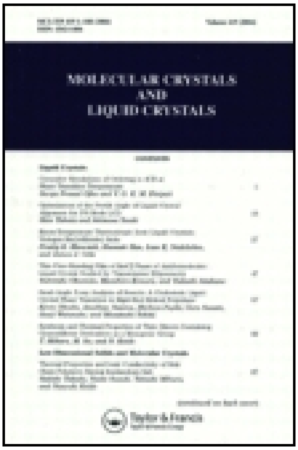

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Novel Synthetic Route to Superconducting-Insulating Nanohybrids

Jin-Ho Choy [a], Soon-Jae Kwon [a] & Eue-Soon Jang [a]

[a] National Nanohybrid Materials Laboratory, Division of Chemistry & Molecular Engineering, Seoul National University, Seoul, 151-742, Korea

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Novel Synthetic Route to Superconducting-Insulating Nanohybrids

JIN-HO CHOY, SOON-JAE KWON and EUE-SOON JANG

National Nanohybrid Materials Laboratory, Division of Chemistry & Molecular Engineering, Seoul National University, Seoul 151–742, Korea

We have developed novel organic-inorganic (cuprate) hybrid superconductors. For the first time, long-chain organic moiety was incorporated into the Bi-based cuprate superconductor through intercalative complexation. The separation between superconducting cuprate layers is systematically controlled by modifying the size of the organic intercalant, giving rise to a critical clue to the relation between superconducting transition temperature (T_c) and the dimensionality in the layered high-T_c compound. It is revealed that the T_c value is not affected by the layer separation between cuprate layers, i.e. interlayer coupling. The present nano-hybrids are expected to be a good model compound to understand the high-T_c superconductivity as well as molecular level quantum-well. In addition, the hybrids are believed to be excellent precursor materials for superconducting particles and thin film or wire.

Keywords: intercalation; intercalative complexation; nanohybrid; intercalant; cuprate

INTRODUCTION

The intercalation of organic molecule into the layered high-T_c superconductor has been regarded as the best way to create low dimensional superconductors, because the organic intercalation leads to free modulation of interlayer distance without changing in the crystal lattice of oxide block. The Bi-O double layers in the layered Bi-based cuprate superconductors, $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m=1, 2, and 3; Bi2201, Bi2212, and Bi2223), are weakly bound along the *c*-axis, in which guest molecules can be intercalated remaining the internal structure of the cuprate blocks unchanged. Here, we tried to develop low-dimensional high-T_c superconductors by intercalating *n*-alkyl chain derivatives into Bi-based cuprates superconductor. The organic intercalation into these rigid Bi-based cuprate was carried out based on the synthetic strategy of intercalative complexation[1]. In this work, we represent the novel synthetic route to organic-cuprate hybrid superconductors and their practical applications such as superconducting nanoparticle and thin film.

EXPERIMENTAL

The Bi-based superconductors, $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (BSCCO), were prepared by the conventional solid state reaction as reported previously [2]. HgI_2-intercalates of BSCCO were prepared by two step heating at 190 °C for 2 h and 240 °C for 4 h, where 1 mole of free iodine ($P(I_2) \approx 1$ atm) was added as a transporting agent. The organic-cuprate hybrid compounds, $[(Py\text{-}C_nH_{2n+1})_2HgI_4]$-BSCCO, were synthesized by solvent mediated reaction between HgI_2-intercalates and alkylpyridinium iodide $Py\text{-}C_nH_{2n+1}I$ at 40 - 70 °C for 6 h. The colloidal BSCCO nano-particles are also prepared by the ultrasonic treatment of organic-cuprate nanohybrids in an acetone solvent. The structures and physico-chemical properties of the present organic-intercalates were investigated by the powder X-ray diffraction (XRD), high-resolution transmission microscopy (HRTEM), X-ray absorption spectroscopy (XAS) analysis, and dc-magnetic susceptibility. The particle-size analyses and the scanning electron microscopy (SEM) measurements were performed on the BSCCO colloidal nano-particles and electrodeposited films, respectively.

RESULTS AND DISCUSSION

Organic-cuprate nanohybrids

From our previous study on the mercuric halide intercalates, HgX_2-BSCCO (X = Br, I), it is revealed that the intercalated HgX_2 is stabilized as 2-coordinated molecules[4]. Taking into account the fact that the mercury in the intercalated HgX_2 is coordinatively unsaturated, it is naturally expected that the intercalated mercuric halide should be further ligated[5]. Here, we have tried to intercalate *n*-alkyl chain derivatives in order to develop two-dimensional cuprate layer, testing the suggested high-T_c theories[6-7]. In this scheme, alkyl pyridinium iodide $Py\text{-}C_nH_{2n+1}I$ (n = 1, 2, 4, 6, 8, 10, and 12) was reacted with HgI_2-intercalates, forming a complex organic-salt $(Py\text{-}C_nH_{2n-1})_2HgI_4$ in the interlayer space of Bi-based cuprates. The XRD and HREM analyses for the organic-salt intercalates show lattice expansion along *c*-axis (Δd; basal increment) ranging from 11 Å (n = 1) to 32 Å (n = 12), which indicates that the bi-layer of alkyl chains is stabilized in the interlayer space. As the length of alkyl chain increases, the intercalated alkyl chains are self-assembled in the interlayer space due to the van der Waals energy gain between organic chains. Figure 1 represents the schematic structural model of organic-cuprate nanohybrid. In accordance with our expectation, the coordination number of Hg is changed from two to four upon organic intercalation, being revealed by the EXAFS analyses of the Hg L_{III}-edges for HgI_2-intercalate and organic-salt intercalate, respectively[1][4].

