Phase intergrowth in $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ thin films

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The presence of phase intergrowth in Bi-Sr-Ca-Cu-O thin films, *in situ* grown using a laser-ablation technique, has been investigated. A simple intergrowth model has been used to analyze the experimental x-ray-diffraction patterns of the films and has allowed us to measure the stacking-fault proportion in the films. Rutherford-backscattering spectrometry (RBS) has also been used in order to determine the cationic composition. The Bi/Cu ratio obtained by x-ray-diffraction analysis is in very good agreement with the results of RBS analysis. The intergrowth phenomenon allows one to change the structure continuously from one pure phase to another one, a fact that is experimentally observed when the oxygen pressure during deposition is changed.

INTRODUCTION

Since the first reports of superconductivity in the Bi-Sr-Ca-Cu-O system,[1,2] several superconducting phases have been shown to exist in this compound. The nominal composition of these phases can be described by the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$, which is denoted by the cationic stoichiometry 2:2:($n-1$):n. The most widely studied compounds of the family are, of course, those with lower n, namely 2:2:0:1 ($n=1$, $T_c=10$ K), 2:2:1:2 ($n=2$, $T_c=90$ K), and 2:2:2:3 ($n=3$, $T_c=110$ K) phases, although this latter is difficult to obtain and partial Pb substitution for Bi is needed to stabilize the phase.[3] The higher members of the series are not thermodynamically stable, and have been only obtained as thin films, by using layer by layer deposition techniques up to the compound $n=7$.[4]

The two-dimensional character of these materials is even more pronounced than in the Y-Ba-Cu-O system. In fact, their structure is formed by a stacking of oxide planes along the c axis. The basic unit cell can be described as formed by two subunits: a $Bi_2Sr_2O_x$ subunit with NaCl structure and a perovskitelike $Ca_{n-1}Cu_nO_y$ subunit. The only difference between two consecutive phases is the addition of a double $CaCuO_2$ plane into the perovskite subunit, increasing the c parameter [$c \approx 24.6 + 6.2$ ($n-1$) Å, $n=1,2,\ldots$] but with the same value of the a and b axes parameters (5.4 Å).

The film deposition process is performed out of thermodynamic equilibrium. Moreover, if the growth parameters are not appropriate, nonstoichiometric composition of the films may be induced. That means that if the difference of free energies between two consecutive members of the family is low enough (taking into account their structure similitude), then the occurrence of stacking faults is possible. In the Bi family, intergrowth can be achieved if CuO_y layers of the 2:2:0:1 or $Ca_2Cu_3O_y$ layers of 2:2:2:3 structures are substituted for $CaCu_2O_y$ layers of the 2:2:1:2 structure. These faults have been shown by transmission electron microscopy on single crystals.[5] Thus, even for the compounds with low n (2:2:0:1 and 2:2:1:2), it is necessary to consider the possibility of intergrowth.

In this work, we report a quantitative analysis of such defects, using an intergrowth model that explains our experimental x-ray-diffraction (XRD) data. As a result, it is possible to correlate structural and compositional information. The effect of oxygen pressure during deposition on these defects is also discussed.

EXPERIMENT

Thin films of the Bi-Sr-Ca-Cu-O compound were deposited by the pulsed laser-ablation technique as has been previously reported.[6,7] A frequency tripled Nd:YAG laser (supplied by B. M. Industries) with $\lambda=354$ nm was used. The laser pulses, with a 7-ns duration, 5-Hz repetition rate, and an energy density of 1 J/cm2, were focused via a quartz lens onto a rotating Bi-Sr-Ca-Cu-O target which was placed in a high vacuum chamber (10^{-8} mbar base pressure). Polycrystalline ceramic pellets with $Bi_4Sr_3Ca_3Cu_4O_y$ and $Bi_2Sr_2Ca_1Cu_2O_y$ compositions were used as targets. The growth of the films was carried out on MgO (100) single-crystal substrates, heated in the range 660–700 °C, under pure O_2 atmosphere (about 0.1 mbar). After deposition, substrate temperature and oxygen atmosphere were maintained for ten minutes. Then, the heater was turned off and oxygen was removed in order to cool the films in vacuum down to room temperature. X-ray-diffraction spectra were recorded in the Bragg-Brentano geometry, with an automatized powder diffractometer using Cu $K\alpha$ radiation. These measurements have been performed in the Ecole Supérieure de Physique et de Chimie Industrielles de Paris (ESPCI).

The elemental composition and film thickness were obtained by Rutherford-backscattering spectrometry (RBS).

