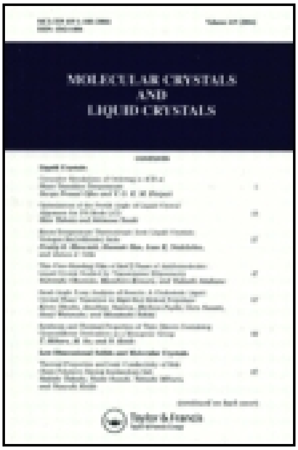

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Mixed Conductors, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_aO_y$ ($0.75 < x < 1.2$, n = 1, 2, and 3)

Young-Il Kim [a] & Jin-Ho Choy [a]

[a] Department of Chemistry, Center for Molecular Catalysis (CMC), Seoul National University, Seoul, 151-742, KOREA

Version of record first published: 04 Oct 2006

To cite this article: Young-Il Kim & Jin-Ho Choy (1998): New Mixed Conductors, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_aO_y$ ($0.75 < x < 1.2$, n = 1, 2, and 3), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 423-428

To link to this article: http://dx.doi.org/10.1080/10587259808042420

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 423–428
Reprints available directly from the publisher
Photocopying permitted by license only

New Mixed Conductors, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$ ($0.75 < x < 1.2$, n = 1, 2, and 3)

YOUNG-IL KIM, and JIN-HO CHOY
Department of Chemistry, Center for Molecular Catalysis (CMC), Seoul
National University, Seoul 151-742, KOREA

New intercalation compounds, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$ ($0.75 < x < 1.2$, n = 1, 2, and 3) have been prepared by the stepwise intercalation of I and Ag into the layered high-T_c superconductor, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$. For all three cases (n = 1, 2, and 3), powder XRD analysis indicated that the Ag-I intercalation expanded the $[Bi-O]_2$ double slabs within host block by ~7.3 Å, with subtle changes in physical properties of the pristine. From the Fourier 1-dimensional electron density mapping and the extended X-ray absorption fine structure (EXAFS) analysis to configure the interlayer structure of Ag_xI_w sublattice, it was revealed that the two-dimensional Ag_xI_w species retained a similar iodine skeleton as found in β–AgI, but with a slightly distorted Ag^+ position. The Ag^+ ionic conductivity of $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$ was turned out to be comparable with that of well known superionic conductors.

Keywords: mixed conductor; superconductor; silver iodide; EXAFS; ionic conductivity

INTRODUCTION

The mixed ionic–electronic conductivity is an essential property for electrode application in various electrochemical systems, and there are increasing interests in the mixed conducting materials. However, only a few materials have been well defined as mixed conductors, due to the complex requirements that they should have simultaneously favorable solid lattice and electronic band structure.[1]

In recent, we have developed a new intercalate, by introducing the Ag–I layer into the cuprate superconductor, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$.[2] Since, in this new hybrid system, the guest and host layers are combined in a molecular level, we could expect a mobile nature of Ag^+ ions in addition to the high electronic conductivity of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$. In this report, we describe the intercalation of Ag–I into $Bi_2Sr_2Ca_{n-1}Cu_nO_y$, the local geometry of Ag–I layer in the interlayer space, and the ionic conductivity of the intercalated Ag^+ ion.

EXPERIMENTAL SECTION

The pristines $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ (n = 1, 2, and 3; $y = 2n + 4 + \delta$) have been prepared by the conventional solid state reaction.[3] For the intercalation of I and Ag, the polycrystalline $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ and Ag powder were homogeneously mixed and pressed into a pellet, which was subjected to the following heat treatments. At first, the silver metal and $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ powders were intermixed, pelletized again, heated at 840 °C for 2 hours, then at 170 °C for 3 hours under an I_2 vapor pressure of ~1 atm., and finally at 190 °C for 10 hours in an open air. The Ag, and I contents in the final phase, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$, could be controlled within the range of $0.75 < x < 1.2$, by varying the initial mixing ratio of Ag to $Bi_2Sr_2Ca_{n-1}Cu_nO_y$.

During the intercalation procedure, powder XRD analysis was performed to monitor the structural evolution of host, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ lattice. In order to probe the local geometry of interlayer Ag–I species, EXAFS spectroscopic analysis was carried out at the Ag K– and I L_3–edges. The ionic conductivity of intercalated Ag^+ ion was examined at 25 ~ 270 °C, by employing both impedance spectroscopy[4] and pulsed method.[5] From the d.c. magnetic susceptibility measurement, the superconducting properties of pristines and their Ag–I intercalates were investigated.

RESULTS AND DISCUSSION

Intracrystalline Structure of Intercalated Ag–I Layer

After each reaction step described in the experimental section (840 °C/ 170 °C/ 190 °C), powder XRD pattern was obtained and interpreted as summarized in Table I. In the iodine atmosphere at 170 °C, it was found that both Ag metal and $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ react with iodine to form AgI and the stage–1 $IBi_2Sr_2Ca_{n-1}Cu_nO_y$, respectively. Further, by raising the reaction temperature and removing the I_2 vapor, the mixture phase of AgI $\oplus$ $IBi_2Sr_2Ca_{n-1}Cu_nO_y$ was transformed into a new single phasic intercalate with a basal increment of ~7.3 Å. The lattice expansion of $\Delta d \approx 7.3$ Å is approximately twice as large as that for the iodine-intercalate,[6] from which we could assume the formation of Ag–I sublattice with iodine double layer.

