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Cubic phase in the Y-Ba-Cu-O system

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A metastable phase in the Y-Ba-Cu-O system has been discovered. The phase is closely related to the high-T_c superconductors and is characterized by a simple-cubic perovskite structure with a lattice parameter of 3.897 Å. A composition Y:Ba:Cu:O = 1.18:1.97:3.05:6.95 was determined using ion-backscattering spectrometry. The material is a black semiconductor and shows no transition to superconductivity down to 4 K. It is an excellent candidate for use in heteroepitaxial structures with the family of rare-earth–alkaline-earth–cuprate superconductors. The cubic phase was prepared as a thin film by excimer-laser ablation.

It has been over three years since the discovery of superconductivity above 90 K in the high-T_c ceramic oxides.[1,2] This group of materials is exemplified by $YBa_2Cu_3O_{7-\delta}$ (1:2:3), which is an orthorhombic perovskite-related superconductor when $\delta < 0.6$, having a continuous range of cell parameters as δ varies.[3,4] We report here an isotropic cuprate, which is closely related to the $YBa_2Cu_2O_{7-\delta}$ materials. It has a cubic structure with a lattice parameter of 3.897 Å. It is proposed that the cubic cuprate is characterized by a simple perovskite ABO_3-type cell. The stoichiometry of the phase has been determined to be near $YBa_2Cu_3O_{9-x}$ with x in the vicinity of 2. We propose that the A cation sites are occupied by a random distribution of Y and Ba ions and that the B cation sites are occupied by Cu ions. The oxygen vacancies are also believed to be randomly distributed. ac magnetic-susceptiblity measurements show no diamagnetic transition down to 4 K. The material was prepared *in situ* as a thin film on single-crystal (100) MgO by excimer-laser ablation.[5] The laser with a wavelength of 248 nm was made to irradiate the rotating $YBa_2Cu_3O_{7-\delta}$ target with a fluence of $\sim 2J/\mathrm{cm}^2$. The heated substrate was located 5–6 cm from the target along a direction roughly perpendicular to the target surface. The substrate was prebaked *in situ* at 700 °C in air just before each run. During deposition, an oxygen pressure of 0.1–0.2 Torr was maintained in the chamber measured some 20 cm from the oxygen jet introduced directly into the plume or onto the substrate. A fresh target surface was prepared immediately prior to each deposition by exposure to about 200 pulses with a shutter introduced before the substrate. The deposition rate was approximately 1–2 Å/pulse and typically 2000 pulses were used to produce a film. After deposition samples were cooled slowly in 150 Torr of oxygen. The cubic phase was produced when the heater block temperature during deposition was near 560 °C. Above 600 °C, the 1:2:3 structure with c axis perpendicular to the substrate surface was observed. At temperatures below about 540 °C insulating amorphous films were produced.

The cubic phase was identified by x-ray diffraction (XRD) and transmission electron microscopy (TEM) at room temperature. Figure 1 gives XRD spectra for a

