

Facile Preparation of Environmental Stable High-Temperature Superconducting Ceramic and Polymer Composites

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A novel facile technique to prepare composite materials based on superconducting ceramics ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) and an acrylate polymer matrix has been developed. The polymer does not have a negative effect on the superconductivity properties of the ceramics. The interpenetrating three-dimensional polymeric network formed within ceramics improves its environmental stability.

I. Introduction

THE high-temperature superconducting ceramic (HTSC) has many applications in modern science and engineering. The usage of HTSC materials is complicated by their high extent of degradation under environmental conditions, like water and carbonic gas. This problem can be solved by using ceramic-polymer composites.^{1–11} Polymer is able to fill the pores in the ceramic and thereby prevents penetration of water vapor inside the ceramic.

Mainly, such composites, based on a polymer matrix, are prepared by impregnating ceramics with a monomer under vacuum for 30 min, followed by an overnight soaking (12 h), then the monomer is polymerized.⁴ We have developed a novel facile technique to impregnate a fine-porous ceramic by cryogenic cooling and high vacuum. This technique can even fill very fine pores in a short time (<30 min). It enables to avoid a long monomer saturation time and thereby reduces the duration of contact between the monomer and the ceramic; thus, the negative effect of a monomer on the HTSC can be prevented.

II. Experimental Procedure

The composite materials of a superconducting ceramic with organic polymers (polyethylene-glycol-dimethacrylate or its

copolymer with styrene) were prepared and studied. The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (Bi-2212) ceramic was used as a superconducting phase because it is a well-known superconductor and its degradation properties have been studied extensively.¹²

The solid-state synthesis¹³ was used for the preparation of superconducting ceramics. Owing to the high volatility of Bi_2O_3 , a two-stage precursor method was used to prepare the samples. The first stage involved the synthesis of precursor material by homogeneous mixing of all elements except Bi. The starting materials with the appropriate ratios of SrCO_3 , CaCO_3 , and CuO were mixed in an agate mortar. The mixtures were calcined at $850^\circ\text{--}870^\circ\text{C}$ in air for 24 h. In the second stage, the required amount of Bi_2O_3 was added to the precursor material by co-milling. The powders were then compacted into disks of 10-mm diameter and approximately 2-mm thickness at 1 GPa. The pellets were sintered at 800°C for 48 h in air with two intermediate grindings and compactations. Then, the samples were quenched at room temperature.

The impregnation process of a ceramic by a polymer is shown in Fig. 1. An organic monomer (ethylene-glycol-dimethacrylate) and initiator (benzoylperoxide) were poured in a flask. Then, the flask was dipped into a Dewar filled with liquid nitrogen. After intense boiling of liquid nitrogen had stopped, we placed a sample of HTSC ceramic on the surface of the frozen monomer and sealed the flask by a cap with a vacuum faucet. Then, we connected it to a vacuum pump (which could provide pressure of 10^{-2} – 10 Pa) and closed the faucet. After that, the flask was taken out of liquid nitrogen and left at room temperature. During thawing, the organic monomer melted, and the ceramic sample was dipped into the liquid monomer, which gradually filled the voids in the material. Finally, a vacuum faucet was opened and the ceramic sample (impregnated with the monomer) was taken out of the flask and polymerized at 80°C for 30 min.

The samples were characterized using powder X-ray diffractometry (XRD; PANalytical, X'Pert Pro, Natick, MA) with $\text{CuK}\alpha$ radiation. The magnetization measurements were carried out in a Quantum Design SQUID magnetometer (San Diego, CA). The resistivity was measured by the standard four-probe method in the temperature range from room temperature down

