

Room temperature (2a x 2b) superstructure formed in Sr-substituted Bi₂ (Sr_{1.6}Y_{0.4})CaCu₂O_y single crystals

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Room temperature ($2a \times 2b$) superstructure formed in Sr-substituted $\text{Bi}_2(\text{Sr}_{1.6}\text{Y}_{0.4})\text{CaCu}_2\text{O}_y$ single crystals

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Abstract

Yttrium-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) superconducting single crystals with a nominal Sr-deficient composition of $\text{Bi}_2(\text{Sr}_{1.6}\text{Y}_{0.4})\text{CaCu}_2\text{O}_y$ ($\text{BS}_{1.6}\text{Y}_{0.4}\text{CCO}$) have been investigated by transmission electron microscopy (TEM). In addition to the normal Y-doped phase which has the similar structure as that of the 2212 phase, a new phase has been observed which is also based on the 2212 structure but a ($2a \times 2b$) superstructure (a and b are lattice parameters) was found superimposed on the intrinsic modulation structure. Regions containing the normal Y-doped 2212 phase and the new phase, respectively, arrange alternately along the a -direction and the interface planes are parallel to the (100) lattice planes. A much higher Y concentration than the nominal value has been detected for the new phase and an ordering in CuO_2 planes of the 2212 structure is suggested to be responsible for the formation of the ($2a \times 2b$) superstructure. © 1997 Elsevier Science B.V.

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Keywords: Bi–Sr–Y–Ca–Cu–O; Microstructure; Transmission electron microscopy

1. Introduction

The study on effects of elemental substitution or chemical doping on the properties of high transition temperature (T_c) superconductors are helpful to elucidate many features of the mechanism for superconductivity. For example, a wide range of elemental substitutions in superconducting compounds were carried out in an attempt to identify functions of the substituting elements. For the 2212 phase, much attention

is generally devoted to the substitution by Ln^{3+} ions ($\text{Ln} = \text{Y}, \text{Nd}, \text{Eu}, \text{Gd}$ or Lu) especially by Y^{3+} [1–22]. It has been found that the substitution of Ca^{2+} by Y^{3+} in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ ($\text{BSC}_{1-x}\text{Y}_x\text{CO}$) introduces a reduction of the hole carrier concentration [8,20] and T_c decreases with increasing x value. A superconducting–non-superconducting transition takes place when $x = 0.3$ – 0.6 [1,3,4,6–8,13,16,18,20]. In these earlier studies, the decrease or disappearance of T_c was attributed to a redistribution of the excess oxygen or the valence change of Cu ions.

From the structure point of view, two remarkable features have been noticed for the partially Ca-substituted $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$: one is the con-

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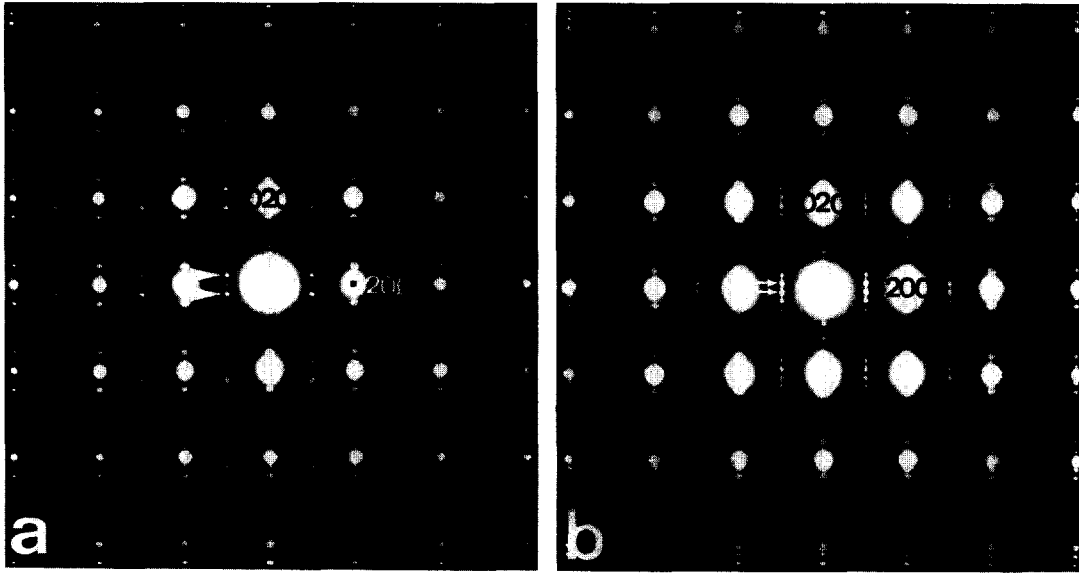


