JOURNAL OF SOLID STATE CHEMISTRY 98, 245–251 (1992)

The Modulation of the Monoclinic $Bi_2Sr_2CuO_{6+\delta}$ Phase

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Received November 26, 1990; in revised form November 21, 1991

A polycrystalline sample of the monoclinic phase $Bi_2Sr_2CuO_6$ has been prepared. The displacive modulation, also present in other compounds of the Bi–Sr–Ca–Cu–O system, has been investigated by means of both electron diffraction and electron microscopy. The modulation is commensurate but it is affected by a strong instability. Discommensurations produce an incommensurate modulation that, in our sample, does not have a well ordered periodicity; this is likely due to a partial disorder of the excess oxygen atoms. A higher-order superstructure (eightfold), also found in the same preparation, is also affected by discommensurations.

Introduction

The superconducting phase in the Bi–Sr–Cu–O system was believed to have the composition $Bi_2Sr_2CuO_6$ as deduced from crystal structure refinements (*1, 2*). Nevertheless, some Sr deficiency is generally found by electron microprobe analysis (*3, 4*). In fact, it is known that in the Bi–Sr–Cu–O system a solid solution $Bi_2Sr_xCuO_6$($x \simeq 1.5$–1.9) exists (*5*). Although the exact values of x may also depend on the Bi content, which seems to be frequently in excess (*6*), the stoichiometric value ($x = 2$) does not seem to be included in the existence range of the solid solution.

Chakoumakos *et al.* (*5*) showed that the ideal composition $Bi_2Sr_2CuO_6$ has a new layered structure with a shorter stacking repeat ($c \simeq 23.6$ Å as deduced from the d_{001} spacing in the assumption that it was still pseudotetragonal) while maintaining the magnitude of the basal plane ($a = b \simeq \sqrt{2}a_p$, $a_p \simeq 3.8$ Å). This new phase was called the "collapsed phase" and is non superconducting. Roth *et al.* (*7*) found that their crystals having the ideal composition $Bi_2Sr_2CuO_6$ had monoclinic symmetry (S.G. *C2/m* or *Cm*). There is then no collapsing, and the decreasing of the d_{001} spacing observed by Chakoumakos *et al.* (*5*) is only due to the change from orthorhombic to monoclinic symmetry. The cell dimensions found, having a commensurate lattice, were $a = 24.493(2)$ Å, $b = 5.4223(5)$ Å, $c = 21.959(2)$ Å, and $\beta = 105.40(1)°$. Nevertheless they also reported that incommensuration effects were sometimes observed by diffraction.

In any case the modulation would correspond to a fourfold ordering, while a fivefold one is observed in the related superconducting phase (*8*).

In a previous paper (*9*) we showed that in the Sr-poorest phase ($1.3 < x < 1.6$) of the pseudotetragonal $Bi_2Sr_xCuO_y$ solid solution, an incommensurate fourfold modulation is

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0022-4596/92 $5.00

present. Hence we proposed the existence of an incommensurate–commensurate transformation as a function of the Sr content. A possible model for the transformation was discussed in the assumption of Tarascon's model (*10*) (insertion of oxygen atoms in the Bi–O double layers). Evidence of a higher-order superlattice in the monoclinic phase was also reported and the family $Bi_{2m}Sr_{2m}Cu_mO_{6m+1}$ ($m > 1$) with $a \simeq 24.5$ Å, $b \simeq \sqrt{2}a_p$, $c \simeq m\sqrt{2}a_p$, $\beta \simeq 105.5°$ ($a_p \simeq 3.8$ Å) was proposed (*9*).

In view of the apparent capability for oxygen accommodation shown by this compound, we focused on studying the monoclinic phase by means of electron diffraction and electron microscopy. We present here a more detailed study of the modulation of the monoclinic phase $Bi_2Sr_2CuO_6$ that reveals a variety of order–disorder phenomena.

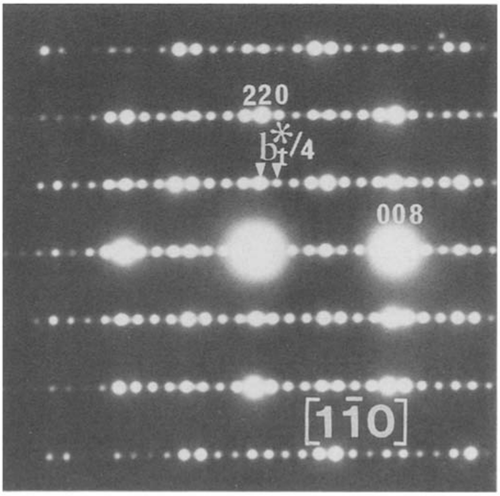

FIG. 1. Electron diffraction pattern of a crystallite from the monoclinic phase in the Bi–Sr–Cu–O system showing a commensurate modulation along the c^*_{monoc}-axis ($q = \frac{1}{4} b^*_{tet}$). Zone axis $[1\bar{1}0]_{monoc}$.

