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X-Ray Diffraction Investigation of the Tetragonal–Orthorhombic Transition in $YBa_2Cu_3O_{6+x}$ in the Temperature Range $300 < T < 1020$ K

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Several materials of general formula $YBa_2Cu_3O_{6+x}$ with $0 \leq x \leq 1$ have been prepared with accurately known composition using precision gas titration techniques. For each composition, the conversion between the tetragonal and orthorhombic phases at temperatures from ambient to $T \leq 1020$ K has been followed using high temperature X-ray diffraction. For $x \leq 0.4$, the phase is tetragonal; for x values of 0.43, 0.45, 0.5, and 0.7, conversion occurs within the temperature ranges 420 K $< T <$ 470 K, 470 K $< T <$ 520 K, 520 K $< T <$ 720 K, and 920 K $< T$ 1020 K, respectively. For $x = 0.9$ and $x \approx 1$ the orthorhombic phase is present for all $T <$ 1020 K. These data indicate that the kinetics of the oxygen ordering, which results in superlattice formation and phase conversion, are fast for temperatures as low as $T \approx 350$ K.

Introduction

For the system $YBa_2Cu_3O_{6+x}$, with $0 \leq x \leq 1$ and $T = 300$ K, a tetragonal phase ($0 \leq x < \sim 0.4$), and a phase or phases with orthorhombic distortion ($x > \sim 0.4$) have been shown to exist (*1–3*). For the latter range, and in particular for $x \approx 0.6$, superlattice formation which results in cell doubling in the basal plane has been shown to exist by neutron diffraction studies (*4*). For $x \approx 1$, the resulting material has a superconducting transition, $T_c = 90$ K; within the lower x range are compositions close to $x = 0.6$ which exhibit $T_c = 55$ K. A partial phase relationship, (x,T), based upon high resolution X-ray data for the system, where phase conversion occurs for the temperature and composition ranges 790 K $< T <$ 945 K and $0.59 < x < 0.66$, respectively, has been reported (*5*). In addition, X-ray and neutron diffraction data are available for portions of (x,T), from samples prepared either by using thermal quenching to maintain an oxygen stoichiometry which had been establishcd at elevated temperatures, (*2, 6*), or by *in situ* measurements (*7, 8*). The present study, using high temperature X-ray diffraction techniques, was undertaken to determine the temperature of the tetragonal–orthorhombic phase transition for several materials in the system $YBa_2Cu_3O_{6+x}$, with particular emphasis on the range $0.4 < x < 0.5$. The materials were prepared with accurately known x, at low temperature, by the method of gas titration. This technique ensures isothermal uptake of oxygen during sample preparation and does not subsequently depend upon rapid quenching to maintain the preparation stoichiometry.

Experimental

The precursor $YBa_2Cu_3O_{6+x}$ was prepared by sintering compressed pellets of a stoichiometric mixture of Y_2O_3, $BaCO_3$, and CuO at 1120 K. All starting compounds were Johnson Matthey Puratronic Grade, of ci-

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ther 99.999% or 99.99% purity. This treatment was followed by grinding and annealing the compressed product under flowing O_2 at 1120 K, then slowly cooling to ambient temperature in O_2. Using the parent batch, samples of selected x were prepared within a stainless steel reactor in the following way. The parent aliquots of $m \approx 1.2$ g were first deoxygenated to $YBa_2Cu_3O_6$ by heating under vacuum $\{p(O_2) < 0.05$ Pa$\}$ at $T = 1020$ K for 16 hr. The temperature was then lowered to $T = 720$ K, and oxygen was admitted to the reactor from a stainless steel manifold. The volumes of the reaction system, manifold and reactor, were calibrated (total volume, $V \approx 50$ cm^3), and the quantity of O_2 which was added to $YBa_2Cu_3O_6$ from the titration manifold was calculated to give the desired final stoichiometry. The oxygen uptake was rapid, with 98% reaction occurring in 2 min. An equilibration period of 2 hr was allowed before slow cooling to ambient temperature, with an additional 1 hr hold at $T = 570$ K. During cooling, the quantity of oxygen absorbed was less than 0.1% of the total uptake and, for the series of samples, the final oxygen pressures were 5 Pa $< p(O_2) < 85$ Pa for $0.3 < x < 0.9$. The resulting oxygen stoichiometry was calculated by volumetric methods, using the calibrated volumes of manifold and reactor, and assuming ideal gas law behavior for oxygen. The product was unloaded and stored in a high purity argon dry box. The calculated stoichiometries have uncertainties from all sources which are estimated at $x \pm 0.01$.

