Smart meta-superconductor MgB$_2$ constructed by the dopant phase of luminescent nanocomposite

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On the basis of the idea that the injecting energy will improve the conditions for the formation of Cooper pairs, a smart meta-superconductor (SMSC) was prepared by doping luminescent nanocomposite Y$_2$O$_3$:Eu$^{3+}$/Ag in MgB$_2$. To improve the superconducting transition temperature ($T_C$) of the MgB$_2$-based superconductor, two types of Y$_2$O$_3$:Eu$^{3+}$/Ag, which has the strong luminescence characteristic, with different sizes were prepared and marked as m-Y$_2$O$_3$:Eu$^{3+}$/Ag and n-Y$_2$O$_3$:Eu$^{3+}$/Ag. MgB$_2$ SMSC was prepared through an ex situ process. Results show that when the dopant content was fixed at 2.0 wt.%, the $T_C$ of MgB$_2$ SMSC increased initially then decreased with the increase in the Ag content in the dopant. When the Ag content was 5%, the $T_C$ of MgB$_2$ SMSC was 37.2–38.0 K, which was similar to that of pure MgB$_2$. Meanwhile, the $T_C$ of MgB$_2$ SMSC doped with n-Y$_2$O$_3$:Eu$^{3+}$/Ag increased initially then decreased basically with the increase in the content of n-Y$_2$O$_3$:Eu$^{3+}$/Ag, in which the Ag content is fixed at 5%. The $T_C$ of MgB$_2$ SMSC doped with 0.5 wt.% n-Y$_2$O$_3$:Eu$^{3+}$/Ag was 37.6–38.4 K, which was 0.4 K higher than that of pure MgB$_2$. It is thought that the doping luminescent nanocomposite into the superconductor is a new means to improve the $T_C$ of SMSC.

Improving the superconducting critical transition temperature of materials is an important scientific and technical problem in condensed matter physics and materials science. Recently, Fausti et al. used mid-infrared femtosecond pulses to transform non-superconducting La$_{1.675}$Eu$_{0.2}$Sr$_{0.125}$CuO$_4$ into a transient 3D superconductor. A similar method was also applied to investigate YBa$_2$Cu$_3$O$_{6.5}$ and K$_3$Bi$_2$I$_6$ using minute, single-wall carbon nanotube inclusions. In accordance with homogeneous system theory, Smolyaninov et al. stated that a superconducting metamaterial with an effective dielectric response function that is less and approximately equal to zero may exhibit high $T_C$, and they verified this theory in their subsequent experiments. Recently, Cao et al. investigated correlated insulator behavior at half-filling in magic-angle graphene superlattices and reported the realization of intrinsic unconventional superconductivity in a 2D superlattice created by stacking two sheets of graphene that are twisted relative to each other at a small angle. Another important method for studying superconductivity is the topological superconductors, which have attracted great attention in condensed matter physics. However, obtaining a practical superconductor with high $T_C$ remains difficult.

The superconductivity of MgB$_2$ was discovered in 2001. MgB$_2$ is a promising material with large-scale applications because of its excellent superconducting properties and simple crystal structure. Considering that the $T_C$ of MgB$_2$ is close to the McMillan temperature limit, developing an effective experimental method to improve the $T_C$ of MgB$_2$ is beneficial to its practical application and to the understanding of the superconducting mechanism. Chemical doping is a simple, effective, commonly used method to change the $T_C$ of superconducting materials. However, many experimental results have confirmed that conventional chemical doping decreases the $T_C$ of MgB$_2$. To date, no effective method has been developed to improve the $T_C$ of MgB$_2$. The use of metamaterial structures to achieve special properties is an important method developed in recent decades, and it provides a new approach to improve the $T_C$ of superconducting materials.

