y$_2$O$_3$/Eu$^{3+}$III) with different EL intensities were prepared by a hydrothermal method [30]. Each MgB$_2$-based superconductor doped with one of the four dopants was prepared by an ex situ process. The obtained XRD spectra show that the dopants did not react with MgB$_2$. The $T_C$ measurements indicated that the addition of dopant exerts an impurity effect that decreases the $T_C$ and an EL exciting effect that increases the $T_C$. Apart from the EL intensity, the micromorphology and degree of dispersion of the dopants also affect the $T_C$.

2 Model

Figure 1a shows the microstructure model of the smart meta-superconductor. The hexagons represent MgB$_2$ microparticles, and the rectangles represent Y$_2$O$_3$/Eu$^{3+}$ nanorods. The nanorods disperse uniformly around the microparticles. Figure 1b provides a diagram of the four-probe method used to measure the resistance–temperature curve. Measurement of resistance was carried out in a low-temperature range in a liquid helium cryogenic system (Advanced Research Systems Company). The two electrodes at the two ends are connected to a direct current (DC) source. The constant current is 100 mA. Two intermediate electrodes are connected to a voltmeter. The constant current that can generate a local electric field, as shown in Fig. 1c.

**Fig. 1** a Model for the smart meta-superconductor, b diagram of the four-probe method, and c diagram of the local electric field.
A voltage drop between the two MgB$_2$ particles occurs during the measurement, in which case the two MgB$_2$ particles act as the electrodes of the voltage source. The voltage drop produces a local electric field that can excite the intermediate nanorods to generate EL, which strengthens the electron–phonon interaction and improves the TC. In this study, we investigated the combined effects of the dopant and EL on the $T_C$ of MgB$_2$-based superconductors.

### 3 Experiment

#### 3.1 Preparation of MgB$_2$ Power

Traditional solid-phase sintering was used to synthesize the MgB$_2$ bulk sample. In brief, magnesium and boron powders were mixed at an atomic ratio of 1.1:2. The mixture was then ground for 20 min in an agate mortar in a glove box, after which the mixture was transferred into a mold and pressed into cylindrical tablets at 20 MPa for 10 min. Finally, the tablets were placed in tantalum vessels and then sintered at 800 $^\circ$C in a closed high-purity Ar atmosphere for 2 h. The heating rate was set to 10 $^\circ$C min$^{-1}$, and the cooling rate was set to 5 $^\circ$C min$^{-1}$. The MgB$_2$ powder was obtained by finely grinding the tablets.

#### 3.2 Preparation of Doped MgB$_2$-based Superconductors

Four types of dopants (Y$_2$O$_3$, Y$_2$O$_3$/Eu$^{3+}$I, Y$_2$O$_3$/Eu$^{3+}$II, and Y$_2$O$_3$/Eu$^{3+}$III) of different EL intensities were prepared by a hydrothermal method and were marked as A, B, C, and D. The molar ratio of yttrium and europium in B, C, and D was 0.95:0.05. The samples were prepared by an ex situ process. For convenience of description, symbols were used to represent the samples. For example, symbol A1 denotes an MgB$_2$-based superconductor in which dopant A accounts for 1 wt %. The same letter and number combination format was used to represent the dopant type and weight percent in the other samples. Furthermore, a pure MgB$_2$ sample, which was marked as P, was similarly produced by the ex situ process [31].

### 4 Results and discussion

Figure 2a–d show the SEM images of dopants A, B, C, and D. Y$_2$O$_3$ nanorods of about 2-μm length and 150-nm diameter are shown in Fig. 2a–c. The nanorods in the three images are highly similar. Figure 2d displays the SEM image of dopant D. Apart from some nanorods, many micron-sized blocks were observed. The addition of europium did not change the micromorphology of the dopants. However, it changed the EL intensities, as shown in the EL spectra of the four dopants in Fig. 2e. Y$_2$O$_3$ is not an electroluminescent material in itself. Acting as the luminescence center, europium renders Y$_2$O$_3$/Eu$^{3+}$, a strong phosphor. The EL intensity of dopant C is nearly three times as high as that of dopant B. The EL intensity of D is the highest in the spectra. All the EL curves show that the strongest peak was centered at 613 nm, with a half-width of about 8 nm, which suggests superior monochromaticity. The EL spectra were obtained at room temperature. Moreover, we detected the same EL
phenomenon for dopants B, C, and D at liquid nitrogen temperature. The unchanged EL properties at low temperature are consistent with the results of another report [32].

