Intercalation of Nitric Oxide into Double-layered Cuprate Superstructure

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The substituted double-layered cuprate, $La_{1.5}Ba_{0.5}SrCu_2O_6$, characterized by the $3a \times 3a$ superstructure, incorporates large quantities of gaseous nitric monoxide *via* intercalation.

Intercalation chemistry of layered mixed oxides attracts much attention from structural as well as functional viewpoints. Generally, however, layered mixed oxides are rather difficult to use as intercalation hosts except for simple ion exchange reactions, because of their much higher charge density of layers compared to those of clay materials. Thus, previous studies of this area were limited to several conventional materials such as titanates and niobates. We now report the rapid intercalation of nitric oxide into the double-layered cuprate, $La_{2-x}Ba_xSrCu_2O_6$.

The layered cuprate $La_{2-x}Ba_xSrCu_2O_6$ was prepared by calcination of powder mixtures of La_2O_3, $BaCO_3$, $SrCO_3$ and CuO at 1050 °C in dry air. The product was treated with water vapour (20 kPa) at 60 °C for 48 h prior to the reaction with NO, which was carried out at 250 °C in a conventional flow reactor. A gaseous mixture of 1 vol% NO/He was fed to the sample packed in a quartz tube (6 mm i.d.). The uptake of NO was determined with an online gas chromatograph with a Porapack-Q column. Rapid NO uptake was observed for $x \geqslant 0.5$; the absorption rate was initially *ca.* 1.0 mol mol^{-1} min^{-1} and gradually decreased with time. After 90 min of the reaction, the amount of cumulative NO uptake exceeded 0.6 mol (mol $cuprate)^{-1}$. Such a large NO uptake suggests that the reaction is not limited to near the surface of the cuprate (BET surface area of the sample less than 2 m^2 g^{-1}). The rate of NO uptake was strongly dependent on the temperature, being negligible below 100 °C or above 300 °C. Also, the NO uptake could not be observed over the cuprate unless pre-treated with water vapour.

Changes of the crystalline phase during the reaction with water vapour and NO were studied by powder XRD and TEM observation. The XRD patterns of the sample (x = 0.5) as prepared in dry air was similar to that of the tetragonal double-layered cuprate, so-called '2126' type, which is related to tetragonal La_2CuO_4 by replacing the layer of octahedra by a double layer of CuO_5 pyramids (see Fig. 2).[1,2] However, the [001] electron diffraction apparently demonstrates the $3a \times 3a$ superlattice reflection [Fig. 1(*a*)]. This superstructure was observed only at $x \approx 0.5$, probably resulting from the ordered substitution of Ba in the interlayer La/Sr matrix. La and Sr appear to be randomly distributed over interlayer sites as pointed out by Nguyen *et al.* for $La_2SrCu_2O_6$.[1] Another possibility is that the superstructure is due to non-stoichiometry of oxygen. Because of Ba substitution for La, the oxygen content must deviate from the ideal value for $La_2SrCu_2O_6$. From the $[1\bar{1}0]$ diffraction [Fig. 1(*b*)], the conditions of reflection are hkl, $h + k + l = 2n$, which agree with those of $La_2SrCu_2O_6$ with the I_4/mmm space group.[1] The interlayer distance of the double-layered cuprate is reflected by [00l] rows as represented in Fig. 1(*c*). The fresh sample showed the periodicity of d_{002} = 1.0 nm, which is close to that of unsubstituted $La_2SrCu_2O_6$. As can be seen from the decreased spacing of the [00l] reflection spots, the interlayer periodicity increased discretely to d_{002} = *ca.* 1.2 nm on exposure to saturated water vapour at 60 °C for 48 h. A further increase of the interlayer periodicity was brought about by the subsequent reaction with 1%NO/He at 250 °C. In this case, d_{002} increased to *ca.* 1.4 nm after 0.6 mol (mol $NO)^{-1}$ was absorbed into the sample [Fig. 1(*d*)]. These changes of the d_{002} value coincided with the shift of the (002) X-ray reflection to lower angles. During these processes, not only was there an absence of structural change along the *ab* plane but also precipitation of second phases was not observed from electron and X-ray diffraction measurements. These results suggest that absorbed H_2O as well as NO molecules should be intercalated into the interlayer spacing of the bulk material.

Fig. 2 shows the typical TEM image of the corresponding sample (x = 0.5, water-treated) before and after NO uptake at 250 °C. The most typical contrast of the image [Fig. 2(*a*)] consists of rows of small white dots lined up along *a* and separated by black dots correlating to Ba, La or Sr. These lead to two types of black-contrast lines with different widths. Evidently, these contrasts reflect the two different types of interlayers, I and II in Fig. 2, which face the base and the top of CuO_5 pyramids, respectively. Even in the NO-intercalated sample [Fig. 2(*b*)], the same layered structure was retained, but the interlayer distance was apparently expanded to produce larger white dot-contrast in a row along *a*.