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On the basis of metamaterials, our group investigated the effects of ZnO electroluminescent (EL) material doping on the superconductivity of BSCCO in 2007 and attempted to change the $T_c$ of this superconductor\(^45\). Meanwhile, it is proposed that the combination of chemical doping and EL excitement, that is, doping EL materials in superconducting materials to form a meta structure, may be an effective method to improve the $T_c$ of superconductors\(^45\). On the basis of these results, a smart meta-superconductor (SMSC) model for improving the $T_c$ of materials has been proposed recently. In this model, the dopant phase is used to inject energy through its EL under the external field to strengthen the Cooper pairs, thereby achieving the purpose of changing the $T_c$. Zhang et al.\(^44\) prepared MgB$_2$ doped with Y$_2$O$_3$:Eu$^{3+}$ particles through an in situ process. Tao et al.\(^45\) prepared MgB$_2$ doped with Y$_2$O$_3$:Eu$^{3+}$ nanoparticles with different EL intensities through an ex situ process. Their results indicated that doping EL materials is favorable for the improvement of $T_c$ compared with conventional doping, which always reduces the superconducting transition temperature of the sample. In addition, similar experimental results were obtained by replacing Y$_2$O$_3$:Eu$^{3+}$ with Y$_2$O$_3$:Eu$^{3+}$/Ag nano-rod particles. Meanwhile, results also indicated that the $T_c$ can be changed by adjusting the Y$_2$O$_3$:Eu$^{3+}$ concentration and EL exciting current\(^46\). However, there are some problems need to improve in the experiments. Y$_2$O$_3$:Eu$^{3+}$ particles or flakes tended to agglomerate during the preparation process and its EL intensity was weak\(^44-47\). The quality of commercial MgB$_2$ was poor and its superconducting transition width ($\Delta T$) is 4.6 K\(^46-47\). Further experiment and improvement will be needed. Moreover, the dopants would decrease the $T_c$ in the case of double dopants, i.e., simultaneous incorporation of Y$_2$O$_3$:Eu$^{3+}$ and nano-Ag into MgB$_2$\(^45\).

In this paper, a kind of new phase of luminescent nanocomposite Y$_2$O$_3$:Eu$^{3+}$/Ag was prepared by compounding nano Ag into the Y$_2$O$_3$:Eu$^{3+}$ matrix directly\(^48\). The luminescent intensity of Y$_2$O$_3$:Eu$^{3+}$/Ag is three times higher than that of Y$_2$O$_3$:Eu$^{3+}$ due to the composite illumination of EL and photoluminescence (PL). Two kinds of nanocomposite illuminator Y$_2$O$_3$:Eu$^{3+}$/Ag with different sizes, namely, micro Y$_2$O$_3$:Eu$^{3+}$/Ag (m-Y$_2$O$_3$:Eu$^{3+}$/Ag) and nano Y$_2$O$_3$:Eu$^{3+}$/Ag flakes (n-Y$_2$O$_3$:Eu$^{3+}$/Ag), are prepared. Meanwhile, a new kind of commercial MgB$_2$, with a small $\Delta T$ of 0.8 K was used. SMSC was prepared by doping Y$_2$O$_3$:Eu$^{3+}$/Ag in MgB$_2$ through an ex situ process\(^49\). The $T_c$ of the MgB$_2$-based superconductor is investigated by changing the Ag content in the dopant phase, the sizes of the dopant phase, and the doping concentration. The results indicate that the $T_c$ of MgB$_2$ doped with 0.5 wt.% n-Y$_2$O$_3$:Eu$^{3+}$/Ag is 37.6–38.4 K, which is 0.4 K higher than that of pure MgB$_2$, which further confirmed that the SMSC is a new way to improve the critical transition temperatures.