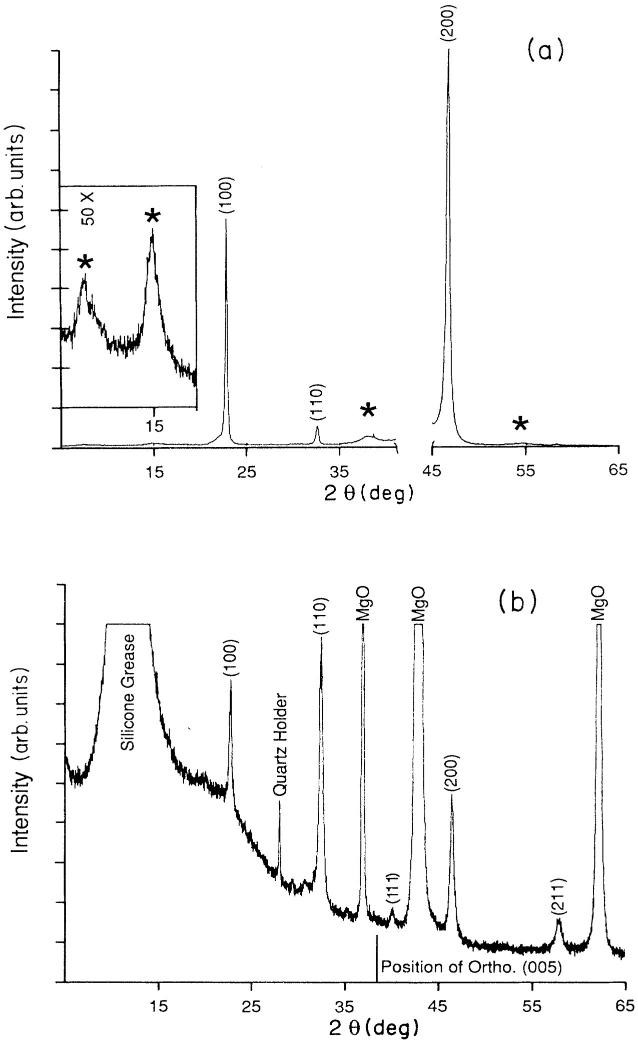

FIG. 1. X-ray diffraction spectra. (a) As-prepared thin film spectrum of a substrate heater temperature of 560 °C. (*) denotes (00l) peaks from the interfacial orthorhombic layer. The MgO substrate region between 42° and 45° was not scanned. (b) Spectrum from randomized powder obtained from same film as in (a) showing simple-cubic structure.

cubic-phase film prepared at 560 °C in Fig. 1(a) and for the scraped randomized powder of the same sample in Fig. 1(b). Both spectra were taken in the usual powder diffraction geometry. Figure 1(a) shows very prominent lines from the film which, if an orthorhombic-1:2:3 (ortho-1:2:3) structure were assumed, would be assigned to the (0k0) reflections of a predominantly *b*-axis-oriented (crystalline *b* axis perpendicular to film surface) thin film. Present as well is a small peak at 32.8° which would correspond to the (013) line of the ortho-1:2:3 phase. Also seen are weak broad lines which correspond to the $(00l)$ reflections of the *c*-axis-oriented ortho-1:2:3 structure. It will be shown later by TEM that these weak $(00l)$ lines originate in a very thin layer of *c*-axis-oriented 1:2:3 material at the interface to the substrate. The spectrum of Fig. 1(b) can be indexed assuming a simple cubic cell whose lattice parameter is given by 3.897 ± 0.004 (1σ) Å. Absent in Fig. 1(b) are any reflections at positions corresponding to $(hkl < 3)$ lines of the 1:2:3 structure. Also missing are any reflections (hkl) for which $l \neq 3n$ where n is an integer. The largest *d* spacing detected in the spectrum of Fig. 1(b) is 3.897 Å. This means that the major component of the film is not the ordinary 1:2:3 phase but instead a cubic phase.

The interpretation of the XRD data is made clear by Fig. 2(a), which shows a high resolution TEM (HRTEM) micrograph, and Fig. 2(b), which shows the corresponding electron diffraction pattern of a cubic film grown on (100) MgO. Details of the sample preparation and instrumentation have been reported previously.[6] The micrograph imaged at 200 kV clearly shows the interface between the film and substrate. Immediately above the interface, several unit cell thicknesses of the usual *c*-axis-oriented 1:2:3 material are seen, identifiable by the distinct 11.7 Å spacings. The thickness of the *c*-axis interfacial layer correlates well with the widths of the $(00l)$ XRD peaks. Beyond a distance which is typically less than ten unit cell thicknesses, the film structure switches abruptly to the cubic phase. Though not visible in the micrograph, the film was observed to remain cubic up to the surface. Some small regions of (110)-oriented cubic material were also found in the film. Apparently these regions are what gave the small peak at 32.8° in Fig. 1(a). Figure 2(b) is a select area electron diffraction pattern from a region encompassing the substrate and the entire film thickness. Two cubic patterns are observed, one due to the substrate and the other due to the film. The alignment of the diffraction patterns reveals the excellent alignment of the crystallographic axis directions of film and substrate and indicates local epitaxy for the cubic film. The epitaxial relationship has been carried through the interfacial layer. Such alignment was found at each position of the sample that was studied. The HRTEM images and the electron diffraction patterns establish the following simple crystallographic relationship between the cubic phase and the MgO substrate:

$$\{100\}_{\mathrm{cubic}} \| \{100\}_{\mathrm{MgO}} \ .$$

Although it is not possible to distinguish between the [100] and [010] directions of the orthorhombic interfacial layer, it is clear from the HRTEM lattice images that these directions are aligned, at least locally, with the crystallographic axis directions of the MgO substrate. Very weak $(00l)$ reflections of a 1:2:3 phase, caused by the interfacial layer, were observed in electron diffraction as is indicated by the arrow in Fig. 2(b).