Fig. 1. [001] SAED patterns for (a) the normal Y-doped 2212 phase, and (b) the Y-doped phase based on the 2212 structure but with a modulation period twice as that in (a). Arrowheads in (a) indicate the typical 2212-type satellite reflections and small arrows in (b) indicate the satellite reflections corresponding to the double (2λ) modulation period in real space.

tinuous decrease of the c -parameter with increasing Y content [3,4,6,7,9,15,20]; another is the formation of a phase (denoted hereafter as $(2212)_{2\lambda}$) with a modulation period approximately twice as that (λ) of the normal 2212 phase [2,8,20,22]. Selected-area electron diffraction (SAED) patterns along the [001] zone-axis of the normal 2212 phase and the $(2212)_{2\lambda}$ phase are shown in Figs. 1a and 1b, respectively. Note the different spacing between satellites along the b^* -direction. In a previous study, we pointed out that the $(2212)_{2\lambda}$ phase is closely related to, and often coexists with, the normal Y-doped 2212 phase and Y concentration in the $(2212)_{2\lambda}$ phase is much higher than that in the coexisted 2212 phase [22]. Y^{3+} ions in $(BiO)_2$ -SrO rock-salt blocks in the 2212 structure have been suggested to be responsible for the formation of the $(2212)_{2\lambda}$ phase [22]. In order to examine more about the effects of Y-substitution on the 2212 structure, we prepared Sr-substituted 2212 single crystals with a nominal composition of $Bi_2Sr_{1.6}Y_{0.4}CaCu_2O_y$. TEM investigations revealed formation of the normal Y-doped 2212 phase and a new phase with a $(2a \times 2b)$ superstructure ($a \approx b = \sqrt{2}a_p$, p refers to the perovskite unit cell).

2. Experimental

Single crystals with a nominal composition $Bi_2(Sr_{1.6}Y_{0.4})CaCu_2O_y$ and $Bi_2Sr_2CaCu_2O_y$ were grown by a traveling-solvent floating-zone technique. Details about the preparation process can be found in Ref. [23]. The as-grown single crystals present a plate-like shape with the minimum size along the c -direction. For the Sr-substituted crystals, superconductivity takes place at an onset transition temperature (T_c , onset) of about 40 K which is derived from ac-susceptibility measurements. After annealing at 500°C for 48 h in air followed by 72 h at 400°C and quenched to room temperature, the T_c , onset becomes 57 K.

Samples for TEM characterization were prepared from annealed crystals. The surface of the TEM samples is set to be parallel to the (001) crystallographic planes therefore TEM observations along the c -direction can be performed. A segment of the crystal was crushed into small pieces and these small crystal pieces with random orientations were dispersed on Ni grids so that it is possible to study the structure along directions perpendicular to the c -direction. Samples were examined by a JEOL 4000 EX (400 kV) and a Philips CM20 (200 kV) transmission electron

microscope equipped with a Link system for energy-dispersive X-ray spectroscopy (EDS).

3. Structural characterization

In spite of the Sr-deficiency in the samples studied, a well characterized 2212 structure is found in most areas. θ - 2θ X-ray scan with the incident Cu ($K\alpha$) X-ray beam at an angle θ with respect to the crystal plate revealed only the $(00l)$ reflections of the normal Y-doped 2212 phase with a c -value of 30.38 Å. Small shoulders have been observed for the $(00l)$ peaks at the higher angle side, implying an “impurity” with a similar structure but a smaller c -value of 30.30 Å compared with the normal Y-doped 2212 phase. Accord-

ing to the intensity of reflections, we can conclude that only a small volume of such impurity exists. We will demonstrate later that this impurity corresponds to a 2212-type phase with a new structural modulation.