Experimental

A polycrystalline sample with nominal composition $Bi_2Sr_{2.1}CuO_y$ was prepared by ceramic processing. The appropriate ratios of Bi_2O_3, $SrCO_3$, and CuO (Merck A.R.) were mixed and calcined in air at 800°C for 24 hr in platinum crucibles. The product was pressed into pellets and then treated again in platinum crucibles at 840°C for 24 hr.

The composition of the compound obtained was determined by analytical electron microscopy (AEM) using a JEOL 2000FX apparatus. Data were collected from different thin crystallites put on a nylon grid coated with carbon film. The composition was calculated using the ratio method (*11, 12*).

X-ray diffraction experiments were done on a Siemens D-500 instrument. Silicon was used as internal standard.

Electron diffraction and electron microscopy were performed on a JEOL 2000FX microscope. Several fresh samples were prepared and observations were done carefully so as to avoid irradiation effects.

Results and Discussion

The composition determined for the sample with nominal composition $Bi_2Sr_{2.1}CuO_y$ corresponds to the formula $Bi_{2.1(1)}Sr_{2.01(1)}CuO_y$. The numbers in parentheses indicate the standard deviation of the average value determined from 12 crystallites. The obtained values point to the ideal composition $Bi_2Sr_2CuO_6$, although a broad spread of bismuth contents is observed.

The corresponding X-ray diffraction pattern can be indexed with the monoclinic cell proposed by Roth *et al.* (*7*). The refinement by the least-squares method of the *d*-spacing data gave the cell parameters $a = 24.49(2)$ Å, $b = 5.412(5)$ Å, $c = 21.93(1)$ Å, and $\beta = 105.5(1)°$. The *a*, *b*, and *c* parameters can then be related to the corresponding values of the pseudotetragonal solid solution ($a_{tet} = \sqrt{2}a_p$, $c_{tet} = 24.6$ Å) by $a_{monoc} \simeq c_{tet}$, $b_{monoc} \simeq a_{tet}$, and $c_{monoc} \simeq 4\, b_{tet}$.

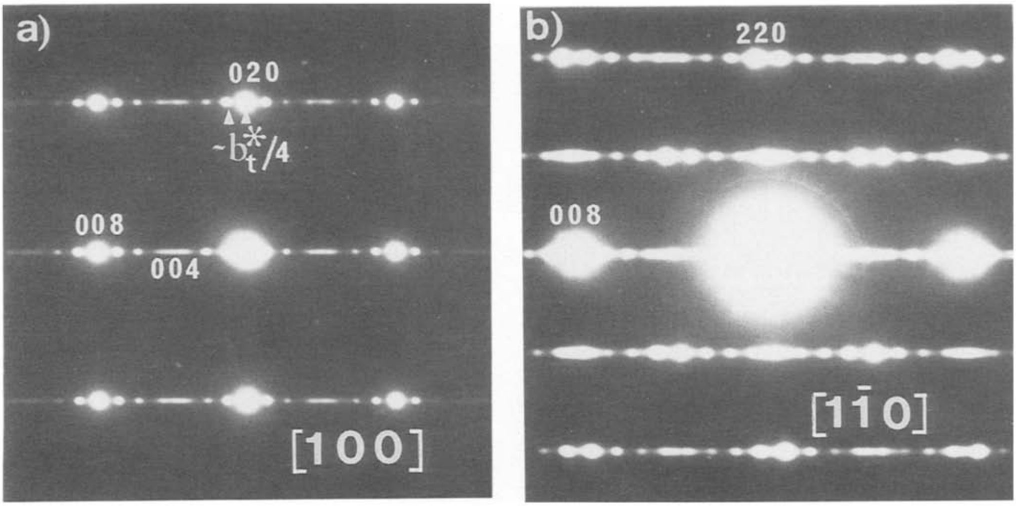

FIG. 2. Typical electron diffraction patterns of a crystallite from the monoclinic phase affected by streaking along the c^*_{monoc} direction. The modulation is incommensurate with $q = 0.263\ b^*_{\mathrm{tet}}$. Zone axis $[100]_{\mathrm{monoc}}$ (a); zone axis $[1\bar{1}0]_{\mathrm{monoc}}$ (b).

