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Possible structural phase transition near 210 K of single-phase Bi(Pb)-Sr-Ca-Cu-O superconducting ceramics

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Ultrasonic measurements on 2:2:1:2 and 2:2:2:3 single-phase samples of Bi-Sr-Ca-Cu-O and Bi(Pb)-Sr-Ca-Cu-O have been carried out. It was found for the first time that there is an anomalous structure change near 210 K in these Bi-based superconducting ceramics. Detailed studies revealed that the sudden change in sound attenuation and velocity is an isothermal-like process. Thermal analysis and specific-heat measurements proved that this anomalous change has characteristics of a phase transition. X-ray diffraction experiments showed sudden increases in lattice constants a and c, indicating some fine-structure changes during this transition.

The discovery of superconductivity at temperatures above 100 K in Bi-Sr-Ca-Cu-O systems[1] has further stimulated the efforts to identify the relevant superconductivity mechanisms involved. The Bi-Sr-Ca-Cu oxide system forms a new class of structure containing more than just corner-sharing Cu-O polyhedra and no one-dimensional Cu-O chain. The structure difference must result in some different behavior when approaching the superconducting transition. In this paper, we will report the first observation of a possible phase transition near 210 K of this system by ultrasonic, thermal analysis, specific-heat, and x-ray diffraction measurements.

Seven samples were used in this study, which can be divided into four groups, i.e., $Bi_2Sr_2CaCu_2O_{8+x}$, $Bi_2Sr_2Ca_2Cu_3O_{10+x}$, $(Bi_{1-y}Pb_y)_2Sr_2CaCu_2O_{8+x}$, and $(Bi_{1-y}Pb_y)_2Sr_2Ca_2Cu_3O_{10+x}$, with $y=0.15$–0.20. The Pb-doped samples were prepared in Tsinghua University by the standard method of solid-state reaction using Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO of analytic purity. The mixtures were reacted in air at 820°–850°C for 60–120 h followed by slow cooling to room temperature. In order to obtain samples with a single phase, special care must be taken to control the sintering temperatures and the oxygen pressure properly.[2] Two of the samples were prepared by Peking University and one was offered by the University of Science and Technology of China (USTC), of which the nominal compositions and the sintering processes were considerably different; e.g., the sample from USTC was quenched in nitrogen. All samples, however, were proved to be of single-phase 2:2:1:2 or 2:2:2:3 structure by x-ray diffraction experiments. Resistivity measurements showed that the zero-resistance temperature T_{c0} was between 74 and 85 K for the 2:2:1:2 phase and between 107 and 112 K for the 2:2:2:3 phase.

The anomalous changes were first observed in ultrasonic experiments. MATEC 7700 series equipment was used for both longitudinal and transverse ultrasound wave measurements with 5–15-MHz quartz or $LiNbO_3$ transducers bound by water-free Nonaq Stopcock grease. The low-temperature conditions were achieved by two methods: One is in an Air Products closed-cycling refrigerator (300–10 K) with a vacuum better than 5×10^{-3} Torr; the other is a conventional nitrogen Dewar (300–78 K) with nitrogen gas for heat exchange. The rate of temperature change was controlled within 0.3–0.5 K min^{-1} or slower and the accuracy of temperature was better than ±0.1 K. The sound velocity was measured by the pulse-echo overlap method and the change in attenuation was measured by a double-echo comparison technique. Results from both closed-cycling refrigerator and conventional Dewar were consistent with each other.

The typical temperature dependence of the sound attenuation and velocity when cooling the sample is shown in Fig. 1. It can be seen that there is a remarkable sudden rise in velocity near 210 K and a sudden drop near 190 K, forming a small but clear peak. Correspondingly, a similar sudden rise and sudden drop in attenuation appear at the exact same temperatures, forming a sharp attenuation peak. When heating the sample immediately after cooling (Fig. 2), the anomalous sudden changes in velocity and attenuation shift towards 235–243 K. Results from transverse sound-wave measurements are consistent with the longitudinal ones. Frequency-dependent (5–15 MHz) measurements showed that no detectable shift of the peak position can be found within the frequency range, though the height of the anomalous peak does increase with in-

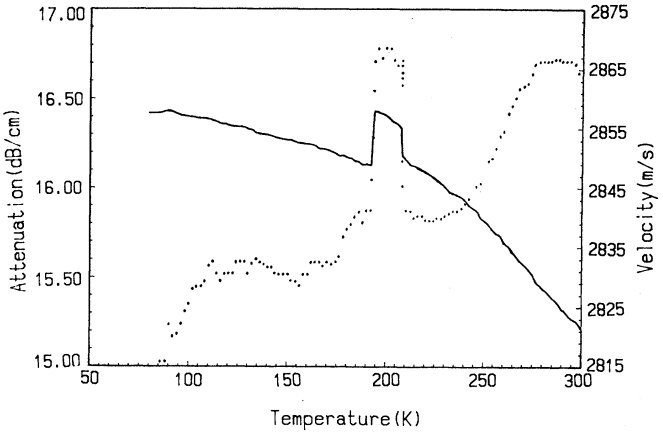

FIG. 1. Temperature dependence of the changes in longitudinal sound velocity (solid curve) and attenuation (dotted curve) at 10 MHz for sample 3 (2:2:1:2 phase) when cooling the sample. Anomalies near 210 K are remarkable.