Fig. 2 shows the typical $[001]$ and $[110]$ SAED patterns taken from the Y-doped 2212 phase formed in most areas of the present single crystals. Typical 2212-type incommensurate modulation with a modulation period of about $5b$ ($b \approx 5.4$ Å) in real space is presented by the satellite reflections in the $[001]$ SAED pattern shown in Fig. 2a. However, a new phase was found to grow adjacent to the normal Y-doped 2212 phase in some regions which can be a few tens of microns in linear size along the $(a-b)$ plane. This is depicted in a bright-field image shown in Fig. 3a. Quite periodic intergrowth of two regions can be seen due to different image contrast: slabs with a darker contrast (marked by the letter B) and slabs with a brighter contrast (marked by the letter I) have a width of about 0.5 and 1 μm , respectively. The $[001]$ SAED patterns from region I and region B are shown in Figs. 3b and 3c, respectively, and the diameter of the selected area is about 0.2 μm on the sample surface. According to the 2212 characteristics shown in Fig. 3b, region I contains the normal Y-doped 2212 phase (denoted as $(2212)_I$ phase). In Fig. 3c, typical 2212 characteristics are also presented including the incommensurate modulation along the b^* -direction. However, extra $(hk0)$ reflections appear at $h = m/2$ and $k = n/2$ ($m, n = 0, 1, 3, 5, \dots$), giving rise to additional reflection rows as indicated by arrowheads. These additional reflections indicate a new superstructure with a $(2a \times 2b)$ unit cell ($a \approx b \approx 5.4$ Å). This commensu-

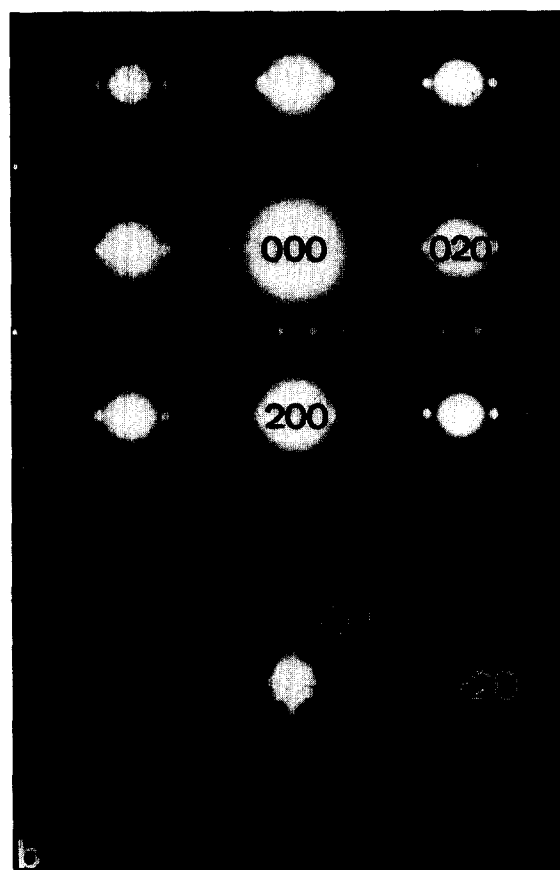


Fig. 2. (a) $[001]$ and (b) $[110]$ SAED patterns taken from $\text{Bi}_2\text{Sr}_{1.6}\text{Y}_{0.4}\text{CaCu}_2\text{O}_y$ single crystals. Main reflections are indexed. 2212-type modulation can be seen in (a) as presented by satellite reflections.