RESULTS AND DISCUSSION

Depending upon the precise growth conditions, pure 2:2:1:2, 2:2:0:1 or multiphase films can be obtained. In fact 2:2:$(n-1)$:n pure phase means $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ structure and $Bi_2(Sr,Ca)_{n+1}Cu_nO_y$ composition due to the mixing of Sr and Ca in their respective sites.[8] Multiphase samples are easily identified by recording their x-ray-diffraction spectra (see Fig. 1), since one can separately observe the Bragg peaks corresponding to each phase. For instance, in a sample composed of a mixture of 2:2:0:1 and 2:2:1:2 textured materials [Fig. 1(a)], the Bragg peaks can be completely indexed by two series of lines (00$2l$) and (00$2l'$), with the c lattice parameters equal to 24.6 and 30.8 Å, respectively. These lines are the ones of the pure 2:2:0:1 phase [Fig. 1(d)] and 2:2:1:2 one [Fig. 1(b)]. This phenomenon implies that pure 2:2:0:1 grains and pure 2:2:1:2 ones are present in the sample. But many XRD spectra have only one set of lines, which does not correspond exactly to the spectra of a pure phase. To understand these spectra, another kind of mixture of both phases has been studied: intergrowth. Intergrowth introduces stacking faults of one phase in a grain of another one. Thus, the long-range periodicity of the structure along the c axis disappears and the effect of intergrowth on the XRD patterns has been studied.

Figure 2 shows the simulation of the XRD intensity spectra, in θ–2θ geometry, for films constituted by 50 cells, $p\%$ with 2:2:0:1 structure and $(100-p)\%$ with 2:2:1:2 structure, randomly distributed. We consider a film with the c axis oriented perpendicular to the substrate, in which only (00l) lines appear. Assuming similar structure factors F for each phase, this x-ray-diffraction intensity can be written as

$$I(\theta,p)=F\left|\sum_{n=1}^{50} e^{iS_n}\right|^2$$
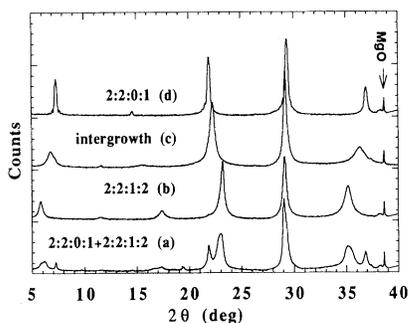
FIG. 1. XRD patterns recorded in θ–2θ geometry of a 2:2:1:2-2:2:0:1 multiphase structure (a), (a) 2:2:1:2 single-phase film (b), a 2:2:0:1-2:2:1:2 intergrowth structure (c), and a 2:2:0:1 single-phase film (d).
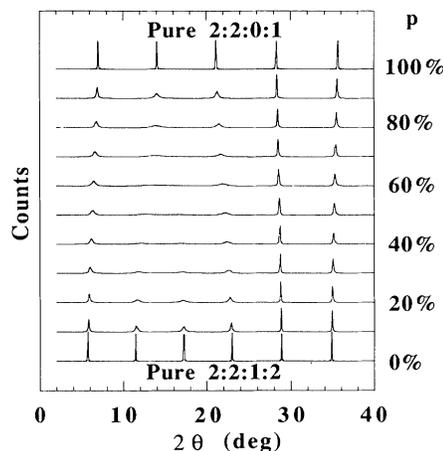
FIG. 2. Simulation of the XRD patterns in θ–2θ geometry of films with intergrowth structures along the c axis [$p\%$ 2:2:0:1 cells, $(1-p)\%$ 2:2:1:2 cells] for $p=0, 10, 20, \ldots, 100\%$.

with

$$S_n = \frac{4\pi \sin(\theta)}{\lambda}[c_n d_{2:2:0:1} + (n-c_n)d_{2:2:1:2}] ,\qquad (1)$$

$c_0=0$; $c_{n+1}-c_n=0$ with a probability $1-p$, and $c_{n+1}-c_n=1$ with a probability p, $\lambda=\lambda_{Cu}=1.54$ Å, $d_{2:2:0:1}=12.3$ Å, and $d_{2:2:1:2}=15.4$ Å. The c-axis parameter is twice the distance between $Bi_2Sr_2O_y$ subunits.

We have plotted in Fig. 2, $I(\theta,p)$ for $p=0, 10, 20, \ldots, 90, 100\%$, averaged over 100 random structures for each p. These data show that there is a continuous change from the spectrum of a pure 2:2:0:1 phase sample to that of a pure 2:2:1:2 one. This evolution of the spectrum appears as a continuous shift and broadening of the peaks, as well as a splitting or a fusion of two Bragg peaks, since when c (or the number of CuO_2 planes in the cell) increases the number of peaks also increases. We observe, as previously noticed by Tarascon et al. on their bulk samples,[5] that if the (00i) peak of the pure A phase is close to a (00j) peak of the pure B phase, in the case of intergrowth of A and B, the corresponding peak is less shifted and broadened and it remains intense. On the contrary, if the (00i) peak is far from any (00j) peak, the corresponding peak is shifted, broadened, and its intensity goes nearly to zero when the intergrowth ratio is maximum ($p=50\%$).