Figure 3 shows the SEM images (Fig. 3a–e) and XRD spectra (Fig. 3f) of the partial samples. The SEM images show that the MgB$_2$ particles are mainly about 1–3 μm and are irregularly shaped. Y$_2$O$_3$ nanorods are also observed (Fig. 3b–e). In addition to some nanorods, many Y$_2$O$_3$ blocks are present, as shown in Fig. 3e. The dispersion of dopants in MgB$_2$ is not uniform. The four dopants are believed to not react with MgB$_2$ during the ex situ process. Figure 3f shows the corresponding XRD spectra of the samples. XRD results show that the main phase of the samples is MgB$_2$. We observed the existence of the Y$_2$O$_3$ phase in the doping samples. Combined with the SEM results, the dopants were confirmed to be unreactive to MgB$_2$. The XRD patterns also indicate that the samples doped with Y$_2$O$_3$/Eu$^{3+}$ are similar to that doped with Y$_2$O$_3$ for the effective incorporation of Eu into the lattice of Y$_2$O$_3$. In addition, MgO was present in all the samples, which was formed during the preparation of MgB$_2$. The SEM images and the XRD spectra of the other samples with different dopants of different amounts are similar.

Figure 4 presents the temperature dependence of the resistivity ($R$–$T$) of the pure MgB$_2$ and MgB$_2$ doped with Y$_2$O$_3$. To discuss in detail the change in $T_C$, we marked three characteristic temperatures, $T_C$, onset ($T_C^{on}$), and offset ($T_C^{off}$), on each $R$–$T$ curve [33, 34]. The purple curve shows the $R$–$T$ curve of pure MgB$_2$ (P). The $T_C$ of pure MgB$_2$ is 35.8 K. The $T_C^{on}$ and $T_C^{off}$ of pure MgB$_2$ are 36.9 and 35.1 K, respectively, which are lower than the critical temperature of pure MgB$_2$ produced by the in situ process. The major cause of the phenomenon is that the samples in the ex situ process were exposed longer to air compared with those included in the in situ process, which increased the MgO content and consequently decreased the $T_C$. The $T_C$ of the doping samples are lower than that of pure MgB$_2$ and decreases with increasing Y$_2$O$_3$ content. These results indicate that the addition of Y$_2$O$_3$ causes an impurity effect that can decrease the $T_C$.

Figure 5 presents the temperature dependence of the resistivity of pure MgB$_2$ and MgB$_2$ doped with Y$_2$O$_3$/Eu$^{3+}$I. The $T_C$ of pure MgB$_2$ is the highest because the impurity effect decreases the $T_C$. However, the $T_C$ does not always decrease with increasing dopant B content. The critical temperature of B2 is higher than that of B1, which is not consistent with the impurity effect. Apart from the impurity effect, dopant B is suggested to cause another effect, which contributes to the improvement of the $T_C$.

Comparison with dopant A, dopant B contains a small amount of europium. Europium, which hardly changes the

![Fig. 3](image1)  
**Fig. 3** SEM images of a P, b A1, c B2, d C3, and e D3; f corresponding XRD spectra of the samples