Table 1

Structure parameters a , b , c and modulation wavelength λ for the Y-doped 2212, $(2212)_I$, and $(2212)_{2a}$ phases. Y-doped 2212 denotes $\text{Bi}_2\text{Sr}_{1.6}\text{Y}_{0.4}\text{CaCu}_2\text{O}_y$ phase formed in most areas of the Sr-substituted crystals. $(2212)_I$ and $(2212)_{2a}$ denote Y-doped 2212 phases with the normal 2212-type modulation and the new $(2a \times 2b)$ modulation, respectively (Fig. 3). The compositions for these three phases were determined (see Table 2). $\Delta a = \Delta b < \pm 0.04$ Å (SAED), $\Delta c < \pm 0.01$ Å (X-ray diffraction), $\Delta \lambda < \pm 0.4$ Å (SAED)

Phase	a (Å)	b (Å)	c (Å)	λ (Å)
Y-doped 2212	5.41	5.42	30.38	26.7 (4.9b)
$(2212)_I$	5.41	5.45	30.30	24.8 (4.6b)
$(2212)_{2a}$	5.29	5.44	30.30	24.3 (4.5b)

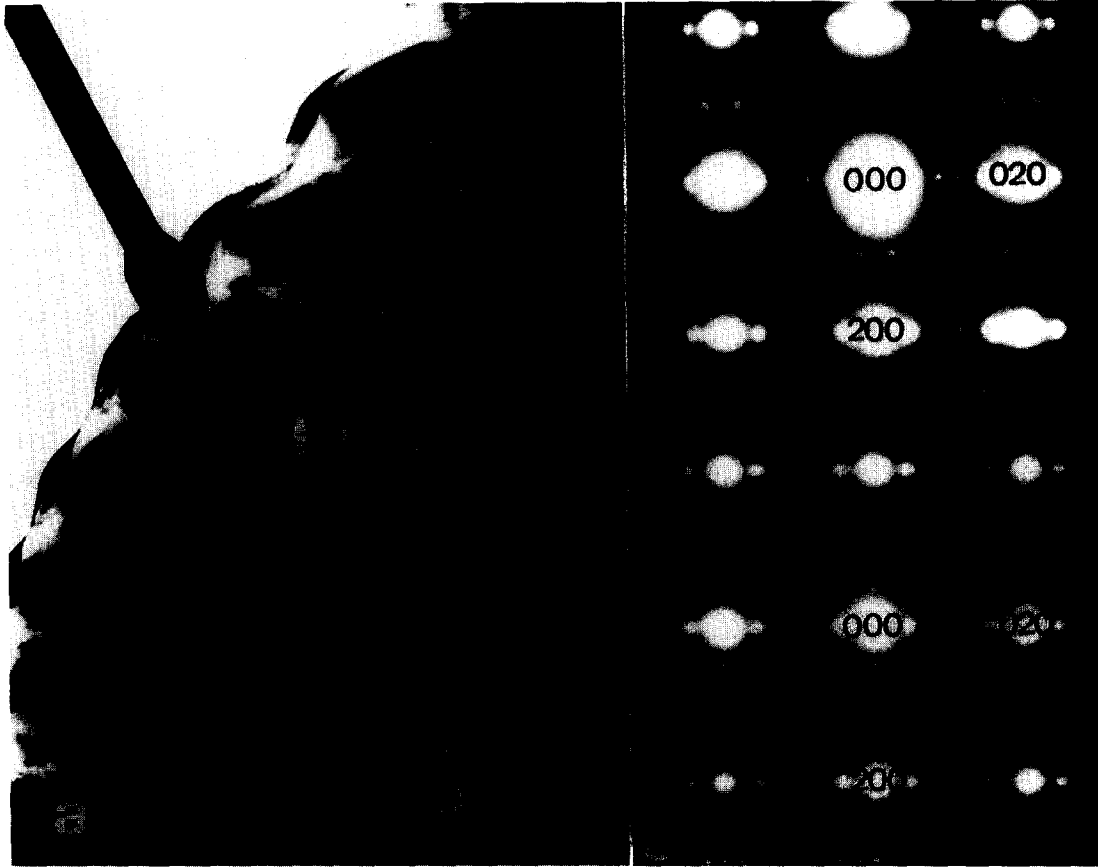


Fig. 3. (a) [001] bright-field image showing alternately arranged slabs (marked by letters B and I) with a darker and a brighter contrast, respectively, formed in the Sr-substituted crystals. SAED patterns obtained from the regions I and B are shown in (b) and (c), respectively. Additional reflection rows corresponding to the $(2a \times 2b)$ modulation in real space are indicated in (c).