Interestingly, lattice expansion along the *c* axis after exposure to water vapour and NO occurred only at $x \geqslant 0.5$. Barium species with strong basic character seems indispensable to promote the solid–gas reaction with H_2O and NO. Mixed oxides containing Ba and Cu are well known to be reactive to nitric oxides.[4–7] As in previous reports by Machida *et al.*,[4,5] for instance, Ba–Cu–O mixed oxides react readily with gaseous NO, but in that case the solid–gas reaction produces barium nitrate or nitrite, which were not observed in the present system. The solid–gas reaction between NO and the double-layered cuprate is characterized by the absence of such a second phase precipitation. *In situ* FT-IR measurement during the intercalation showed the appearance of absorption peaks ascribable

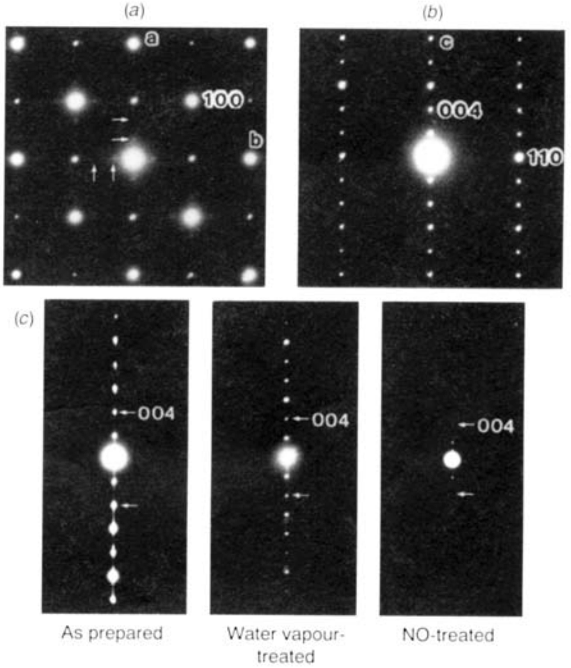

Fig. 1 Electron diffraction patterns of $La_{1.5}Ba_{0.5}SrCu_2O_6$: (*a*) [001] and (*b*) $[1\bar{1}0]$ patterns of as-prepared sample; (*c*) [00l] rows observed in [hk0] patterns of as-prepared, water vapour-treated and NO-treated samples. Arrows in (*a*) indicate superstructure reflections.

to OH stretching (3600 cm^{-1}) and ONO stretching vibrations (1385 and 1270 cm^{-1}), but the absence of HOH bending and any other N–O vibrations. Thus, intercalated H_2O and NO are converted to hydroxide and nitrite ions, respectively, in the interlayer spacing.

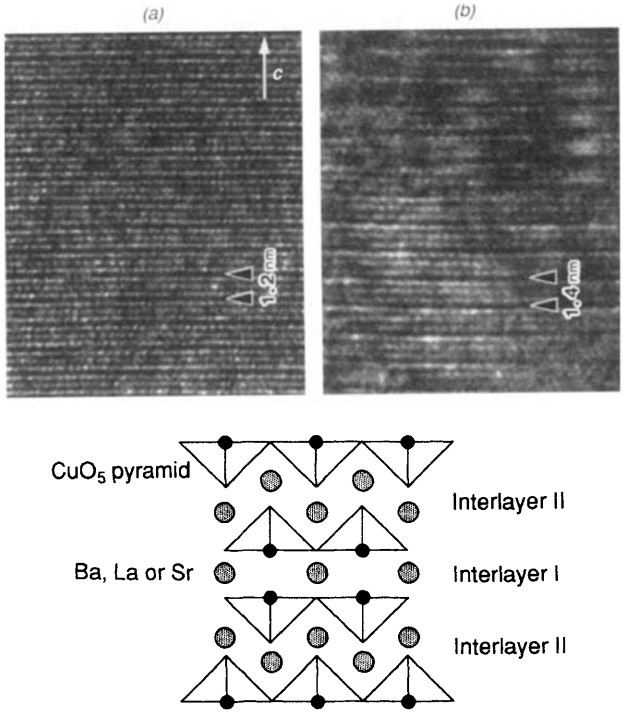

Fig. 2 TEM image with incident beam parallel to *ab* plane: (*a*) water vapour-treated, (*b*) NO-treated sample

The resulting intercalation compound between NO and the double-layered cuprate was stable in air up to *ca.* 300 °C. Some of the intercalated NO was eliminated by heating to 500 °C, but the rest remained even after heating to 800 °C. Recently, a new superconductor containing nitrate groups in a '123-type' cuprate was reported by Raveau and coworkers.[7,8] They introduced nitrate groups into the cuprate by using $Ba(NO_3)_2$ as a starting material. The present study demonstrates another continent route for the introduction of nitrate groups into layered cuprates, which might be a possible way to develop a new superconductor. Actually, since the NO intercalation resulted in a large chemical shift (+0.8 eV B.E.) of the Cu $2p_{3/2}$ XPS signal, the intercalated NO molecules must lead to strong charge transfer with Cu. The NO-intercalation is to be expected to control the electroconductivity of the double-layered cuprate.

Financial support by Nissan Science Foundation and The Sumitomo Foundation is gratefully acknowledged.

Received, 29th November 1994; Com. 4/07300B

References

1 N. Nguyen, L. Er-Rakho, C. Michel, J. Choisnet and B. Raveau, *Mater. Res. Bull.*, 1980, **15**, 891.
2 R. J. Cava, B. Batlogg, R. B. van Dover, J. J. Krajewski, J. V. Waszczak, R. M. Fleming, W. F. Peck, L. W. Rupp, P. Marsh, A. C. W. P. James and L. F. Schneemeyer, *Nature*, 1990, **345**, 602.
3 K. Tabata, H. Fukui, S. Kohiki, N. Mizuno and M. Misono, *Chem. Lett.*, 1988, 799.
4 M. Machida, K. Yasuoka, K. Eguchi and H. Arai, *J. Chem. Soc., Chem. Commun.*, 1990, 1165.
5 M. Machida, S. Ogata, K. Yasuoka, K. Eguchi and H. Arai, *Proc. Int. Cong. Catal.*, 1993, 2645.
6 H. Arai and M. Machida, *Catal. Today*, 1994, **22**, 97.
7 A. Maignan, M. Herview, C. Michel and B. Raveau, *Physica C*, 1993, **208**, 116.
8 M. Hervieu, C. Michel and B. Raveau, *Chem. Mater.*, 1993, **5**, 1126.