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Intercalation Reaction of $Bi_2(Sr,Nd)_2CuO_y$ $Bi_2Sr_2(Ca,Gd)Cu_2O_y$ and Related Compounds With Iodine*

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With iodine vapour treatment of various single crystals of Bi-Sr-Ca-Ln(Rare earth element)-Cu-O system, the stage-1 iodine-intercalation compounds of $Bi_2(Sr,Nd)_2CuO_y$(2201), $Bi_2Sr_2(Ca,Gd)Cu_2O_y$ or $Bi_2Sr_2CaCu_2O_y$(2212) and Bi_8SrCaO_{14} have been prepared. x-ray diffraction and transmission electron microscope analysis indicate that iodine layer of thickness 3.2~3.5 Å is formed between two Bi_2-O_2 layers.

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Attention has been paid to layered intercalation compounds for a long time. A variety of host lattices that can incorporate atomic or molecular guest species have been examined, e. g., graphite[1] and layered dichalcogenides of transition metal.[2] Superconductivity, lattice distortions, etc. can be modified significantly by intercalation.[3–5] A number of the intercalation compounds of transition metal dichalcogenides are superconductors.[6,7] X. D. Xiang *et al.*, have found a stage-1 intercalation compound of $Bi_2Sr_2CaCu_2O_y$ with iodine recently.[8] They showed that iodine intercalation does not affect superconductivity of host compound. In this letter, we report a series of iodine intercalated compounds of Bi-Sr-Ca-Ln(Rare-earth element)-Cu-O system and Bi_8SrCaO_{14} prepared by means of a high-pressure technique. It is evident that a iodine-layer of thickness 3.4 Å is formed between the Bi_2-O_2 layers of these host compounds by x-ray diffraction and transmission electron microscope (TEM) analysis.

Various single crystals of Bi-Sr-Ca-Ln-Cu-O system and Bi_8SrCaO_{14} used in our experiments are grown by flux method. The detailed technique has been described elsewhere.[9,10] The sizes of all the single crystals used in this experiment are about 2×3×0.2 mm. The crystals and a small amount of solid iodine are put into a high-pressure vessel, kept at 200°C for 10 days under the pressure about 10 atmospheres, then cooled to room temperature. The x-ray diffraction analysis is made by Japan Rikaku D/Max-γA x-ray diffractometer with monochromatic high-intensity Cu(K_α) radiation (λ=1.5418 Å) and TEM observation is carried out on an H-800 Analysis Electron microscope respectively.

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After iodine vapour treatment, the habit planes of various single crystal samples are still smooth. The rocking curves measured from single crystals $Bi_2(Sr,Nd)_2CuO_y$, $Bi_2Sr_2(Ca,Gd)Cu_2O_y$, and Bi_8SrCaO_{14} after iodine intercalation by the double-crystal diffractometer method are shown in Fig. 1. The symmetry of each curve indicates that the samples intercalated keep the forms of single crystals, however, small angle grain boundary and lattice distortion are increased.

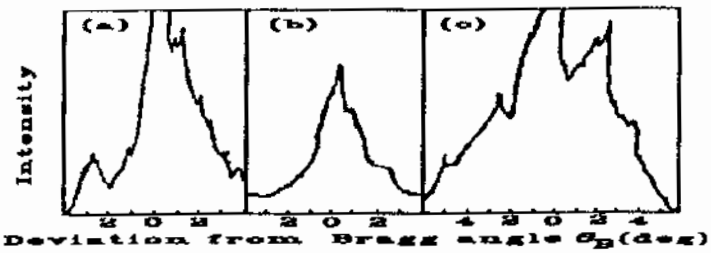

Fig. 1: Rocking curves of single crystals $Bi_2(Sr,Nd)_2CuO_y$ (a), $Bi_2Sr_2(Ca,Gd)Cu_2O_y$ (b) and Bi_8SrCaO_{14} (c) after iodine intercalation.

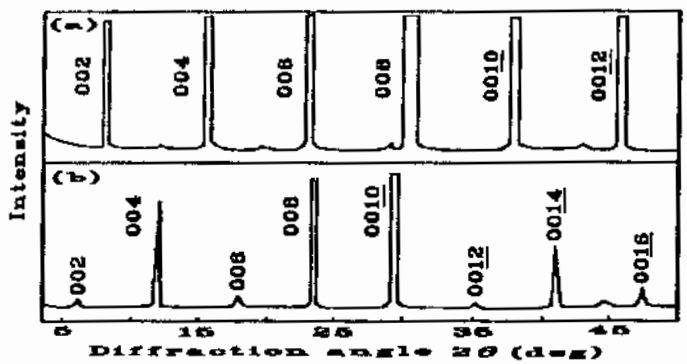

Fig. 2: Multiple-order diffraction pattern of $Bi_2(Sr,Nd)_2CuO_y$ (a). Before iodine intercalation, (b). After iodine intercalation.