rate superstructure superimposes on the intrinsic 2212 incommensurate modulation to form a new phase. We denote this new phase as $(2212)_{2a}$ phase hereafter. The interface planes between B and I regions are parallel to the (100) planes of the 2212 structure. Lattice parameters a and b as well as modulation wavelength λ for the $(2212)_I$ and $(2212)_{2a}$ phases can be determined directly from the corresponding [001] SAED patterns (Figs. 3b and 3c) and a summary of lattice parameters determined by TEM and X-ray diffraction is given in Table 1.

Fig. 4 is a [001] lattice-fringe image from the region B (see Fig. 3a). $11 \text{ \AA} \times 12 \text{ \AA}$ lattice meshes are recognized. Black (or white) fringes, the 11 \AA apart along the a -axis are due to the a -axis component ($2a \approx 11 \text{ \AA}$) of the $(2a \times 2b)$ modulation, while the 12 \AA lattice spacing along the b -axis is

the projected period of the normal 2212-type modulation ($\lambda = 24 \text{ \AA}$) on the (001) plane. Therefore, Fig. 4 indeed confirms two superstructures superimposed on each other. However, the fact that the 11 \AA period ($2b \approx 11 \text{ \AA}$) is too weak to be visible along the b -direction implies an anisotropic feature of the $(2a \times 2b)$ superstructure.

SAED patterns obtained by tilting the samples in the electron microscope allow us to rule out the possibility of double diffraction as the reason of the $(2a \times 2b)$ modulation, and moreover to verify a close relation between the $(2212)_{2a}$ phase and the 2212 phase. By using convergent-beam electron diffraction (CBED) along the [001] direction of the crystal, we were able to obtain the structural information along the c -direction as we have demonstrated in our previous paper [22]. We found that no differ-

Table 2

Chemical composition determined by EDS for the Y-doped 2212, (2212)₁ and (2212)_{2a} phases (see definitions for these phases in the caption of Table 1). The composition for the Y-free 2212 phase determined by electron microprobe is also listed as a comparison. Experimental error < ±0.1

Phase	Nominal formula	Determined composition
Y-doped 2212	Bi _{2.0} Sr _{1.6} Y _{0.4} CaCu _{2.0} O _y	Bi _{2.0} Sr _{1.7} Y _{0.5} Ca _{0.8} Cu _{1.8} O _y
(2212) ₁	Bi _{2.0} Sr _{1.6} Y _{0.4} CaCu _{2.0} O _y	Bi _{2.0} Sr _{1.7} Y _{0.6} Ca _{0.8} Cu _x O _y ^a
(2212) _{2a}		Bi _{2.0} Sr _{1.8} Y _{1.0} Ca _{0.7} Cu _x O _y ^a
Y-free 2212	Bi _{2.0} Sr _{2.0} CaCu _{2.0} O _y	Bi _{2.03} Sr _{2.00} Ca _{0.98} Cu _{2.00} O _{8.26} ^b

^a *x* not quantitatively determined.

^b Determined by electron microprobe.

ence exists between *c*-parameters for the (2212)₁ and (2212)_{2a} phases within experimental error. Therefore the slightly lower *c*-lattice parameter of 30.30 Å detected by X-ray diffraction could correspond to both the (2212)₁ and (2212)_{2a} phases, while the higher *c*-lattice parameter of 30.38 Å is known for the normal Y-doped 2212 phase formed in most areas of the samples. The CBED results also indicate that the (2*a* × 2*b*) commensurate modulation occurs only in the (*a*–*b*) planes.