It was further shown by tilting experiments that the apparent absence of the 1:2:3 phase in the majority of the film was not due to a fortuitous alignment of the electron beam along the [001] direction of a 1:2:3 film. With the specimen oriented as in Fig. 2(a), a rotation was performed around the normal to the surface and lattice fringe images were taken at various intervals up to 45°. Whereas the distinct 11.7 Å spacings of the ortho-1:2:3 interfacial layer remained for each rotation interval as expected, no such spacing could be seen in the material above the interfacial layer. Additionally, a second cross section specimen of the same sample cut orthogonally to

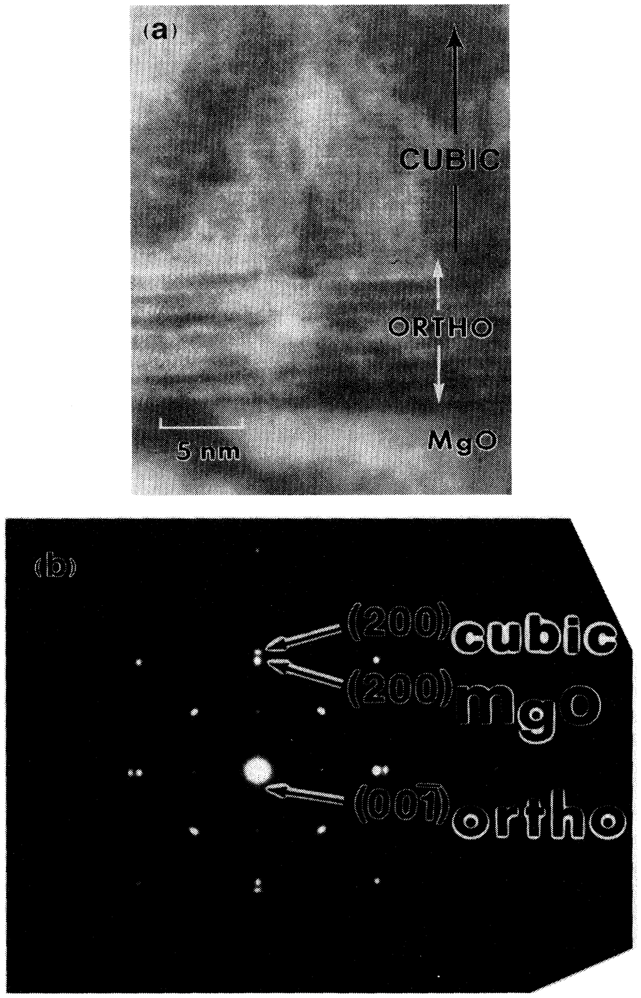

FIG. 2. (a) High resolution TEM of the film substrate interface region for a cubic Y-Ba-Cu-O film on MgO. The *c*-axis-oriented orthorhombic-1:2:3 interfacial layer is interposed between the substrate and the cubic film. (b) Select area diffraction pattern of interface region.

the first was prepared. The second specimen revealed the c-axis-oriented interface layer as in Fig. 2(a), but neither HRTEM nor electron diffraction were able to detect a significant fraction of the ordinary 1:2:3 phases or any amorphous material in the bulk of the film.

The stoichiometry of the cubic phase was studied by Rutherford-backscattering spectrometry (RBS) using 2.0 MeV He ions and by inductively coupled plasma atomic emission spectroscopy (ICP). Metal stoichiometry derived by RBS using an average over two cubic films was found to be Y:Ba:Cu$=(1.18:1.97:3.05)\pm 5\%$. ICP analysis of a similar film gave a metal ratio in agreement with the above numbers. In all samples studied, a small excess of Y relative to the 1:2:3 phases was observed. Oxygen stoichiometry determined by RBS was found to be 6.95 ± 0.5 based on the above metal stoichiometry.

The RBS measurements also revealed that the composition was uniform throughout the entire thickness of the film. Furthermore, ion-channeling measurements were performed on the cubic films. Although the minimum yield was only about 71%, the mere observation of ion channeling is a clear manifestation of the high crystalline quality and long range order in this material.