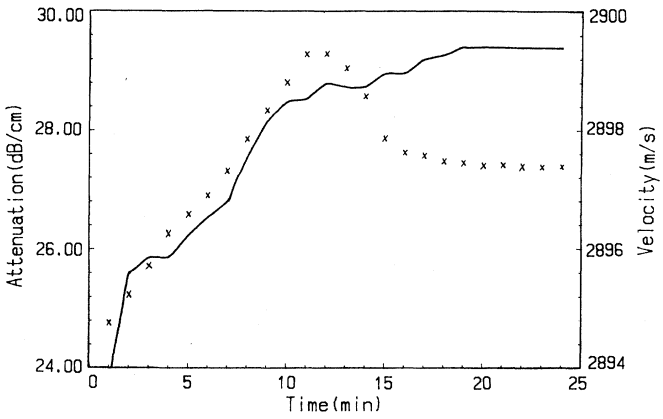

FIG. 3. Time dependence of the changes in longitudinal sound velocity (solid curve) and attenuation (dotted curve) at 10 MHz for sample 1 at 209.0 ± 0.1 K. The continuous changes in velocity and attenuation lasted for more than 20 min.

creasing frequency.

Detailed investigations revealed that the above sudden changes observed in temperature-dependent measurements are probably isothermal-like processes (or more accurately, these anomalous changes are completed within 0.1–0.2 K, considering the accuracy of the Air Products temperature controller is ±0.1 K). The observed time dependence of changes in sound velocity and attenuation at 209.0 ± 0.1 K is shown in Fig. 3. It has been proved that the thermal equilibrium can be achieved within 2 min since the step of the change of the temperature in our experiments is very small (only 1–2 K). So the measured velocity and attenuation usually show stable values as soon as the thermal equilibrium is realized. However, at the temperatures where the sudden anomalous changes occur, the gradual and continuous changes in velocity and attenuation can last for more than 20 min. It is well known that ultrasonic measurement is a very sensitive volume probe for subtle structure change. The above phenomenon indicates that some kind of structure change occurs. Such structure change is essentially a continuous process though it looked like an abrupt change in the temperature-dependent experiments.

The above phenomenon is reproducable. Results from three successive cooling-heating cycles, which lasted for 48 h, were consistent with each other (sample 1). Exactly the same results were obtained for sample 1 after an interval of three months. Seven samples of the four different groups were examined and all of them showed similar anomalies near the same temperatures. Considering that these samples were prepared by three different laboratories with considerably different technological processes, it can be concluded that the anomalous structure change near 210 K is sample independent.

In order to investigate the physical origin, thermal analysis, specific-heat measurements, and x-ray diffraction experiments were carried out. Two independent thermal-analysis experiments (for heating only) were performed in a DuPont 990-type differential thermal analysis (DTA) (for sample 1) and a DuPont 1090-type

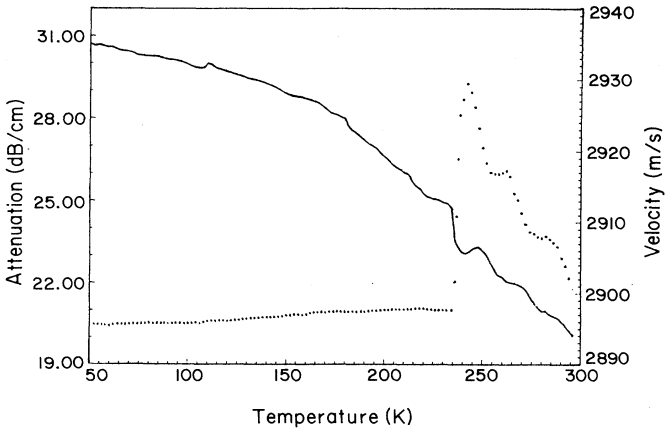

FIG. 2. Temperature dependence of the changes in longitudinal sound velocity (solid curve) and attenuation (dotted curve) at 10 MHz for sample 1 (2:2:2:3 phase) when heating the sample immediately after cooling. The anomalies shift towards 234 K.

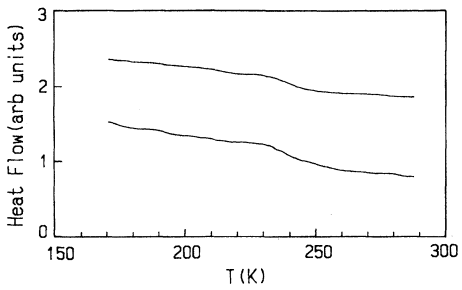

FIG. 4. DTA results for sample 1 (upper curve) and DSC results for sample 2 (lower curve).