**Experiment**

**Preparation of m-Y$_2$O$_3$:Eu$^{3+}$/Ag and n-Y$_2$O$_3$:Eu$^{3+}$/Ag.** Y$_2$O$_3$ and Eu$_2$O$_3$ were weighed (the atomic ratio of Y and Eu is 0.95:0.05) and dissolved in a beaker with excess concentrated hydrochloric acid and subsequently heated and dried at 70°C for 2h to obtain a white precursor. One of the precursor was dissolved in 4 mL of deionized water to form a solution, and ammonium oxalate was added to it dropwise. The solution was subsequently stirred vigorously at 2°C in a temperature-controlled water bath. A certain amount of AgNO$_3$ was added to the solution after being stirred for 30 min. After another 30 min of stirring, the pH value of the solution was adjusted to 9–10 by adding NaOH. The final solution, designated as solution A, was obtained after another 30 min of stirring. Another precursor was also prepared into solution with 24 mL benzyl alcohol. Octylamine (4 mL) was added dropwise to the solution, which was subsequently stirred for 1 h. Afterward, a certain amount of AgNO$_3$ was added to the solution. After stirring for another hour, another solution was obtained and designated as solution B. Solutions A and B were then transferred to two reaction kettles, respectively. A hydrothermal reaction occurred at 160°C for 24 h. The products were washed several times with deionized water and absolute ethanol and sintered at 800°C for 2 h to form Y$_2$O$_3$:Eu$^{3+}$/AgCl. After illumination, the Y$_2$O$_3$:Eu$^{3+}$/AgCl transformed into two kinds of luminescent Y$_2$O$_3$:Eu$^{3+}$/Ag nano-rod composite with different Ag contents. Meanwhile, Y$_2$O$_3$:Eu$^{3+}$/Ag nano-rod composite with different Ag concentrations was prepared by changing the AgNO$_3$ content. In this paper, Ag contents uniformly refers to the initial atomic ratio of Ag and Y. For example, 5% Ag means that the initial nominal atomic ratio of Ag to Y is 0.05:0.95. Meanwhile, similar method was applied to synthesize Y$_2$O$_3$ and Y$_2$O$_3$:Sm$^{3+}$.

**Preparation of MgB$_2$-based SMSC.** At a certain ratio, commercial MgB$_2$ powder (Alfa Aesar) and the luminescent nanocomposite Y$_2$O$_3$:Eu$^{3+}$/Ag were weighed and prepared into an alcohol solution. The two suspensions were sonicated for 20 min, then the dopant was added dropwise to MgB$_2$. After sonication for more than 20 min, the mixed solution was transferred to a culture dish. Subsequently, the culture dish was placed in a vacuum oven at 60°C for 4 h to yield a black powder. The powder was pressed into a pellet with a diameter of 11 mm and a thickness of 2 mm and placed in a small tantalum container, which was annealed at 800°C for 2 h in high-purity argon atmosphere. The MgB$_2$-based superconductor doped with luminescent nanocomposite materials of different sizes and Ag contents was synthesized to investigate the $T_c$ of SMSC.

**Results and Discussion**

Figure 1a shows the EL spectra of Y$_2$O$_3$, Y$_2$O$_3$:Eu$^{3+}$/Ag, m-Y$_2$O$_3$:Eu$^{3+}$/Ag, and n-Y$_2$O$_3$:Eu$^{3+}$/Ag. The Ag content of the luminescent nanocomposite materials was 5.0%. It shows that Y$_2$O$_3$ is a non-EL material and becomes a kind of EL material after the addition of a small amount of Eu element. The results also indicate that the EL intensity of the luminescent m-Y$_2$O$_3$:Eu$^{3+}$/Ag nanocomposite and n-Y$_2$O$_3$:Eu$^{3+}$/Ag is remarkably improved primarily due to the composite luminescence of the electroluminescence of Eu$^{3+}$ centric and the surface plasma-enhanced photoluminescence of Ag. Among the four dopants, n-Y$_2$O$_3$:Eu$^{3+}$/Ag had the highest EL intensity. Figure 1b shows the SEM image of m-Y$_2$O$_3$:Eu$^{3+}$/Ag. The surface size and thickness of the m-Y$_2$O$_3$:Eu$^{3+}$/Ag flake are approximately 300 nm and 30 nm, respectively. Figure 1c,d show AFM images of n-Y$_2$O$_3$:Eu$^{3+}$/Ag and Fig. 1d presents a cross section of the AFM image in Fig. 1c. Figure 1e,f show TEM images of n-Y$_2$O$_3$:Eu$^{3+}$/Ag. It can be seen that the
The surface size of n-Y2O3:Eu3+/Ag was 20 nm, and its thickness was approximately 2.5 nm, which is much smaller than that of m-Y2O3:Eu3+/Ag.