The fourfold superstructure is clearly seen by means of electron diffraction. Figure 1 shows an electron diffraction pattern taken with the beam parallel to the [1$\bar{1}$0] direction. The spots are equally spaced, so the modulation is commensurate and the pattern can be fully indexed with the above cell. In connection with the solid solution $Bi_2Sr_xCuO_6$, $x < 1.9$ (where incommensurate ordering is found), this could be interpreted as an incommensurate–commensurate transformation that occurs when the Sr content reaches the ideal content. This transformation is accompanied by a structural distortion to lower symmetry. On the other hand, it appears that the commensurate ordering, which may be due to the full occupancy of Sr sites (*9*), must be rather unstable, since the majority of the electron diffraction patterns revealed the presence of monoclinic crystallites exhibiting incommensurate modulations with periodicities close to the one observed for the commensurate phase.

Figure 2 shows two electron diffraction patterns taken along [100] and [1$\bar{1}$0] mono-

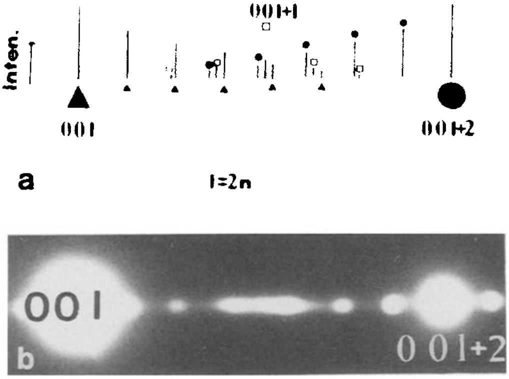

FIG. 3. (a) A schematic intensity distribution along the c^* direction of both substructure and satellite reflections in electron diffraction experiments for an incommensurate modulation ($q = 0.263\ b^*$). Satellite intensities are expected to vary with the satellite order. The $00l$ ($l = 2n + 1$) substructure reflection has a weaker intensity than the $00l$ ($l = 2n$) substructure reflection, and hence the satellites of the former will be weaker than those of the latter. (b) Observed intensity distribution of the same modulation in the same direction. The strong streaking is observed near the $00l$ ($l = 2n + 1$) substructure reflections.

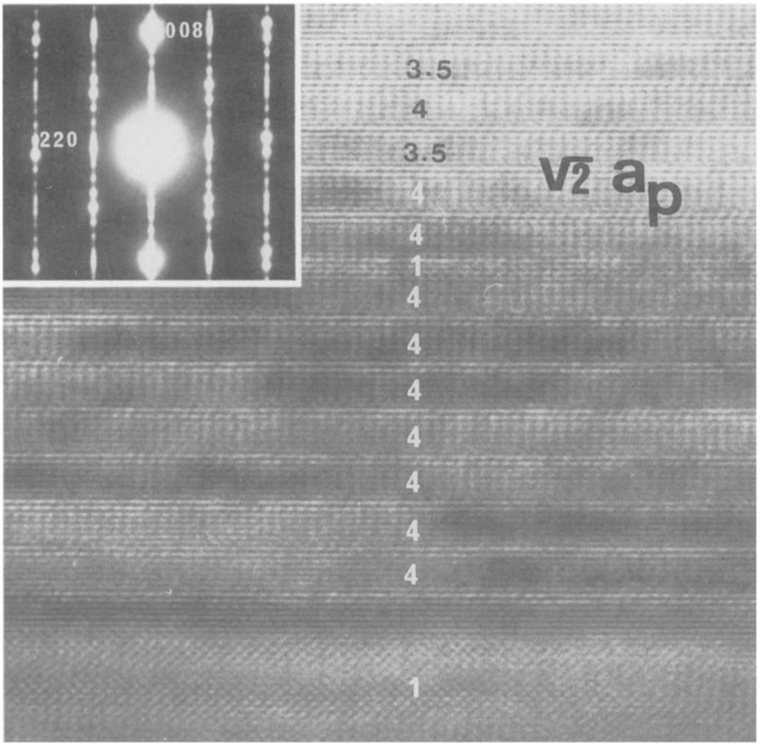

FIG. 4. Electron micrograph of a crystallite showing three different areas where the oxygen excess content is different. The number on the fringes indicates the number of $\sqrt{2}a_p$ blocks that the fringe contains along the c-axis. Fringes with $4\sqrt{2}a_p$ and $3.5\sqrt{2}a_p$ dimension would correspond with the presence of an additional oxygen atom every eight or seven Bi atoms rows, respectively. There are also areas (bottom) where the perovskite substructure $\sqrt{2}a_p \times \sqrt{2}a_p$ can be seen, indicating the absence of oxygen excess. The inset shows the corresponding electron diffraction pattern.