TABLE I Phase identification from the powder XRD pattern analysis after each reaction step.

	840 °C/ 2h open air	170 °C/ 3h $P(I_2) \approx 1$ atm.	190 °C/ 10h open air
Phase	Pristine/ Ag	I-intercalate/ AgI	Ag-I-intercalate
Δd^*	-	3.6 Å	7.2 ~ 7.3 Å

*Lattice expansion of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$

For better understanding of the intracrystalline structure of guest Ag–I layer, we have utilized the EXAFS spectroscopy,[7] together with the Fourier 1-dimensional electron density (ρ_z) mapping[8] for the Ag–I intercalates.

Using the XRD (*00l*) intensities, ρ_z profile was calculated along the crystal *c*–axis of $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$, from which we could find out the informations about stacking sequence of guest species. For the comparison with the empirical data, ρ_z was simulated based on the probable structure models of Ag–I sublattice. Among the various assumptions, the best coincidence occurred when Ag ions are distributed in two layers between the exterior I layers, as ····[Bi-O] / I / Ag / Ag / I / [Bi-O]···· .

The raw EXAFS spectra recorded in a transmission mode, have been processed according to the standard procedure; i) background subtraction, ii) k^r–weighting (r = 2 for Ag *K*–edge, and 3 for I L_3–one), and iii) Fourier filtration.[7] Then a non-linear least squares curve fitting was carried out to the Fourier first coordination shell EXAFS, in order for the determination of the structural parameters such as bond distance, coordination number, and Debye-Waller factor. From both edges, the Ag–I bond length was found to be ~2.78 Å, as in the reference β–AgI. On the other hand, the coordination number around the Ag and I were determined to be 4 and 3, respectively, indicating that the I ions are interfaced with the [Bi–O] plane of host block.

Mixed Conductivity of $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$

Upon Ag–I intercalation, the superconducting property of the pristine $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ was maintained with only a slight decrease in the transition temperature (T_c). For the phases with n = 1, 2 and 3, the T_c depressions were 5 K, 12 K, and 13 K, respectively. The ionic conductivity of interlayer Ag^+ ion has been measured by the impedance spectroscopy and pulsed method, which can measure the partial ionic contribution in a mixed ionic-electronic conductor. As expected from the well established solid state theory, the Ag^+ ionic conductivity increases monotonously with the Ag^+ concentration and the ambient temperature. Over 100 °C, all the Ag–I intercalates exhibit superionic conductivity of $\sim 10^{-2}\ \Omega^{-1}\cdot cm^{-1}$, together with the electronic one of $\sim 10^{-1}\ \Omega^{-1}\cdot cm^{-1}$. The noble mixed conductivity of $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$ can be ascribed to its regularly interstratified structure consisting of the metallic $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ block and the ionic conducting Ag-I layer.

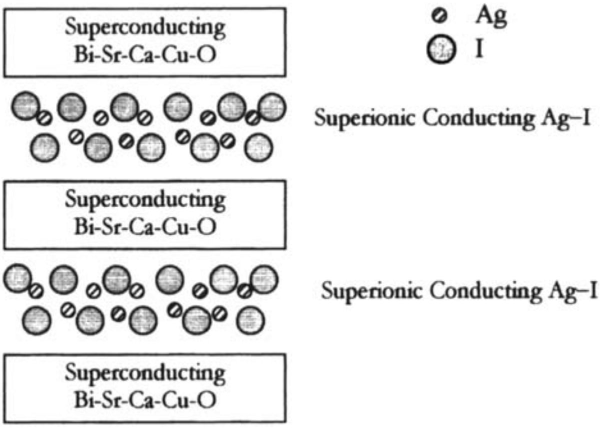

FIGURE 1 Schematic representation of the interstratified structure in the mixed conductor, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$.

As illustrated in Fig. 1, two different kinds of materials are assembled into a nanocomposite, $Ag_xI_wBi_2Sr_2Ca_{n-1}Cu_nO_y$, where the combination of heterogeneous components led to the unique conducting property.

Acknowledgments

This research was in part supported by the Ministry of Education (BSRI-96-3413), and by the the KOSEF through the Center for Molecular Catalysis (CMC).

References

[1.] W. J. Weber, H. L.Tuller, T. O.Mason, and A. N. Cormack, *Mater. Sci. Eng. B*, **18**, 52(1993).
[2.] J.-H. Choy, N.-G. Park, Y.-I. Kim, S.-H. Hwang, J.-S. Lee, and H.-I. Yoo, *J. Phys. Chem.*, **99**, 7835(1995).
[3.] A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi, and K. Uchinokura, *Phys. Rev. B*, **41**, 6418(1990).
[4.] J. R. Macdonald, *J. Chem. Phys.*, **61**, 3977(1974).
[5.] R. T. Johnson. Jr, R. M. Biefield, M. L. Knotek, and B. Morosin, *J. Electrochem. Soc.*, **123**, 680(1976).
[6.] X.-D. Xiang, S. Mackerman, W. A. Vareka, A. Zettl, J. L. Corkill, T. W. Barbee III, and M. L. Cohen, *Nature*, **348**, 145(1990).
[7.] B. K. Teo, in *EXAFS : Basic Principles and Data Analysis* (Springer-Verlag, Berlin, 1986), pp. 45–52.
[8.] M. F. C. Ladd, and R. A. Palmer, in *Structure Determination by X-ray Crystallography* (Plenum Press, New York, 1985), p. 270.