Figure 2a shows the SEM image of pure MgB2. The size of the MgB2 particle was approximately 0.1–1 μm. The TC of the samples was determined based on the R–T curve, which was measured using a four-probe method in a liquid helium cryogenic system developed by the Advanced Research Systems Company. Figure 2b shows the normalized R–T curve of pure MgB2 and indicates that the onset temperature (Ton) and offset temperature (Toff) of pure MgB2 were 38.0 and 37.2 K, respectively. The ΔT of pure MgB2 was 0.8 K. Figure 2c shows the XRD spectra of pure MgB2 and partially doped samples, in which the standard card of MgB2 (PDF#38-1369) is demonstrated using black vertical lines. The results showed that the XRD spectrum of pure MgB2 (black curve) matched the standard card of MgB2 well, except for the inevitable small amount of the MgO phase. The red and blue curves represent the XRD spectra of MgB2 doped with 2.0 wt.% m-Y2O3:Eu3+/Ag and 2.0 wt.% n-Y2O3:Eu3+/Ag, respectively. The Ag content was 5.0%. The main phase of the doped samples was MgB2. Moreover, apart from a small amount of the MgO phase, the Y2O3 phase was also found in the XRD spectra of the doped samples. The XRD spectra of the other doped samples were similar.

Figure 3 shows the normalized R–T curves of MgB2 doped with m-Y2O3:Eu3+/Ag with different Ag contents. On the basis of the results of our previous study, the content of m-Y2O3:Eu3+/Ag in the four samples was fixed at 2.0 wt.%. The Ag contents of m-Y2O3:Eu3+/Ag in the four samples were 1.0%, 4.0%, 5.0%, and 8.0%, as shown in the figure, and their Tc values were 34.8–35.6, 36.0–36.8, 37.2–38.0, and 34.8–35.6 K, respectively. The Tc of the doped samples initially increased then decreased with the increase in Ag content. Meanwhile, the corresponding doped sample had the highest Tc when the concentration of m-Y2O3:Eu3+/Ag was fixed at 2.0 wt.% and the Ag content was 5.0%, which is equal to that of pure MgB2. The experimental results are similar to those of our previous studies, that is, doping EL materials may improve Tc in several cases compared with conventional doping, which always reduces the Tc of the sample. As a dopant, m-Y2O3:Eu3+/Ag exerts an impurity effect that decreases Tc. Meanwhile, as an EL material, m-Y2O3:Eu3+/Ag exerts an EL exciting effect that increases Tc. The samples doped with 0.5 wt.% n-Y2O3:Eu3+/Ag had the highest Tc of 37.6–38.4 K, which is 0.4 K higher than that of pure MgB2. However, the impurity effect of the dopant dominated when the doping concentration increased to a high range, which led to a low Tc. These results indicate that doping luminescent nanocomposite materials effectively adjusts and improves Tc at an appropriate doping concentration.