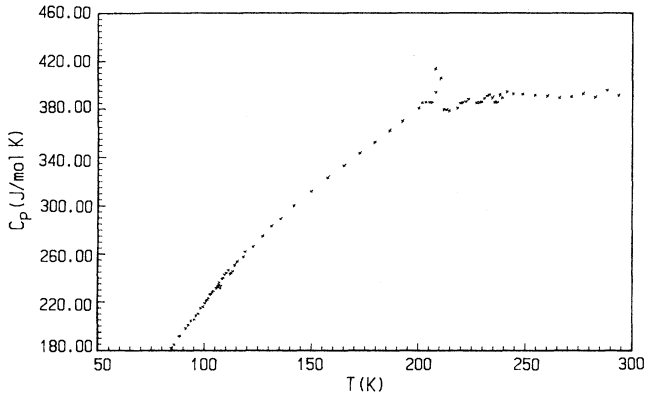

FIG. 5. Specific heat of $Bi_{1.70}Pb_{0.30}Sr_2Ca_2Cu_3O_{10+x}$. Clear anomaly near 210 K can be seen.

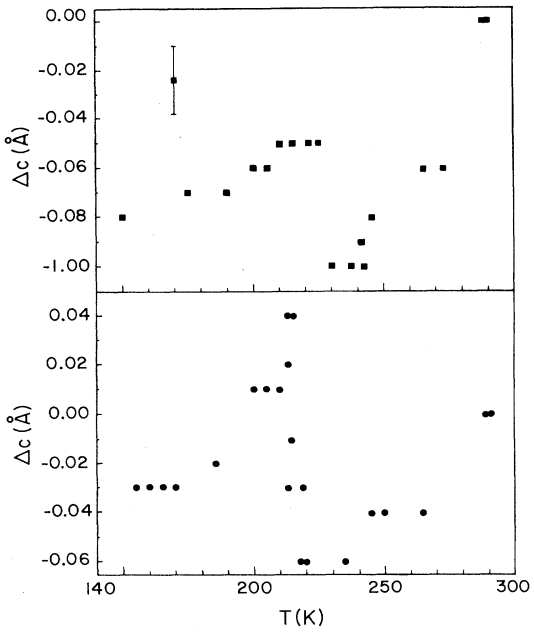

FIG. 6. Temperature dependence of the relative changes in lattice constants c (2:2:2:3 phase) obtained from x-ray diffraction experiments when cooling (●) and heating (■) the sample.

differential scanning calorimetry (DSC) (for sample 2), respectively. It can be seen from Fig. 4 that both curves show similar specific-heat changes between 230 and 245 K, though no heat-flow peak (or dip) can be observed, implying that a phase transition occurred. This was confirmed by our recent specific-heat measurements. The measurements were conducted in the Chinese National Institute of Metrology with an accuracy better than 1%. The total weight of samples used was 8 g. A clear anomalous peak with ΔC_p near 20 J/mol K can be observed near 210 K (Fig. 5). X-ray diffraction experiments also showed an anomalous sudden increase in lattice constants near this temperature (Fig. 6), though no distinct change in diffraction patterns was observed. The above x-ray diffraction results show that the framework of the lattice structure does not change in this temperature region; however, some subtle changes in fine structure, e.g., bonding length or bonding configuration, could occur. The possible tilt or stretch of a Cu—O or Bi—O bond will result in an anomalous increase in lattice constant, leading to a structural phase transition. Further investigations, e.g., neutron diffraction experiments, are being conducted.

It is interesting to point out that in our early investigations we found that there are ultrasonic anomalies near 170 and 250 K for $YBa_2Cu_3O_{7-y}$ superconductors,[3] which are accompanied with anomalous changes in specific heat[4] and lattice constant.[5,6] Now similar anomalous changes near 210 K for the Bi(Pb)-Sr-Ca-Cu-O superconductors were also observed. Such lattice instability occurring at the temperature $T \approx 2T_c$ might be, like the case in $A15$ compounds, a general characteristic for the perovskite superconducting ceramics and might have close relation with their high-T_c superconductivity. The difference between the anomalies, however, in the two systems is considerable, which is hardly surprising if the difference in structure is taken into account. The structure readjustment in $YBa_2Cu_3O_{7-y}$ is a rather slow process, e.g., the sound attenuation peaks are rather wide with a gentle slope, which was related to the ordering readjustments of oxygen atoms,[5,7,8] whereas for the Bi-based systems, there is no one-dimensional Cu-O chain and no evidence for diffusion movements of any atoms. The possible stretch or tilt of Cu—O or, Bi—O bonds are quite fast processes and thus might result in a sharp anomalous peak in sound attenuation.

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