clinic directions, respectively. Although the patterns are affected by streaking along the c_{monoc} direction, they can be indexed using the same monoclinic cell. As can be seen the streaking is more evident near to the (hkl) $k + l = 2n + 1$ reflections of the monoclinic substructure, i.e., without considering the modulation (the spot labeled 004 would be 001 in the substructure). This effect seems to be due to two different reasons. First, the modulation is now incommensurate ($c_{\text{monoc}} \simeq 3.8\ b_{\text{tet}}$) with a large modulation amplitude as deduced from the presence of high-order satellites. Second, the (hkl) $k + l = 2n + 1$ reflections of the monoclinic substructure are in this case weaker than those corresponding to $k + l = 2n$, as is evident from Fig. 2a comparing, for example, the spot labeled 008 (004 in the substructure) with the spot 004 (001 in the substructure). Hence the satellites of the former kind of reflections will be weaker than those corresponding to the latter reflections. In Fig. 3a we show a schematic distribution of satellite positions and their respective intensities where, as expected, these vary with the satellite order. In the observed distribution (Fig. 3b) the streaked areas would correspond to the accumulation of satellites originating from different basic

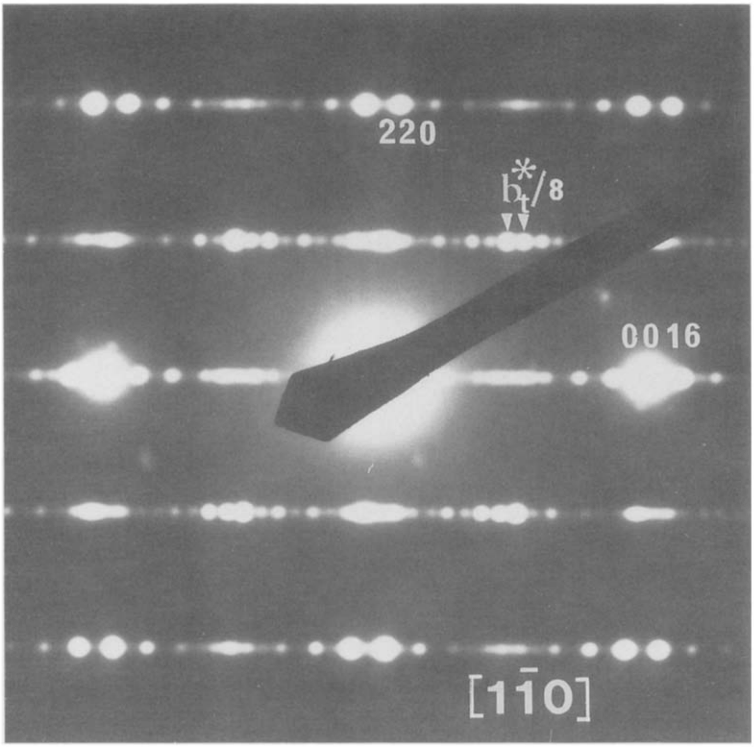

FIG. 5. [110] zone axis of a crystallite from the monoclinic phase showing the presence of an eightfold commensurate modulation along c^* ($c = 8b_{tet}$).

reflections. Nevertheless, in addition to this, streaking is also observed near the first-order incommensurate satellites of the (hkl) $k + l = 2n$ substructure reflections, (for example, first-order satellites of the spot labeled 008 (002 in the substructure) of Fig. 2a), indicating that the periodicity of the modulation is not well ordered. In accordance with this, the corresponding micrograph, Fig. 4, shows a lack of regularity along the c_{monoc} direction. The separation, along that direction, of most of the fringes, is $4\sqrt{2}a_p$. This would correspond to the introduction of an extra oxygen every fourth unit cell, i.e., each eight Bi atom rows (*10*). The presence of some fringes of $3.5\sqrt{2}a_p$ dimension (extra oxygen each seven Bi atom rows) and areas of fringes separated by $\sqrt{2}a_p$, which implies either no extra oxygen or one extra oxygen every two Bi atom rows, would produce the disordering effect that we showed in the corresponding electron diffraction pattern, although it can not solely justify the strong streaking near the hkl ($k + l = 2n + 1$) reflections of the monoclinic substructure (see above).