For X-ray diffraction measurements, quartz capillaries of length 4 cm × diameter 0.5 mm were quickly loaded in air, the free volume in the capillary above the sample then being minimized by filling with silica powder which previously had been degassed by heating under vacuum at $T > 1020$ K. The capillary was then immediately sealed with low vapor pressure epoxy. The short length of capillary which contained the epoxy remained just outside the furnace assembly during data collection and did not experience a temperature exceeding $T = 350$ K. Assuming 0.5 packing efficiency of the powders, the estimated total free volume within the capillary after loading is $V \approx 3 \times 10^{-3}$ cm^3. Diffraction data were obtained on a Stoe 2-circle powder diffractometer, equipped with a Stoe high temperature graphite furnace attachment. The radiation used was CuK_α, from which CuK_β was eliminated by reflection from a curved, crystalline graphite monochromator; this also focused the diffracted beam onto the detector slits, thereby optimizing instrument resolution. The data collection geometry was Debye–Scherrer, with the sample capillary rotating within a narrow cylindrical cavity in the body of the graphite furnace. Due to the thermal gradient within the furnace, temperature uncertainities were $T \pm 10$ K. Data were collected by step-scanning, with a step width of $2\Theta = 0.04°$ and a counting time of 120 sec per step. After first ensuring, with measurements over the full 2Θ range, that no additional phases were present, the data collection was limited to five selected "fingerprint" ranges in 2Θ, these being up to 4.5° in width and centered approximately on 32.5°; 39.5°; 46.5°; 58.5°; and 68.0°. Initial data were collected for samples with $x = 0.0$, 0.3, 0.5, 0.7, 0.9, and 1.0 at each of $T = 295$, 520, 720, 920, and 1020 K, which served to locate the (x,T) range of interest. Subsequent samples were prepared with $x = 0.40$, 0.43, 0.45 and studied over a reduced temperature range, 295 K $< T <$ 520 K, with smaller temperature increments. Following data collection at the elevated temperatures, the X-ray spectrum of each sample was re-collected at 295 K to ascertain bulk reversibility, and also to demonstrate the integrity of the capillary seal throughout the measurement sequence. If any oxygen exchange due to a leak in the capillary had occurred, then a composition shift, Δx, would be experienced by the sample upon equilibration

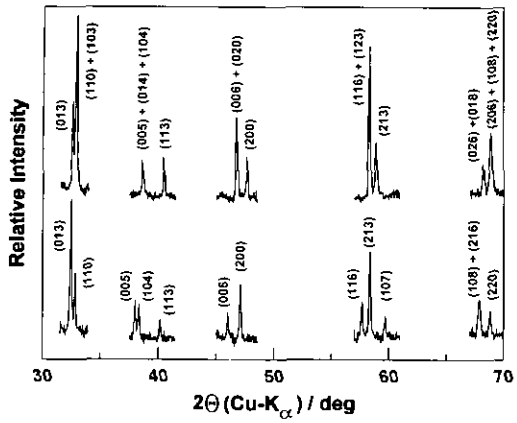

FIG. 1. X-ray spectra for $YBa_2Cu_3O_{6+x}$ for $x = 0$ (lower curve set) and $x = 1$ (upper curve set), shown for each of the 5 "fingerprint" ranges in 2Θ which were investigated. The indices for the lower and upper data are based upon the tetragonal and orthorhombic lattice, respectively. Data were obtained at $T = 295$ K with monochromated CuK_α radiation.

during cooling, which consequently would be manifested in the X-ray spectrum.

Results and Discussion

Shown in Fig. 1, as an example of the X-ray spectra for the overall ranges investigated, are data obtained at 295 K from compositions prepared at the lower and upper composition limits, i.e., at $x = 0$ and $x \approx 1$. These are the spectra which correspond to tetragonal and orthorhombic symmetry, respectively. As x increases the c-axis decreases and, once the orthorhombic range is entered, this is accompanied by changes in the basal plane which result in a decreasing a-axis and an increasing b-axis. In consequence there is approximately a 2% reduction in cell volume as x passes from the lower to the upper phase limit. Shown in Table I to illustrate this trend are the lattice parameters derived from the samples at 295 K; cell constants measured at higher temperatures exhibit similar trends.

Of the 2Θ ranges over which data were collected, that for $44.0° < 2\Theta < 48.5°$ was selected to show most clearly the result of the structural changes which occur as (x,T) varies. This range includes the reflections (006) and (200) for the tetragonal phase, the latter splitting into a doublet (020) + (200) as the orthorhombic distortion becomes dominant, and then (020) + (006) coalescing as the fully loaded oxygen composition is approached and c approximates $3b$. The appearance of this portion of the X-ray spectrum for all sample compositions is shown in Fig. 2. The spectra at all T and x are sharp, with the exception of those at the highest temperatures for $x = 0.9$ and 1.0. For these compositions the experimental conditions result in the desorption of sufficient O_2 from the sample into the remaining free volume of the capillary to produce what is almost certainly an inhomogeneous sample, which consequently shows broader diffraction peaks. The quantity of O_2 exchange experienced by any particular sample depends upon T and x, but apart from those cases identified above, the maximum stoichiometric shift due to the effect of temperature is calculated from the thermodynamics (*1,9–11*) for the system $YBa_2Cu_3O_6 + O_2$, {i.e., from $p(O_2$ desorption) and capillary $V \approx 3 \times 10^{-3}$ cm^3} to be $\Delta x < 0.005$ for $T < 520$ K and $\Delta x < 0.01$ at higher T. Reversibility to the phase state which was ini-