EDS analyses are performed in B, I regions and regions containing only the normal Y-doped 2212 phase. The electron beam probes areas with a diame-

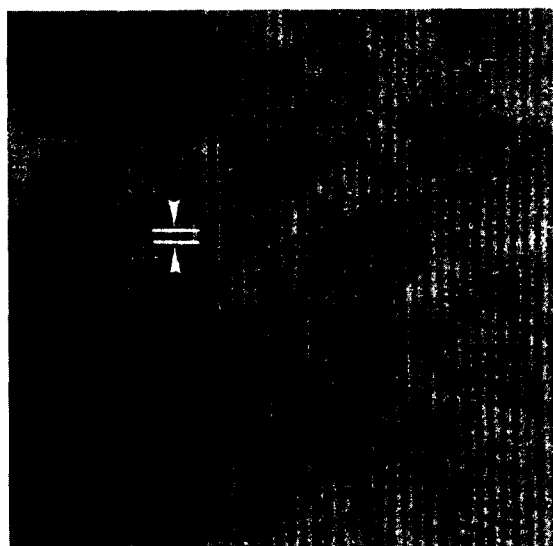


Fig. 4. [001] lattice-fringe image showing a 11 Å × 12 Å lattice-fringe meshes which are a consequence of the overlap between the normal 2212-type modulation and the (2*a* × 2*b*) modulation.

ter of about 0.2 μm. The results are listed in Table 2. Some important points should be noted. First of all, inhomogeneous and phase-related Y³⁺ concentration was found, e.g. compared with other areas, a high average concentration of Y³⁺ in the (B+I) region was detected. A direct consequence of this high Y³⁺ concentration is the decrease of the λ value for the (2212)₁ and (2212)_{2a} phases formed in the (B+I) region with respect to the normal Y-doped 2212 phase formed in other areas. This is in agreement with a tendency of λ change upon Y-doping reported by other groups [7,8,14,15,17]. The Ca contents in the (2212)₁ and (2212)_{2a} phases are all below the nominal value and decrease with increasing Y³⁺. This can only be explained by the partial substitution of Y³⁺ for Ca²⁺ in both phases. However, a higher Y³⁺ concentration for the (2212)_{2a} phase does not yield a lower Sr²⁺ content compared with the (2212)₁ phase, as would be expected from a Y³⁺ substitution for Sr²⁺. We thus speculate that Y³⁺ ions favor to occupy the pre-existed Sr²⁺ vacancies or to replace Ca²⁺ ions in the SrO planes. The Bi content is constant in all regions examined. We did not obtain a quantitative Cu content for the (2212)₁ and (2212)_{2a} phases because of the large experimental error due to the copper washers used to mount the samples for ion-milling during TEM sample preparation. However, there exists a definite evidence from the composition analyses on crushed pieces of the same crystal that the Cu content is quite deficient in the highly Y-doped 2212 phase (Table 2). This Cu-deficiency (Cu_{1.8}) is more significant than Cu_{1.92–1.95} reported by Alméras et al. [25]. Based on Tables 1 and 2, we confirmed that the (2212)₁ phase shown in Fig. 3 is

just the normal Y-doped 2212 phase, while changes in both microstructure and composition occurred for the $(2212)_{2a}$ phase. However, due to the small area and not quite successful isolation of the $(2212)_{2a}$ phase, the physical property is still unknown for this new phase.

4. Discussion

The effect of Y-doping on microstructure may be different depending on the occupation site of Y^{3+} in the 2212 structure. As a result, the 2λ or the $(2a \times 2b)$ superstructures could be formed under different conditions. We will now elaborate this in some more detail.

4.1. Model for the 2λ modulation: Y^{3+} ordering in the SrO planes

According to our previous study, the presence of Y^{3+} in the SrO planes could be the origin of the 2λ period in the $(2212)_{2a}$ phase [22]. The presence of Y^{3+} in the SrO planes was reported by Alm eras et al. [25] and two kinds of positions for Y^{3+} in the SrO planes are possible. First, it has been reported that Ca^{2+} ions could partly replace Sr^{2+} ions in the SrO planes [5,26–28], therefore Y^{3+} ions may replace these Ca^{2+} ions in SrO planes because of the similar size. Second, Y^{3+} ions could occupy Sr vacancies which often exist in the SrO planes even in the Y-free 2212 phase [29]. These two possibilities could take place simultaneously but the latter one is important for the formation of the 2λ modulation. According to Beskrovnyi et al. [30], Sr vacancies in the SrO planes favor locations in the vicinity of the extra oxygen in the BiO layers (see Fig. 5), the inter-distance between Sr vacancies has a period coincident with λ , which is the intrinsic modulation period along the b -axis. In the Ca-substituted 2212 phase, the amount of Y^{3+} in the SrO plane is not enough to fill all Sr vacancies. A Y^{3+} ordering with the 2λ period along the b -axis is thus formed when only half amount of the Sr vacancies are occupied, i.e. one Y^{3+} for every two Sr vacancies. In this model, the 2λ modulation superimposes on the 2212-type intrinsic modulation as already verified experimentally [22].

