

Preparation and characterization of PEG/Bi2212 nanocomposites

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Abstract. Single-phase nanocomposites of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (Bi2212) with organic polymer have been successfully synthesized for the first time by the foliation-adsorption technique. Colloidal suspension containing exfoliated Bi2212 nanosheets was prepared with a stepwise intercalation method. Poly(ethylene glycol) (PEG) was slowly added into colloids containing Bi2212 nanosheets. X-ray diffraction patterns show that the gallery height of Bi2212 host is expanded from 3.08 nm to 4.91 nm in PEG/Bi2212 nanocomposites. The basal plane expansion of 0.9 nm is in good agreement with the values reported for PEG-containing nanocomposites, suggesting that a PEG bilayer is incorporated within the Bi2212 nanosheets.

1. Introduction

The layered bulk materials are exfoliated into individual sheets, so-called nanosheets, in solution to form colloidal suspensions, being expected to open a new route to synthesize nanoparticles and thin films. One of the most important and attractive aspects of the exfoliated nanosheets is that various nanostructures can be fabricated using them as two-dimensional building blocks. It is even possible to tailor superlattice-like assemblies, incorporating a wide range of materials, such as polymers, into the nanosheets. From a viewpoint of application, the intercalation of large organic molecules provides a new synthetic route to high- T_C superconducting thin-films and nanocomposites by separating superconducting blocks into isolated single sheets.

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (Bi2212) is the noble high- T_C superconductor and has a layered structure, which consists of perovskite blocks separated by weakly-coupled Bi-O double layers. Bi2212 colloidal suspension consisting of exfoliated nanosheets was first reported by J-H. Choy *et al.* [1-2]. In our group, Bi2212 colloids dispersed in acetone were also obtained from intercalated Bi2212 via the $\text{HgBr}_2/\text{Bi2212}$ precursors [3-4].



In this report, we describe the first synthesis of single-phase nanocomposites of Bi2212 with organic polymer by the exfoliation-adsorption technique. This technique [5-7] is one of the most attractive ways if the host materials can be separated into the nanosheets and the polymer is soluble in a solvent. Poly(ethylene glycol) (PEG) is adopted as the guest polymer, because PEG is soluble to organic solvent. The exfoliation-adsorption method, however, may require additional process controls, such as ultrasonic exposure and mechanical stirring, to optimize the synthesis of nanocomposites. This is because the exfoliation-adsorption method is highly dependent on the chemical and physical properties of host inorganic materials and guest organic polymers. These conditions therefore need to be optimized for each synthesis.

2. Experimental

The inorganic starting materials used for all preparations described in this work were analytical reagent grade and used without further purification. Tetrabutylammonium bromide (TBA:Br, Aldrich), dimethylsulfoxide (DMSO, Wako Chemicals), and Poly(ethylene glycol) (PEG, average molecular weight 1000, Wako Chemicals) was also used as received.

Bi2212 hosts were prepared by the solid-state reaction of Bi_2O_3 , SrCO_3 , CaCO_3 , Y_2O_3 , and CuO powders (1-2 μm , Soekawa Chemicals) [8-12]. They were mixed in the ratio of $\text{Bi}:\text{Sr}:\text{Ca}:\text{Y}:\text{Cu} = 2:2:0.8:0.2:2$. The well-mixed powders were sintered at 800°C for 20 h in air. They were pulverized, mixed, palletized and sintered at 870°C for 24 h with air-flow. This process was repeated twice in order to improve the crystallinity and the superconducting transition temperature T_C .