TABLE I

VALUES OF THE CELL PARAMETERS FOR $YBa_2Cu_3O_{6+x}$ AT $T = 295$ K FOR EACH OF THE PREPARED MATERIALS

x	a/Å	b/Å	c/Å
0.0	3.8558(4)		11.830(1)
0.3	3.8596(4)		11.792(1)
0.4	3.8558(4)		11.782(1)
0.43	3.8465(5)	3.8635(5)	11.775(1)
0.45	3.8434(5)	3.8658(5)	11.768(1)
0.5	3.8404(4)	3.8689(4)	11.753(1)
0.7	3.8289(4)	3.8775(5)	11.710(2)
0.9	3.8176(4)	3.8853(5)	11.680(2)
1.0	3.8138(4)	3.8845(5)	11.654(2)

Note. Data were collected from powder samples with monochromated CuK_α radiation. Values in parentheses are esd's.

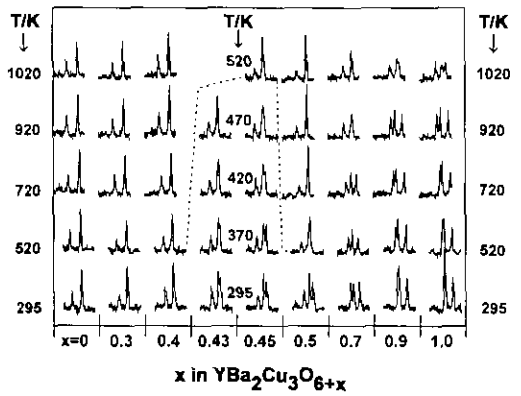

FIG. 2. X-ray spectra for $YBa_2Cu_3O_{6+x}$ in the range $44° \leq 2\Theta \leq 49°$ for all samples, illustrated as a matrix containing data for each composition and temperature. Each vertical column shows data for a fixed value of x, and beside each row is shown the temperature at which each spectrum was collected. The envelope of data enclosed in broken lines for $x = 0.43$ and $x = 0.45$ is shown over a reduced temperature range compared to the remainder of the compositions.

tially present under ambient conditions was demonstrated for all samples except those with $x \geq 0.9$ which had experienced temperatures $T > 920$ K, and where some minor variations in relative peak positions and intensities were observed in X-ray spectra.

From the X-ray data, the relationship of transition temperature with x can be determined. With the onset of the tetragonal–orthorhombic conversion, the (200) reflection at first broadens and then splits into a doublet (200) + (020). By using these criteria, and by observing that, in comparison to the orthorhombic form, the (200) reflection of the tetragonal form is sharper and more intense, the following can be extracted from Fig. 2: for $x \leq 0.4$, no conversion occurs and the phase is tetragonal for all $T <$ 1020 K; for $x > 0.4$, and with, in each case, the composition listed first followed by the best temperature range for the phase conversion: $x = 0.43$, 420 K $< T <$ 470 K; $x = 0.45$, 470 K $< T <$ 520 K; $x = 0.5$, 520 K $< T <$ 720 K; $x = 0.7$, 920 K $< T <$ 1020 K; $x = 0.9$ and $x = 1$, $T >$ 1020 K. The rate of change in transition temperature with x is large, and in agreement with data which have been reported earlier (*5*) for compositions with $0.58 < x < 0.66$. However, for the range $0.40 < x < 0.45$, the transition temperatures are lower by about 50 K than those reported earlier (*8*). The current work extends to lower T and x values, the data for the phase diagram for equilibrated samples of $YBa_2Cu_3O_{6+x}$, and provides additional evidence that the diffusional processes which result in the ordering of oxygen vacancies are still fast for temperatures which are marginally above ambient (*12*, *13*). As a corollary to this, it has also been observed (*9*) that the kinetics of O_2 absorption by $YBa_2Cu_3O_6$ are fast for $T \approx 420$ K, offering the possibility of developing low temperature preparation procedures for a range of single phase oxygen compositions in these and related perovskite materials. These aspects of the results support conclusions of modeling studies (*14*), which predict that long range ordering of oxygen can occur at low temperatures.

Conclusions

The technique of precision gas titration provides a method for preparing samples of $YBa_2Cu_3O_{6+x}$ which are equilibrated during reaction with O_2 and which do not require subsequent quenching to maintain stoichiometry. The tetragonal–orthorhombic transition which occurs in $YBa_2Cu_3O_{6+x}$ with changing x can be observed by X-ray diffraction techniques in powdered samples of these materials at temperatures $T >$ 300 K and $x > 0.4$. Consequently, the temperature ranges for the conversion at various values of x can be determined. For compositions $0.4 < x \leq 0.43$, the transition temperature is close to ambient. The X-ray data obtained at the lower temperatures are interpreted as representing homogeneous sample compositions, which is evidence that materials under these conditions exhibit fast rates of diffusion of oxygen vacancies.

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