The existence of either a commensurate modulation or an incommensurate modulation with closely related periodicity suggests that the well ordered fourfold superstructure is disturbed by discommensurations rather than by a change in the origin of the structural deformation. The structural deviation could lose its coherence by interaction with defects present in the crystal. Such kind of instabilities are able to affect some commensurate modulations (*13*). Some early interesting examples were studied in

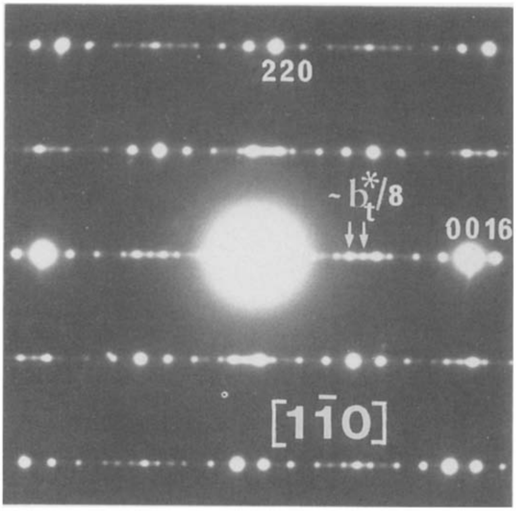

FIG. 6. Electron diffraction pattern showing an incommensurate modulation with periodicity close to eight ($c \simeq 8b_{\mathrm{tet}}$).

neutron- and electron-irradiated samples of 1T-TaS_2 and TaS_3 by means of electron diffraction experiments (*14*). In this case the fraction of defects (displacement of Ta atoms) was related to the irradiation doses.

In any case, in the pseudotetragonal solid solution the quantity of Sr vacancies seems to be large enough to avoid the formation of a commensurate modulation. In the monoclinic phase, AEM experiments have revealed that although the average composition is near $Bi_2Sr_2CuO_6$, there are many crystals with simultaneously a slight Sr deficiency and a Bi excess. As proved in other systems, the kind of discommensurations discussed above can happen at very low concentrations of defects (*14*). Nevertheless, the defects have to be near enough so as to avoid that the perturbed coherence of the structural deviation be adequately matched (*13*). The presence of small quantities of either Sr vacancies, bismuth atoms placed in Sr sites or the disordered oxygen excess, perhaps as a consequence of such defects, could be responsible for the discommensuration. In this respect the electron diffraction pattern showed in Fig. 1 would then correspond to a particularly well ordered crystal.

On the other hand, we have also found the same discommensuration effect in crystals exhibiting a higher periodicity. The $m = 8$ member of the previously proposed (*9*) family $Bi_{2m}Sr_{2m}Cu_mO_{6m+1}$ ($m > 1$) can also be found in either a commensurate or an incommensurate version (see Figs. 5 and 6).

Conclusions

The commensurate modulation of the monoclinic phase that can be related to the full occupancy of the Sr sites is affected by a strong instability. The discommensuration effect disturbing the coherence of the structural deviation produces a similar but incommensurate modulation. So, crystals exhibiting this kind of modulation are easier to find than those with commensurate modulation. Further, the incommensurate fourfold modulation does not have a well ordered periodicity due to the accommodation of different oxygen excess.

The large number of Sr vacancies present in the pseudotetragonal solid solution seems not to allow the existence of an analogous commensurate modulation, and the incommensurate modulation would be the only one found, as we had observed previously (*9*).

The origin of the monoclinic distortion has to be investigated, but this depends on the preparation of a further well ordered monoclinic phase. Work on this matter concerning both the $m = 4$ and $m = 8$ members of the family $Bi_{2m}Sr_{2m}Cu_mO_{6m+1}$ ($m > 1$) is now in progress.

Acknowledgments

We thank Professor A. K. Cheetham for early discussion concerning the problem of Sr vacancies in this system. The authors also thank the "Centro de Microscopía Electrónica," UCM, for technical assistance and CICYT (Grant MAT88/0250) and "Fundación Domingo Martínez" for financial support.

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