Colloidal suspension containing exfoliated Bi2212 nanosheets was prepared with a stepwise intercalation method [3-4]. A large molecule, such as alkylammonium ion, cannot be intercalated directly into the narrow Bi-O layers of Bi2212 host. To increase the gallery height between the Bi-O layers, we prepared the $\text{HgBr}_2/\text{Bi2212}$ precursors prior to the alkylammonium ion intercalation. The intercalated precursor was prepared by the chemical vapour transport technique with Bi2212 and HgBr_2 in a vacuum-sealed quartz ampoule. TBA:Br was then intercalated into $\text{HgBr}_2/\text{Bi2212}$ via the ion exchange method. The molar ratio of $\text{HgBr}_2/\text{Bi2212}$ precursor and TBA:Br was 1:3. They were mixed with 50 mL of DMSO in a Schlenk-type flask. The mixture was vigorously stirred at 70°C for 6 h. Exfoliation of Bi2212 was carried out by sonicating TBA/Bi2212 in DMSO solution. In typical reactions, 0.3 g of TBA/Bi2212 was exfoliated by ultrasonication at ambient temperature in 300 mL of DMSO. Excess PEG polymer (0.9 g) was slowly added into colloids containing Bi2212 nanosheets. The mixtures were stirred, and solid product was precipitated. The nanocomposites were then collected by centrifugation, washed to remove unintercalated polymer, and dried *in vacuo* overnight.

X-ray powder diffraction (XRD) data on samples were collected on a Rigaku RINT Ultima⁺ diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation, by 0.02° 2θ step/0.6 sec between 2 and 120° .

3. Results and discussion

It is well known that the superconducting properties of the oxide high- T_C superconductors are very sensitive to the hole concentration. In the Bi2212 system, the hole concentration can be easily varied by substituting the divalent Ca ion by trivalent rare-earth ions, *e. g.* Y [13]. In this study, host Bi2212 single crystals were prepared at Y content $x = 0.2$, where the highest T_C can be obtained at the optimum hole concentration in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+d}$ system [8-9].

Various layered compounds have been delaminated into their colloidal single-sheets via the so-called soft chemical techniques, which require neither high temperature nor ultrahigh vacuum for preparations. The resulting nanosheets exhibit novel physical and chemical properties due to an extremely small thickness of around 1 nm. Treatment of 0.3 g of TBA/Bi2212 intercalation compound with DMSO of 300 mL after ultrasonication for 200 min in the ice bath yields uniform and transparent colloidal solution. A clear Tyndall light scattering can be observed, indicating the presence of exfoliated Bi2212 nanosheets dispersed in DMSO. The resulting colloidal suspension is stable for a few days. Then black solid is precipitated.

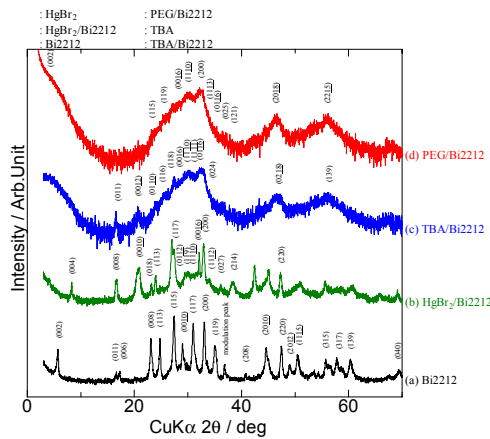


Figure 1. XRD patterns of the host and its nanocomposites; (a) Bi2212 host, (b) HgBr₂/Bi2212, (c) TBA/Bi2212, and (d) PEG/Bi2212 nanocomposite prepared at room temperature.

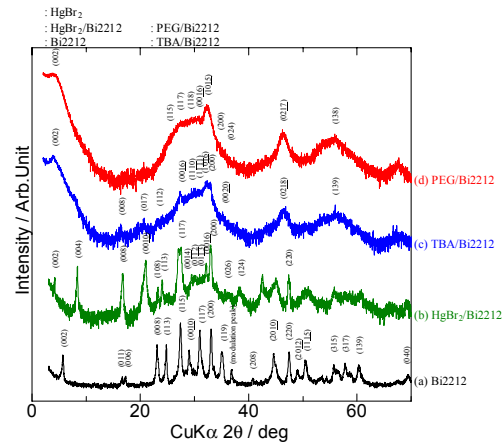


Figure 2. XRD patterns of the host and its nanocomposites; (a) Bi2212 host, (b) HgBr₂/Bi2212, (c) TBA/Bi2212, and (d) PEG/Bi2212 nanocomposite prepared at 70°C.