Table 1: Change of (00L) multiple-order diffraction data before and after iodine intercalation of $Bi_2(Sr,Nd)_2CuO_y$ and $Bi_2Sr_2(Ca,Gd)Cu_2O_y$

(00L)	$Bi_2(Sr,Nd)_2CuO_y$ *d*-Value		$Bi_2Sr_2(Ca,Gd)Cu_2O_y$ *d*-Value	
	Before iodine intercalation	After iodine intercalation	Before iodine intercalation	After iodine intercalation
002	11.65	14.46	15.14	18.00
004	5.89	7.46	7.62	9.22
006	3.94	5.03	5.12	6.19
008	2.96	3.79	3.85	—
0010	2.36	3.04	3.08	3.74
0012	1.98	2.54	2.56	3.13
0014	1.69	2.18	2.20	2.70
0016	—	1.91	1.93	2.36
0018	—	1.70	1.71	—

Although the incorporation of iodine into the host lattices does not destroy their single crystal nature, their crystal structure has been modified considerably. Figures (2a) and 2(b) are typical 00L multiple-order diffraction patterns of $Bi_2(Sr,Nd)_2CuO_y$ before and after iodine treatment. It can be seen that all the multiple-order diffraction lines of Fig. 2(b) are indexed with cell parameter 30.6 Å. It means that the cell parameter of the host crystal along c-direction is expanded from 23.7 to 30.6 Å after intercalation (Table 1). The cell parameters along a- and b-directions do not change as much according to the electron diffraction pattern in Fig. 3, i.e. a=5.41 Å, b=5.42 Å, although one of the two directions is modulated. All these small changes can not be explained simply by heat-treatment of host crystal.[11]

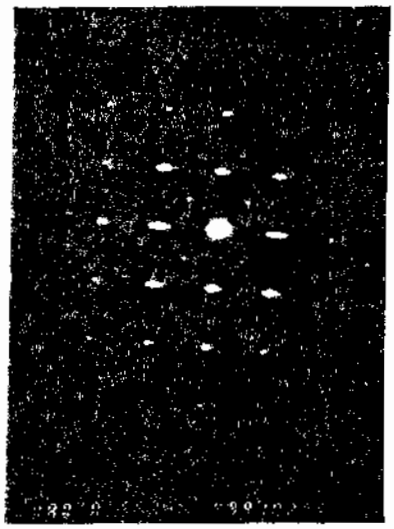

Fig. 3: (00L) electron diffraction pattern of $Bi_2(Sr,Nd)_2CuO_y$ after iodine intercalation.

The 00L multiple-order diffraction patterns of $Bi_2Sr_2(Ca,Gd)Cu_2O_y$ single crystal, which are taken before and after iodine vapour treatment respectively, are shown in Fig. 4. Similar to the result of 2201 host crystal, the lattice constant along c-axis is also increased, from 30.80 to 37.76 Å, which is consistent with the result for iodine intercalation of $Bi_2Sr_2CaCu_2O_y$ reported by X. D. Xiang.[8]

The colour of single crystal compound Bi_8Sr CaO_{14} changes from light yellow to semitransparent dark brown after the same treatment as for 2201 crystal. The (00L) multiple-order diffraction pattern of the host crystal (Fig. 5(a)) has changed to one of the Fig. 5(b), and the latter has a number of additional diffraction lines expressed using asterisk, which can be indexed by c=37.92 Å, while the electron diffraction pattern of the sample made by Bi_8SrCaO_{14} iodine intercalated is almost the same as that of host lattice.[10]

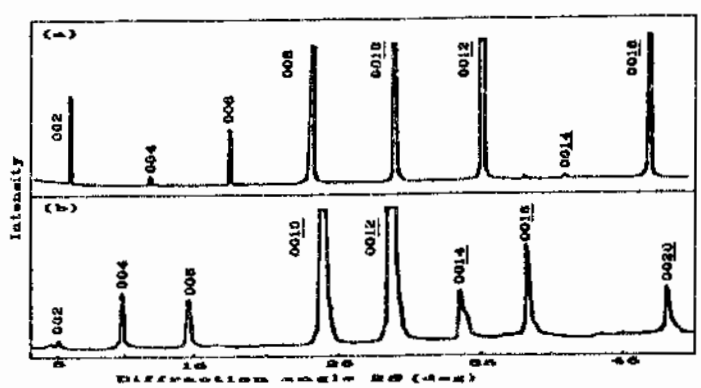

Fig. 4: Multiple-order diffraction pattern of $Bi_2Sr_2(Ca,Gd)Cu_2O_y$ (a). Before iodine intercalation, (b). After iodine intercalation.

It is worthwhile to point out that iodine intercalation reaction is irreversible. Heated at 200°C, the iodine intercalation compounds are destoryed and can not return to the original host. The insertion can not be washed out after these single crystals are dipped into alcohol for 24 h, and the diffraction pattern of crystal does not change.

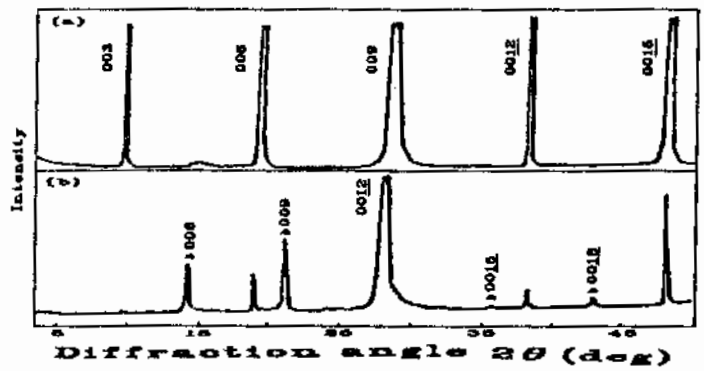

Fig. 5: Multiple-order diffraction pattern of Bi_8SrCaO_{14} (a). Before iodine intercalation, (b). After iodine intercalation.

It can be seen from the description above that after iodine intercalation every Bi_2-O_2 double layer is stretched by an amount of 3.2 to 3.5 Å, and there is no significant change in $a-b$ plane which is parallel to Bi_2-O_2 layer. It is shown that iodine is inserted between two Bi_2-O_2 layers forming the stage-1 iodine intercalation compound. The research on the effect of iodine intercalation of 2201 and 2212 undoped- and doped-rare earth element on superconductivity is in progress.

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