Figure 1(c) shows the XRD pattern of a film in which the structure is an intergrowth of 2:2:0:1 and 2:2:1:2 cells. It can be seen that all the peaks of spectrum (c) are located between the 2:2:0:1 and 2:2:1:2 lines, showing a shift of the peak position that is less important when the 2:2:0:1 and 2:2:1:2 lines are closer, as discussed above. This latter effect is clearly observed at the diffraction peak around $2\theta \sim 29°$, i.e., between (008) and (00$\underline{10}$) reflections of 2:2:0:1 and 2:2:1:2 pure phases, respectively.

Although the shifts of the peak positions are nearly linear as a function of the stacking-faults percentage p, the analysis of Hendricks and Teller[9] has been used in order to simulate more completely the x-ray-diffraction

spectra. Since in these Bi-based compounds the Bi and the Sr species are the heaviest elements ($Z=83$ for Bi and $Z=38$ for Sr, to be compared to $Z=29$ for Cu and $Z=20$ for Ca), we can assume that x-ray scattering is only due to the $Bi_2Sr_2O_y$ subunit electrons and then it is

enough to consider a one-dimensional disordered system (along the c axis) with two characteristic parameters d and $d_{2:2:1:2}$, which are the only allowed distances between $Bi_2Sr_2O_y$ layers. With this assumption, x-ray-diffraction intensities can be written as

$$I(\theta,p)=|F(\theta)|^2\frac{2p(1-p)\{1-\cos[k(d_2-d_1)]\}}{1+p^2+(1-p)^2+2p(1-p)\cos[k(d_2-d_1)]-2p\cos(kd_1)-2(1-p)\cos(kd_2)} , \qquad (2)$$

where p is the stacking-fault percentage, d_1 is the distance between $Bi_2Sr_2O_y$ subunits of the intergrown phase and d_2 is the distance of the 2:2:1:2 phase, $k=4\pi\sin\theta/\lambda_{Cu}$ the scattering vector, θ is the Bragg angle, and $F(\theta)$ is the structure factor of $Bi_2Sr_2O_y$ subunit.

We have used Eq. (2) to analyze the XRD spectra corresponding to more than twenty samples having only one set of lines. The Bragg peaks were indexed as (00$\underline{2l}$) lines of a 2:2:1:2 phase with $p\%$ of stacking faults corresponding to the intergrowth of 2:2:0:1 or 2:2:2:3 phases. Finally, we obtain the p percentage that results from the lowest root-mean-square (rms) deviation value. This deviation was calculated over the seven main XRD peaks. The rms deviation between calculated and observed peak positions corresponding to a pure 2:2:1:2 phase was 0.41°. After simulation using Eq. (2), the rms deviation decreases to 0.036°. This simulation takes into account a correction of the sample position in the diffractometer. A more elaborate model including the intergrowth of the three phases has also been tested, that means one more parameter to fit the same experimental data. The new model does not significantly improve the rms deviation, which is already of the same order of magnitude than the diffractometer resolution (0.02° for 2θ). Thus, a model considering the intergrowth of two phases is enough to explain the experimental data.

The 2:2:1:2 (008) peak is one of the most intense (00$\underline{2l}$) peaks and its shift is considerable (more than one degree). That is why it can be used to determine the stacking-fault proportion in the films. Figure 3 shows the theoretical

shift of this peak as a function of the stacking-fault (2:2:0:1 or 2:2:2:3) proportion p. A linear approximation such as $\bar{p}=(\theta-\theta_{2:2:1:2})/(\theta_i-\theta_{2:2:1:2})$ with $i=2:2:0:1$ or 2:2:2:3 can be used. In this case, the maximum absolute error on p is about 8%. Nevertheless, in our analysis we have used full expressions to obtain p values.