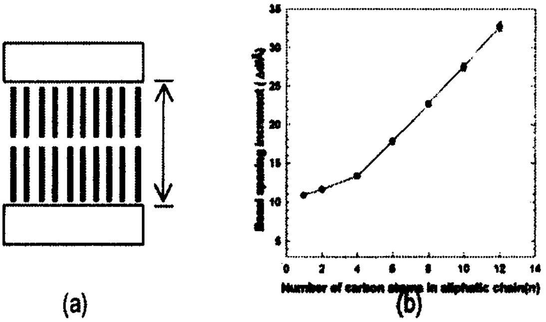

FIGURE 1 (a) Schematic structural model for the organic- cuprate nanohybrid. (b) Basal increments as a function of alkyl chain length in the organic-cuprate hybrids.

Dc-magnetic susceptibility measurements for the present organic-salt intercalates show that the T_c values are nearly not changed in spite of remarkable basal increments, indicating that high-T_c superconductivity is the intrinsic two dimensional nature of CuO_2 plane. The present organic-cuprate hybrid superconductors are expected to be ideal material for studying molecular level quantum wells, because the thickness of the insulating layer can be freely modified by changing the length of the alkyl chain.

Application of organic-cuprate nanohybrids; nanoparticle and thin film

In the present organic-salt intercalates, the chemical interaction between Bi-based cuprate blocks is supposed to vanish due to the large interlayer separation. Based on this idea, we have tried to separate the organic-cuprate nanohybrid into each individual cuprate block through appropriate physico-chemical treatment. Indeed, superconducting colloidal nanoparticles were successfully prepared by exfoliating the organic-cuprate hybrids[8]. From the particle-size analyses and TEM measurement, it is found that the plate-like particles are in the range of 50 - 200 nm. The exfoliated nanoparticles are believed to be excellent precursor materials for the superconducting thin film and wire.

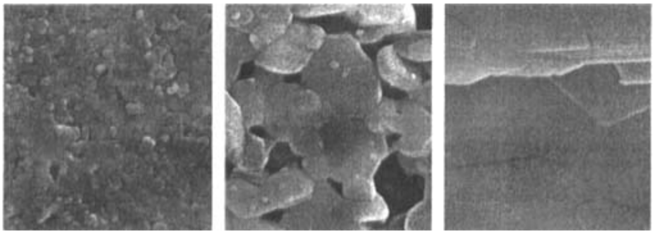

FIGURE 2 SEM images for (a) as-deposited film, (b) heat-treated at 700 °C, and (c) heat-treated at 800 °C, respectively.

By electrodepositing the colloidal particles on Ag-substrate and subsequent heating process, we were also able to demonstrate well developed superconducting thin film. Figure 2 shows the morphologies of as-deposited film and heat treated ones, where the grain-growth from the exfoliated nanoparticles could be clearly seen. This novel synthetic route to superconducting thin film will play an important role in engineering high-T_c materials.

CONCLUSION

We have prepared organic-cuprate hybrid superconductors by intercalative complexation method, where the organic-bilayers are stabilized inbetween the Bi-based cuprate superconductor. From the magnetic susceptibility measurements for the organic intercalates, we were able to conclude that the high-T_c superconductivity is the intrinsic nature of two-dimensional CuO_2 plane. The organic-cuprate intercalates are expected to be an important precursors both for scientific research and practical application such as superconducting thin film and wire.

Acknowledgment

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References

[1] J.-H. Choy, S.-J. Kwon, and G.-S. Park, Science, **280,** 1589 (1998).
[2] A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi, K. Uchinikura, *Phys. Rev. B* **41,** 6418 (1990).
[3] J.-H. Choy, N.-G. Park, S.-J. Hwang, D.-H. Kim, and N.-H. Hur, *J. Am. Chem. Soc.* **116,** 11564 (1994).
[4] J.-H. Choy, S.-J. Hwang, and N.-G. Park, *J. Am. Chem. Soc.* 119, 1624 (1997).
[5] R. Arnek and D. Poceva, *Acta Chem. Scand. Ser. A* 30, 59 (1976).
[6] J. M. Wheatly, T. C. Hsu, and P. W. Anderson, *Nature,* **333,** 121 (1988).
[7] M. Di Stasio, K. A. Muller, and L. Pietronero, *Phys. Rev. Lett.* **64,** 2827 (1990).
[8] J.-H. Choy, S.-J. Kwon, S.-J. Hwang, Y.-I. Kim, and W. Lee, *J. Mater. Chem.*, **9,** 129 (1999).