The precise determination of atomic arrangements in the cubic phase is made difficult by the sample morphology. The usual single-crystal XRD or neutron diffraction techniques are inaccessible to thin films. A crystal structure based on powder XRD and symmetry arguments is proposed. The XRD data of Fig. 1(b) indicate the lattice to be cubic with no distortion to $<0.1\%$. Thus it is argued that there can be no ordering of Y and Ba ions. Also, long range ordering of oxygen vacancies would likely cause displacements of metal ions which would result in some kind of distortion detectable by powder XRD. The above considerations together with the value of the lattice parameter suggest that the obvious choice for a possible solution to the structure is a simple perovskite of the type ABO_3 where Y and Ba ions occupy the A cation sites with random distribution and Cu ions occupy the B sites. Charge balance considerations together with the experimentally observed stoichiometry indicate that vacancies occupy the oxygen sublattice with about two vacancies for every nine anion sites. If the ideal cubic lattice contains cations in the ratio (Y:Ba:Cu)=(1:2:3) then the excess measured Y would suggest approximately 2.3 vacancies per 9 anion sites in the ideal cubic structure as prepared. The structure just described belongs to the space group $Pm3m$. In general the perovskite structure is not stable under high levels of vacancy concentration; however, it is well known that in copper containing perovskite and perovskite-related materials high vacancy levels are possible.[7] This relates to the stability of copper in square-planar or square-pyramidal coordination. The possibility exists that ordering of oxygen vacancies is occurring in the material resulting in a real unit cell of larger dimension; however, this would be difficult to observe given the sample morphology.

Given the close match in stoichiometry, it should be possible to convert the cubic phase to the more stable 1:2:3 material by a thermal treatment in which temperatures high enough to achieve bulk diffusion of cations are attained. The phase change would be primarily a rearrangement of the Y and Ba cations giving the ordered A-site distribution and the corresponding tripled unit cell volume. To test the above suggestion, a cubic film grown on MgO was heated in a furnace at 950 °C in air for 5 min and cooled slowly at the natural rate. XRD revealed a spectrum characteristic of a c-axis-oriented 1:2:3 film confirming a phase transformation to the 1:2:3 material.

The temperature dependence of resistivity for a cubic film grown on MgO indicates a nearly flat but rising value as temperature decreases with a transition to superconductivity observed near 60 K. Magnetically modulated microwave absorption (MAMMA) measurements[8] force us to assign the resistivity transition observed near 60 K in the cubic films grown on MgO to the thin interfacial 1:2:3 layer as no appreciable MAMMA transition is seen near 60 K. This is reasonable in view of the fact that the interfacial layer comprises less than 2% of the film. No MAMMA transition associated with the thin film was detected down to 10 K. Likewise, ac magnetic-suceptibility measurements conducted with the field applied perpendicular to the film surface show no transition down to 4 K. Typical c-oriented ortho-1:2:3 films of equal thickness give large susceptibility signals.

Many groups have reported superconducting Y-Ba-Cu-O films produced by various vacuum deposition processes at relatively low temperatures. For example Geerk *et al.*[9] report Y-Ba-Cu-O films sputtered at 600 °C on MgO substrates which they conclude are a-axis-oriented 1:2:3 films with an a lattice parameter of 3.85 Å. The authors give thin film XRD data that show features similar to our results for cubic films. This includes the existence of weak, broad peaks corresponding to $(00l)$ reflections of the 1:2:3 phase which we attribute in our films to the thin interfacial c-axis-oriented 1:2:3 layer.