4.2. Model for the $(2a \times 2b)$ superstructure: ordering in the CuO_2 planes

In the Sr-deficient $BS_{1.6}Y_{0.4}CCO$ crystals studied in this paper, it is reasonable to assume that the amount of Sr vacancies and Y^{3+} ions in the SrO planes are drastically increased compared with the Ca-deficient $BSCa_{0.6}Y_{0.4}CO$. Consequently, the Y^{3+} concentration is too high to form ordering with either 2λ or $(2a \times 2b)$ periods in the SrO planes. The $(2a \times 2b)$ superstructure is also unlikely to take place in the BiO planes as no interference has been observed between the $(2a \times 2b)$ superstructure and the intrinsic 2212-type modulation, which is mainly determined by the BiO double layers. Although the oxygen content in the BiO planes could be changed significantly in the Y-rich $(2212)_{2a}$ phase, and ordering of oxygen vacancies was proposed to cause the $(2a \times 2b)$ superstructure during *in-situ heating* of Pb or Y-doped Bi–Sr–Ca–Cu–O [13,31–33], the ordering of oxygen vacancy is not the reason for the *room temperature* $(2a \times 2b)$ superstructure reported here because the superstructure remains stable under intense electron beam irradiation which could considerably change the density and distribution of the oxygen vacancies in the BiO layers. Actually, according to the conclusion of Beskrovnyi et al., the substitution of Sr^{2+} or Ca^{2+} by Y^{3+} leads to an increase of oxygen content in the BiO planes and eventually all vacancies available for the excess oxygen in the BiO planes are occupied when $Y_{0.7}$ is reached [34]. Based on this result, no oxygen vacancies can be available in the BiO planes in the $(2212)_{2a}$ structure which contains high Y-doping ($Y_{1.0}$). Although extra oxygen induced by the very high Y^{3+} concentration in the (B+I) region could go to the Ca planes which are known to be able to accommodate excess oxygen [15,16], no $(2a \times 2b)$ superstructure has been observed so far in the Ca planes in a number of studies on Ca-substituted samples. Based on the reasons mentioned above, we figured out that the $(2a \times 2b)$ modulation was not formed in the BiO, SrO or Ca layers.

Considering that the lattice parameters a and b of the 2212 phase are mainly determined by the CuO_2 planes, we suggest that the two-dimensional $(2a \times 2b)$ superstructure was formed in the CuO_2 layers. According to the EDS results, large amount of Cu vacancies existed, which are necessary to balance the extra charge induced by the Y^{3+} -doping. Therefore the