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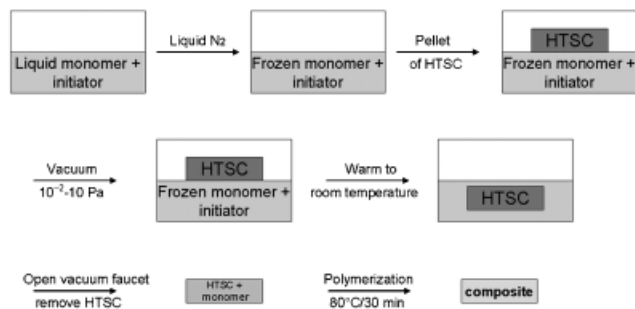


Fig. 1. Schematic procedures of high-temperature superconducting ceramic (HTSC) ceramic/polymer composite preparation.

to 78 K. The environmental stability of the samples was assessed by exposing the samples to various humidity, temperature, and time conditions, and then monitoring the changes in magnetic and the electric properties.

III. Results and Discussion

The XRD powder patterns of the composite and pure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ samples are shown in Fig. 2. The results indicated that the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ceramic phase was retained. Thus, the polymer did not destroy the superconducting phase.

The composites obtained after impregnation and polymerization were investigated for their tolerance to water vapor at different temperatures. To this end, we monitored the changes in the magnetic and electric properties, as well as the phase composition of samples before and after exposure to water vapor.

The resistances of the composites were practically the same as the HTSC ceramics before the impregnation (Fig. 3, curve 1). Both samples demonstrated an abrupt superconducting transition at $T_c = 83$ K. During 30 days of exposure in a humid atmosphere (24.5°C, 87% RH), the resistive properties of pure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ceramic deteriorated with increasing resistivity and decreasing superconducting transition temperature ($T_c = 79$ K), as shown in Fig. 4 (curve 3). However, the resistive properties of the composite remained almost unchanged after exposure to a humid condition (Fig. 3, curve 1—before, curve 2—after).

The measurements of magnetic properties indicated that the superconducting volume fraction after impregnation of a ceramic by a polymer decreased just by 5% (Fig. 4, curve 2) in comparison with pure Bi-2212 ceramic (Fig. 4, curve 1). Such an insignificant decrease of the superconducting volume fraction demonstrates that impregnation of the superconducting ceramic by a polymer has little negative effect on the superconductive properties of the ceramic. A drastic decrease in the superconducting volume fraction by 59% was observed for the pure ceramic (Fig. 4, curve 3) when it was exposed to a humid atmosphere (99% RH, 25°C) for 7 days. At the same time, for

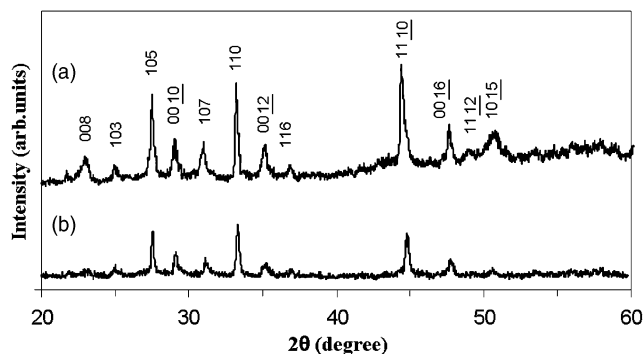


Fig. 2. Powder X-ray diffractometry patterns of (a) the composite and (b) pure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ceramic.

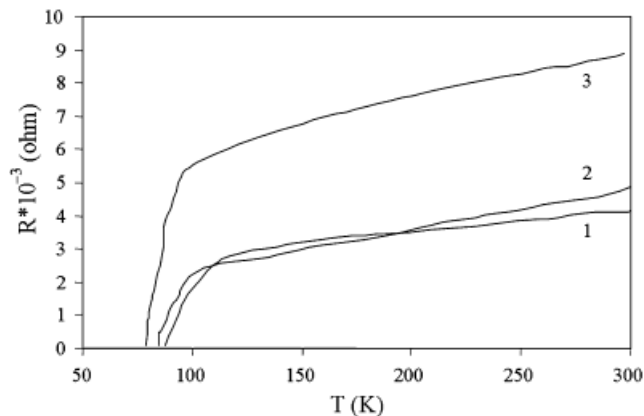


Fig. 3. Plot of resistivity versus temperature for a pure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ceramic and its composite in different environments. Curve 1, both samples before exposure to high humidity (30 days at 20°C and 87% RH); curve 2, composite exposed to high humidity; curve 3, ceramic exposed to high humidity.