The appearance of the interfacial layer and the orthorhombic to cubic phase metamorphosis above it are intriguing observations. The random occupancy of A cation sites and defects in the cubic structure is consistent with the low growth temperatures needed to achieve the phase; however, it is remarkable that the orthorhombic 1:2:3 layer at the MgO interface is always seen. Considering the close lattice match of the cubic and orthorhombic phases, and the large mismatch of each with the MgO substrate, it is reasonable to expect the cubic phase to grow directly from the substrate interface. Perhaps the accommodation of stress in the interfacial layer plays a role in the appearance of the 1:2:3 phase there. Recently, we have found that the metastable phase also grows on the (100) surface of $SrTiO_3$. Using this substrate it was observed by TEM that the c-axis-oriented 1:2:3 interface layer is also present; however, it is typically only about 1–2 unit cell lengths in thickness and in some areas the metastable phase appears to grow directly on the substrate. XRD measurements of the film were unable to resolve the $(h00)$ peaks of the film from those of the substrate. It is therefore possible that the lattice parameter of the phase on $SrTiO_3$ is slightly larger than on MgO. Within the resolution of electron diffraction the phase remains cubic on $SrTiO_3$. The absence of a connected superconducting interfacial layer for the cubic film was confirmed by temperature-dependent resistivity measurements, which showed no transition to superconductivity down to 10 K. Electrical measurements of this film give a more accurate picture of the phase, therefore, than those grown on MgO. The room-temperature resistivity was found to be equal to 0.04 Ω cm and to increase with decreasing temperature.

The cubic structure was also found to occur in low-temperature growth of the Gd-Ba-Cu-O material. The phase was produced under similar conditions as for cubic Y-Ba-Cu-O except that temperatures nearly 20 °C higher were necessary. It is likely that the rare-earth elements that form the 1:2:3 materials will also have their metastable analogues.

The excellent lattice match between orthorhombic and cubic phases as well as their chemical compatibility suggest that useful heteroepitaxial structures might be possible using these materials. Indeed, Josephson-type sandwich structures and superlattices incorporating alternating layers of the orthorhombic and cubic phases have been achieved in our laboratory. It has been observed that the cubic material is stable during subsequent higher temperature (700 °C) growth of the orthorhombic material and that they grow well on each other. A more detailed presentation of these results will appear elsewhere.

It is interesting that the cubic materials as prepared, although closely related in structure and composition to the 1:2:3 materials, are not superconducting down to 4 K. This could be connected with the three dimensionality of the material. It may also be related to the random distribution of oxygen vacancies in the structure which may limit the range of continuous Cu-O linkages. The oxygen content achievable under ordinary conditions may limit carrier concentration and may as well play a role. The close connection between the cubic and the high-T_c phases could provide valuable insight for the understanding of the illusive mechanism of superconductivity in the high-T_c cuprates.

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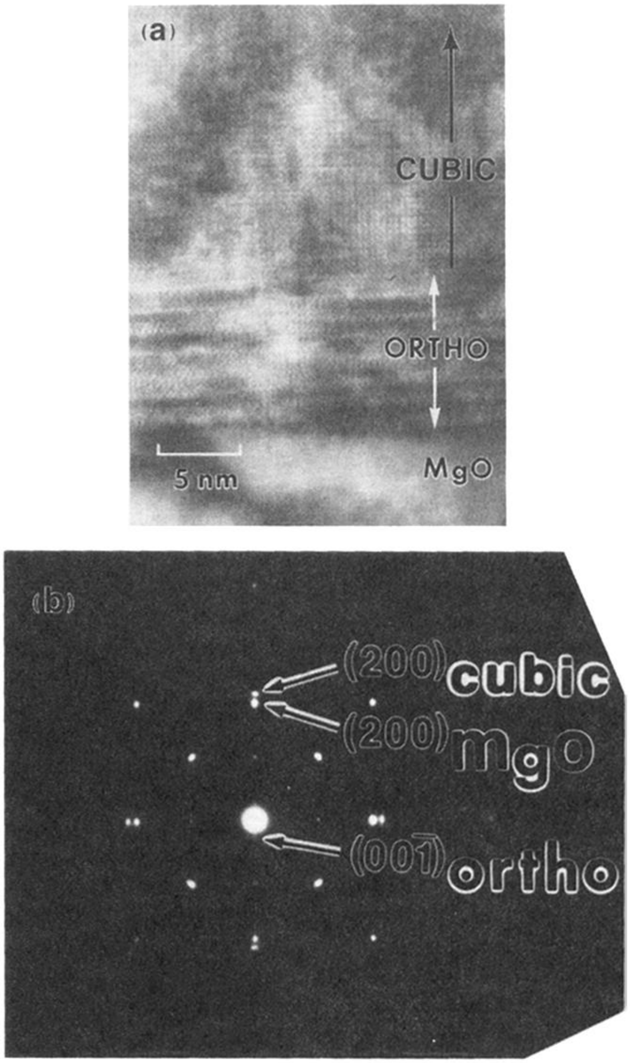

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