Table 1. XRD data for Bi2212 nanocomposites.

Sample	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	Δ <i>c</i> (nm)
Bi2212	0.541	0.541	3.076	—
HgBr ₂ /Bi2212	0.541	0.541	4.384	1.308
TBA/Bi2212	0.541	0.540	5.101	2.025
PEG/Bi2212 ^a	0.543	0.538	4.908	1.832
Bi2212	0.541	0.541	3.076	—
HgBr ₂ /Bi2212	0.541	0.541	4.384	1.308
TBA/Bi2212	0.543	0.539	5.117	2.041
PEG/Bi2212 ^b	0.541	0.540	4.876	1.800

^a Prepared at room temperature.

^b Prepared at 70°C.

Figure 1 shows the XRD pattern of PEG/Bi2212 nanocomposite together with Bi2212 host and its derivatives. The XRD data obtained are summarized in Table 1. In this study, all XRD peaks are assigned by the basic double-block model, although the $(a + b)/2$ shift of the cuprate block may not occur upon Bi2212 intercalation compounds. The observed lattice expansion along the *c*-axis for HgBr₂/Bi2212 precursor, Δ*c* = 1.308 nm, is very near to 1.26 nm of the reported value [3-4]. This suggests that the HgBr₂ monolayer is intercalated between the Bi-O double layers of Bi2212 host crystal. The difference between interlayer spacing of TBA/Bi2212 intercalation compounds and unintercalated Bi2212, Δ*c* = 2.025 nm, is in good agreement with twice of 1.05 nm for the TBA-intercalated α-zirconium phosphate [14]. This means that the TBA⁺ ions reside the single-layer arrangement in the interlayer gallery of Bi2212. HgBr₂/Bi2212 precursor and TBA/Bi2212 intercalation compounds are used to increase the gallery height between the Bi-O layers.

Figure 1(d) shows the XRD pattern of PEG/Bi2212 nanocomposite prepared at room temperature for 7 days. There is no trace of the pristine phase in XRD patterns for PEG/Bi2212 nanocomposite, indicating that PEG polymer is incorporated homogeneously into each Bi2212 layer. It is found that the gallery height of Bi2212 host is expanded from 3.08 nm to 4.91 nm in PEG/Bi2212 nanocomposites. The basal plane expansion of 0.9 nm is in good agreement with the values reported for PEG-containing nanocomposites [6-7]. This suggests that a PEG bilayer is incorporated within the Bi2212 nanosheets.

The experimental conditions of the foliation-adsorption technique need to be optimized for each synthesis. The synthesis time and temperature of PEG/Bi2212 nanocomposites and the molar concentration of Bi2212 colloids are carefully checked. Figure 2(d) shows the XRD pattern of PEG/Bi2212 nanocomposite prepared at 70°C for 7 days. Although the synthesis temperature is elevated from room temperature to 70°C, the other conditions for PEG/Bi2212 nanocomposites are unchanged. A more obvious (002) peak can be found around 4.1° in Fig. 2(d), indicating that the crystallinity of PEG/Bi2212 nanocomposite prepared at 70°C is higher than that prepared at room temperature, although the lattice constants calculated from the assigned XRD peaks are almost same.

4. Summary

The single-phase stage-1 intercalation nanocomposites of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (Bi2212) with organic polymer poly(ethylene glycol) (PEG) have been synthesized for the first time via $\text{HgBr}_2/\text{Bi2212}$ precursors and TBA/Bi2212 intercalation compounds. It is found that the gallery height of Bi2212 host is expanded by 1.8 nm in PEG/Bi2212 nanocomposites. TBA/Bi2212 can be exfoliated into single layers in DMSO, which is stable for a few days after ultrasonication. Further study will be needed to prepare the more stable colloidal suspension of Bi2212 nanosheets, which are useful as a building block for the fabrication of a wide variety of functional nanomaterials.

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