the composites, the superconducting volume fraction decreased only by 41% (Fig. 4, curve 4). Moreover, the temperature dependence of magnetic susceptibility (Fig. 4, inset), the same as resistivity dependence, indicates that the value of the superconducting transition temperature for the pure ceramic decreased after exposure in a humid atmosphere, whereas the T_c value of the composite ceramic remained unchanged.

Figure 5 shows the changes in the relative quantity of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconducting phase in the samples with time in the humid atmosphere. The relative quantity of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ phase was calculated according to the results of XRD analysis. The results indicated that the degradation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ in the composite sample was much slower than that of the pure ceramic.

The above results have shown that the impregnation process of cryogenic cooling and high vacuum is a very effective way of preparing a ceramic composite. A rigid three-dimensional interpenetrating network structure can be completely formed within the ceramic, which had a significant stabilization effect on the superconducting ceramics.

IV. Conclusion

The proposed technique to prepare superconducting ceramic-polymer composite materials is easy and can be carried out in a

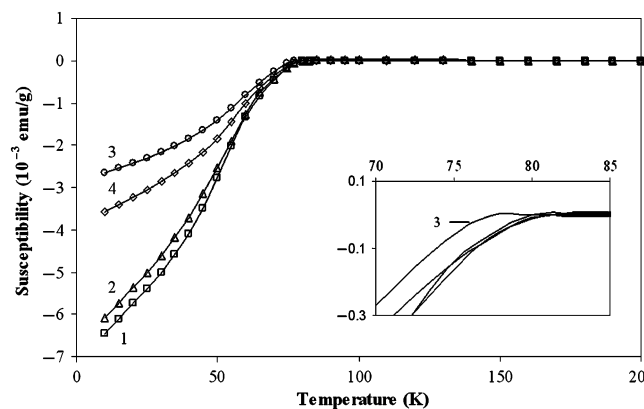


Fig. 4. Temperature dependence of dc-magnetic susceptibility for pure a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ceramic and its composite in different environments. Curve 1, pure ceramic before exposure to high humidity; curve 2, composite ceramic before exposure to high humidity; curve 3, pure ceramic exposed to high humidity (7 days at 25°C and 99% RH), curve 4, composite exposed to high humidity.

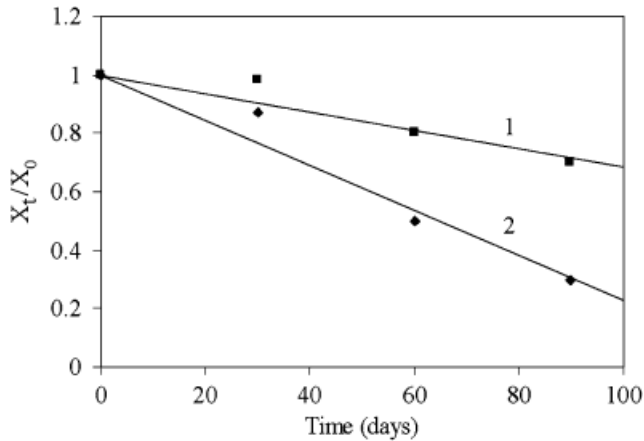


Fig. 5. Plot of the relative quantity of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconducting phase versus time for a composite (curve 1) and a ceramic (curve 2) at 24.5°C, 87% RH.

short time. The polymer does not have a negative effect on the superconducting properties of the ceramic but improves its environmental stability. The interpenetrating three-dimensional polymer network formed within the ceramic is capable of stabilizing the ceramic.

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