The calculated p percentages for our samples vary between 30% of the 2:2:2:3 stacking faults and 95% of the 2:2:0:1 faults. These values have been used to calculate the Bi/Cu ratio for each sample:

$$\frac{Bi}{Cu}=\frac{2}{2-p}\,(2{:}2{:}0{:}1\,/\,2{:}2{:}1{:}2\text{ intergrowth})$$

and   (3)

$$\frac{Bi}{Cu}=\frac{2}{2+p}\,(2{:}2{:}1{:}2\,/\,2{:}2{:}2{:}3\text{ case}) .$$

We have chosen the Bi/Cu ratio to make the analysis because it represents the proportion of $Bi_2Sr_2O_y$ subunits and CuO_2 planes and is the only one that can give suitable information, because of the possibility of substitution between Sr and Ca. The atomic composition of all the films was determined by RBS and the Bi/Cu ratio was also obtained. Comparison of the Bi/Cu ratio obtained by these two different analyses is presented in Fig. 4, showing an excellent correlation between them. This result shows the validity of the model and also provides additional and interesting information. Thus, an excess or lack of Cu with respect to Bi appears as an addition or loss of planes in the crystal structure, respectively. The

FIG. 3. Theoretical shift of the 2:2:1:2 (008) XRD peak position as a function of stacking-fault percentage.
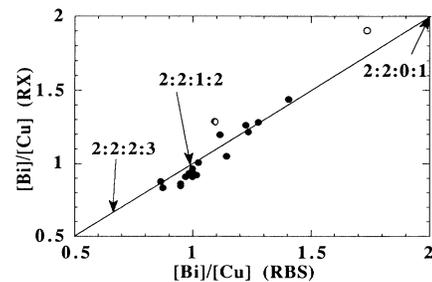
FIG. 4. Comparison of the Bi/Cu ratios obtained from RBS (composition) and XRD (intergrowth) analyses. Open circles (○) represent films in which the Bi/Cu ratio measured by RBS is underestimated due to film roughness.
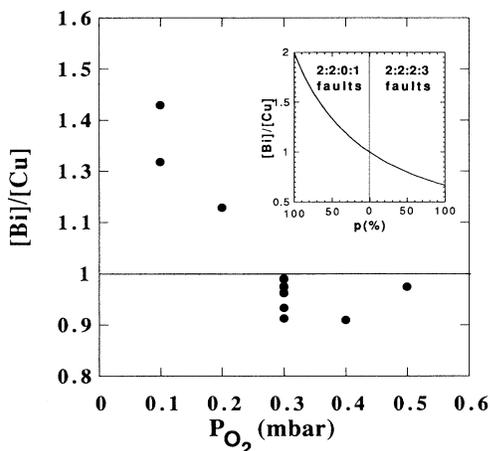
FIG. 5. Influence of oxygen pressure during deposition on the composition and intergrowth structure of the films. The inset shows the Bi/Cu ratio as a function of stacking-fault percentage [see Eq. (3)].

main effect of a slight nonstoichiometry of the films is the presence of stacking faults instead of parasitic phase of the element in excess. Furthermore this correlation shows that substitutions in the Bi or Cu planes are not important.

From Fig. 4 it can also be seen that most of the samples have a significative amount of stacking faults and only a few of them are nearly pure 2:2:1:2 phase. That means that the phase identification of *in situ* grown thin films is not easy. Thus, phase diagrams (deposition pressure vs temperature) such as already reported in the literature[10,11] must be carefully done. The very poor agreement between the various published phase diagrams is certainly due to the intergrowth phenomenon. Therefore, instead of the effect of pressure and temperature on the phase formation, the influence of deposition conditions on the intergrowth of phases must be investigated. In fact, a continuous change from a 2:2:0:1 system to a 2:2:1:2 + 2:2:2:3 one, using the same target, is possible by controlling the oxygen pressure during deposition. In Fig. 5 we show that a variation of the oxygen pressure

from 0.1 to 0.5 mbar allows a change from a 2:2:1:2 film with 60% of 2:2:0:1 to a 2:2:1:2 film with 20% of 2:2:2:3 (see inset, Fig. 5). All these films were grown using a target with 4:3:3:4 cationic composition. This continuous change observed is coherent with the intergrowth model, as has been reproduced in Fig. 2 above.

CONCLUSION

We show in this study that the intergrowth of different phases of *in situ* grown thin films of the Bi-based compounds is a general issue and it is necessary to investigate these kinds of defects in order to grow single-phase films and to improve their physical properties. This effect must be carefully analyzed, since in the XRD spectra of such films only one set of lines appears, as it were single-phase sample. Thus, the calculation of the *c*-axis parameter from the XRD data is not sufficient to identify the different phases present in the films. A calculation of the *c*-axis parameter, which gives a high deviation, probably means that the films contain stacking faults. We have been able to make a quantitative analysis of XRD data using a simple intergrowth model. From this analysis we have obtained the stacking-fault proportion inside the films that appears to be well correlated to the Bi/Cu ratio measured by RBS. This means that stoichiometry defects do not prevent the total crystallization of the *in situ* films in a Bi-Sr-Ca-Cu-O structure but introduce structural faults. It has been shown that continuous change in the structure is achieved as a function of the oxygen pressure during deposition. This study underlines the absence of a well-defined stability limit between the different phases of the Bi family. Further studies are now under way in order to analyze the influence of the laser-ablation parameters on these structural defects.

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