![Fig. 4](image2)  
**Fig. 4** Temperature-dependent resistivity of pure MgB$_2$ (▼), and MgB$_2$-doped with 1 wt % Y$_2$O$_3$ (■), 2 wt % Y$_2$O$_3$ (●), and 3 wt % Y$_2$O$_3$ (▲)
morphology of Y$_2$O$_3$, renders dopant B a strong EL system (Fig. 2). We assume that EL is the key to improving the critical temperature. As shown in Fig. 1c, the current used to measure the R–T curve produces a local electric field that excites the EL of dopant B. In turn, EL excites the crystal lattice vibration, strengthening the electron–phonon interaction and resulting in the improvement of critical temperature. We call this phenomenon as an EL exciting effect. An obvious competitive relationship exists between the impurity effect and the EL exciting effect. The $T_C$ of the doping sample initially increases and then decreases with increasing dopant B content. The EL exciting effect is stronger than the impurity effect when the content of dopant B is 2 wt %. However, when the content increases up to 3 wt %, the $T_C$ decreases. This behavior results from the inability of the nanorods to disperse uniformly in the sample. The increment in content hardly enhances the EL exciting effect but greatly increases the impurity effect.

To study further the impurity effect and the EL exciting effect, we produced samples doped with Y$_2$O$_3$/Eu$^{3+}$II. The critical temperatures of these samples are shown in Fig. 6. As seen from the results, doping does not always decrease the critical temperature. The $T_C$ of C2 is 35.9 K, which is even higher than that of pure MgB$_2$. The increment is not obvious, but it is of great significance. Moreover, compared with the $T_C$ of A2, in which no EL exciting effect occurs, the $T_C$ of C2 has been increased greatly by 2.8 K. This result suggests that the introduction of the EL exciting effect may be an effective method for improving the critical temperature. In addition, the $T_C$ of C1 (C2, C3) is higher than that of B1 (B2, B3), although these samples have the same europium content. We speculate that the enhancement in $T_C$ is caused by the high EL intensity of dopant C, which is nearly three times as high as that of dopant B. Improving EL intensity can enhance the EL exciting effect, consequently improving the critical temperature $T_C$. Such result also indicates that the change in $T_C$ is not induced by the addition of the rare earth element europium.

The critical temperatures of MgB$_2$ doped with dopant D are shown in Fig. 7. Although dopant D exhibits the strongest EL intensity among the four dopants, the critical temperatures of the corresponding samples are not higher than those of the samples doped with other dopants. This outcome is probably due to the micromorphology of dopant D. The diameter and thickness of the Y$_2$O$_3$ block are about...
2 μm and 500 nm, respectively (Fig. 2d). The quantity of the Y2O3 blocks is much less than that of Y2O3 nanorods in the other dopants of the same quality. The points that can produce the EL exciting effect greatly decrease, leading to the increment in the impurity effect and reduction of the EL exciting effect. Dopants with different morphologies have different influences on the critical temperature. It also can be inferred from the result that the TC of D3 is higher than that of D2, which is different from the results shown in Figs. 5 and 6.

5 Conclusion

Basing on the meta-material structure, we designed a smart meta-superconductor consisting of MgB2 microparticles and Y2O3/Eu3+ nanorods. The nanorods can generate an EL exciting effect under a local electric field produced by the current used in measuring the critical temperature. The EL exciting effect contributes to the increment in TC by strengthening the electron–phonon interaction. Four dopants of different EL intensities were synthesized in this study. MgB2-based superconductors doped with different dopants of varying percentages were then prepared. When the doping concentration is 2 wt %, the TC of MgB2 doped with Y2O3 is 33.1 K. Replacing Y2O3 with Y2O3/Eu3+ nanorods, the TC could be improved up to 34.7 or 35.9 K, respectively. The latter is even higher than the TC of pure MgB2. The significant increment is the result of the EL exciting effect. Meanwhile, the following conclusions can be drawn from the results: (1) The dopants induce an impurity effect that decreases the critical temperature. The impurity effect increases rapidly with the increment in dopant content. (2) Dopants with good EL property bring about an EL exciting effect that is favorable to the improvement of the critical temperature. An obvious competition exists between the impurity effect and the EL exciting effect. (3) The EL exciting effect is dependent not only on the EL intensity but also on the concentration, micro-morphology, and uniformity of the dopants dispersed in the sample.

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