**Figure 1.** (a) EL spectra of Y2O3, Y2O3:Eu3+, m-Y2O3:Eu3+/Ag, and n-Y2O3:Eu3+/Ag; (b) SEM image of m-Y2O3:Eu3+/Ag; (c,d) AFM images and (e,f) TEM images of n-Y2O3:Eu3+/Ag.
MgB₂ doped with non-EL materials Y₂O₃ and Y₂O₃:Sm³⁺ were synthesized to prove the conclusions above. Figure 5 shows the normalized R–T curves of MgB₂ doped with Y₂O₃, Y₂O₃:Sm³⁺, Y₂O₃:Eu³⁺, and n-Y₂O₃:Eu³⁺/Ag. The doping concentration was fixed at 0.6 wt.%, and the Ag content in n-Y₂O₃:Eu³⁺/Ag was 5.0%. Results indicated that Tc of MgB₂ doped with non-EL materials Y₂O₃ or Y₂O₃:Sm³⁺ was much lower than that of pure MgB₂, which is different from MgB₂ doped with EL materials at the same concentration. MgB₂ doped with Y₂O₃:Eu³⁺ increased to 36.6–37.4 K due to the EL exciting effect. Meanwhile, MgB₂ doped with the luminescent n-Y₂O₃:Eu³⁺/Ag nanocomposite further increased to 37.0–37.8 K. The results show that doping EL materials facilitates an increase in Tc in several cases compared with conventional doping, which always reduces the Tc of the sample. Meanwhile, luminescent Y₂O₃:Eu³⁺/Ag nanocomposite materials increase the Tc of MgB₂ due to the strong EL intensity.

The results in Fig. 4 show that the optimum concentration of n-Y₂O₃:Eu³⁺/Ag is 0.5 wt.%, which is lower than the value in our previous study due to the small size of n-Y₂O₃:Eu³⁺/Ag. The disadvantages caused by the impurity effect can be reduced if luminescent nanocomposite materials have a small size and are relatively evenly distributed.
distributed in the sample. Moreover, the ΔT of commercial MgB2 in our previous study was too large to accurately determine the influence of the dopant phase on TC. In the current study, a new kind of commercial MgB2 with a small ΔT of 0.8 K was used, and we obtained a similar conclusion, which further proves the effectiveness of this method.

Conclusions
In this paper, two types of luminescent nanocomposite Y2O3:Eu3+/Ag with different sizes were prepared and marked as m-Y2O3:Eu3+/Ag and n-Y2O3:Eu3+/Ag. SEM and AFM images indicated that the surface size and thickness of m-Y2O3:Eu3+/Ag are approximately 300 nm and 30 nm, which are 20 nm and 2.5 nm for n-Y2O3:Eu3+/Ag. The EL spectra showed that the luminescent intensity of Y2O3:Eu3+/Ag is three times higher than that of Y2O3:Eu3+. MgB2 of SMSC was prepared through an ex situ process to improve the TC of the MgB2-based superconductor on the basis of the idea that the injecting energy will improve the conditions for the formation of Cooper pairs. The TC of MgB2 SMSC was determined based on the measured R–T curve by using the four-probe method in a liquid helium cryogenic system. Results show that the TC of MgB2 SMSC initially increased then decreased with the increase in the Ag content when m-Y2O3:Eu3+/Ag content was fixed at 2.0 wt.%. When the Ag content was 5.0%, the TC of MgB2 SMSC doped with 2.0 wt.% m-Y2O3:Eu3+/Ag was 37.2–38.0 K, which was equal to that of pure MgB2. Meanwhile, the TC of MgB2 SMSC doped with n-Y2O3:Eu3+/Ag increased initially then decreased basically with the increase in the content of n-Y2O3:Eu3+/Ag, in which the Ag content is fixed at 5%. The TC of MgB2 SMSC doped with 0.5 wt.% n-Y2O3:Eu3+/Ag was 37.6–38.4 K, which was 0.4 K higher than that of pure MgB2. It is thought that the doping luminescent nanocomposite into the superconductor is a new means to improve the TC of SMSC. However, the increase in the TC remains insufficient. In future work, new dopant phases with improved characteristics will be prepared to increase the TC of MgB2. Meanwhile, we will attempt to apply this method to other superconductors.

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Author Contributions
X.Z. conceived and led the project; Y.L., H.C. and X.Z. designed the experiments; Y.L., H.C., M.W. and L.X. performed the experiments and characterized the samples; all authors discussed and analyzed the results; Y.L. wrote the paper with input from all co-authors; X.Z. and Y.L. discussed the results and revised the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

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