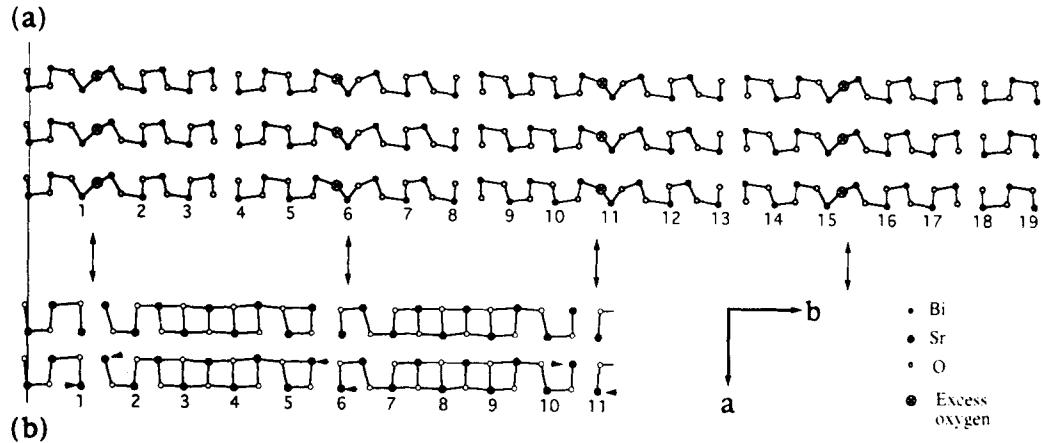


Fig. 5. Configuration of (a) the BiO plane, and (b) the SrO plane refined by Beskrovnyi et al. [29,30]. Sequence numbers in (a) mark the basic unit cells. Arrowheads in (b) indicate the Sr positions which favor to be vacancies. Double-head arrows indicate the modulation period (λ) which is determined by spacing between the positions where excess oxygen atoms are inserted in the BiO plane. Note also the correlation between the modulation period and the separation of the Sr vacancies as indicated by double-head arrows.

$(2a \times 2b)$ superstructure might result from an ordering of Cu vacancies in the CuO_2 planes. In a simplified

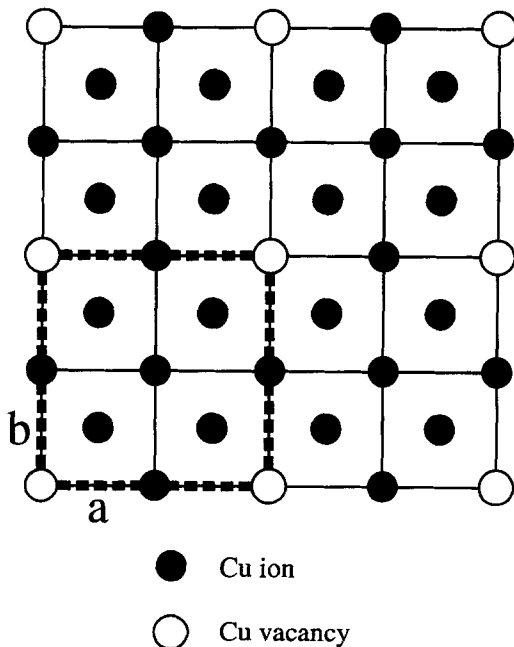


Fig. 6. Schematic drawing of the $(2a \times 2b)$ super unit cell (dashed lines) formed by Cu vacancies in a CuO_2 plane. Only Cu ions and vacancies are displayed in this simplified representation.

model schematically shown in Fig. 6, at least $1/8$ Cu positions are empty to form the $(2a \times 2b)$ superstructure in which the Cu content becomes $\text{Cu}_{1.75}$ which is consistent with the experimental value of $\text{Cu}_{1.8}$ (Table 2). The high Y^{3+} content in the $(2212)_{2a}$ phase could result in a high density of Cu vacancies therefore the formation of the $(2a \times 2b)$ superstructure in the CuO_2 planes is easy to understand. One can also imagine that under favorable growth conditions, Y^{3+} ions could condense around Cu vacancies in the CuO_2 planes to form a Y^{3+} ordering. The significant difference in size and valence between Y^{3+} and Cu^{2+} could yield not only a change of the Cu–O content but also the displacements of Cu and O away from their regular positions in the CuO_2 planes. Such effect was considered as the origin of the $(2a \times 2b)$ superstructures occurring in other superconducting ceramics [35].

5. Conclusion

In Sr-substituted $\text{Bi}_2\text{Sr}_{1.6}\text{Y}_{0.4}\text{CaCu}_2\text{O}_y$ single crystals, the phase which is based on the 2212 structure but has the new $(2a \times 2b)$ commensurate superstructure, was observed growing alternately with the normal Y-doped 2212 phase. A considerably higher Y^{3+} concentration has been detected for this new phase compared with the adjacent normal Y-doped 2212 phase. Our experimental evidence supported the conclusion that the $(2a \times 2b)$ superstructure was formed in the CuO_2 planes.

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