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Ultrasound anomalies in single-phase $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ superconducting ceramics

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Abstract. Ultrasonic anomalies near 200 K in single-phase $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ ($x = 0$–0.2, $n = 1, 2$) superconducting samples were observed by velocity and attenuation measurements of both longitudinal and transverse sound waves. The remarkable isothermal-like anomalous changes near 200 K indicate that there are possible structural changes or phase transitions in the samples. On comparison with $YBa_2Cu_3O_{7-y}$, the different behaviours in ultrasonic anomalies are attributed to the differences in structure. It is suggested, however, that the lattice instability appearing near $T \approx 2T_c$ may be a common feature of the existing superconducting perovskites and may have some relation to their high T_c.

1. Introduction

In our early ultrasonic investigations, we found that there are possible structural changes or a lattice instability near 250 K, 160 K and above T_c in a $YBa_2Cu_3O_{7-y}$ superconducting ceramic (He *et al* 1987), which was confirmed by the results of other groups (Horie *et al* 1987, Laegreid and Fossheim 1988, Deng *et al* 1988). Slightly different results were also reported (Almond *et al* 1987, Wang *et al* 1987, Ewert *et al* 1987, Suzuki *et al* 1988). For the new suerconducting systems Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O, no report has been published so far. One of the reasons may be the difficulties in preparing suitable samples. The objective of this work has been to examine the ultrasonic characteristics of Bi(Pb)–Sr–Ca–Cu–O systems and to compare them with the characteristics of the similar superconducting ceramic $YBa_2Cu_3O_{7-y}$.

2. Experimental details

Six samples were used in this study; they can be divided into four groups, as follows: $Bi_2Sr_2CaCu_2O_{8+y}$, $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_{8+y}$, $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ and

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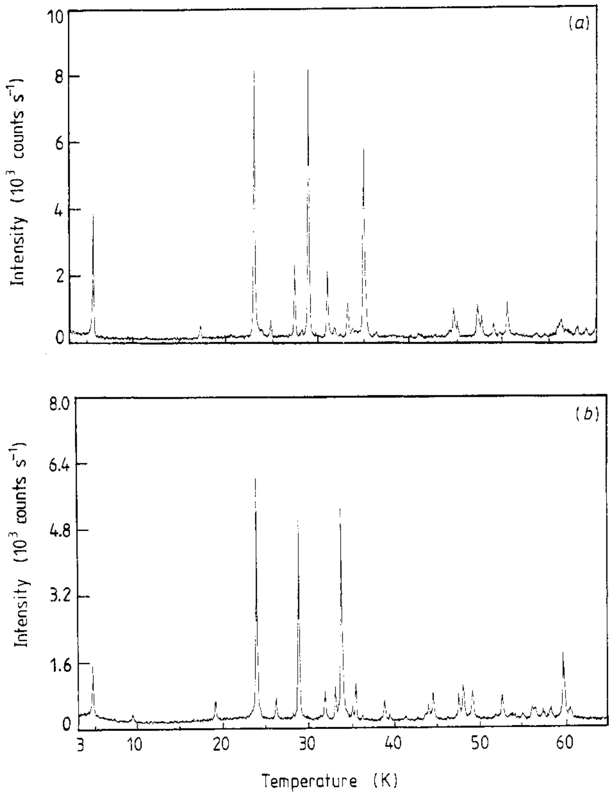

Figure 1. Typical x-ray diffraction spectra of single-phase (*a*) $(Bi_{0.85}Pb_{0.15})_2Sr_2CaCu_2O_{8+y}$ and (*b*) $(Bi_{0.85}Pb_{0.15})_2Sr_2Ca_2Cu_3O_{10+y}$ polycrystalline samples.

$(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_{10+y}$ single-phase polycrystalline samples. They were all prepared by the usual powder ceramic method. Powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and PbO (for Pb-doped samples only) were ground and mixed together in the appropriate anion proportions to yield the desired stoichiometry of the reacted compounds. In order to obtain samples with a single phase, special care must be taken to control the sintering temperatures and the oxygen pressures properly (Endo *et al* 1988). After sintering, the Pb-doped samples were slowly cooled to room temperature whereas the other samples were usually quenched in air. The resulting samples are cylindrical pellets with a diameter of 10–16 mm and a thickness of 3–5 mm. X-ray diffraction results proved that they were all of a single-phase (2212) or (2223) layered structure. Typical x-ray diffraction patterns are shown in figure 1. Resistivity measurements showed that the zero-resistance temperatures T_c were between 74 and 85 K for the (2212) phase samples and between 107 and 112 K for the (2223) phase samples. During the revision of this manuscript, an additional sample (BK0401) was kindly offered to us by the University of Science and Technology of China and examined at Tsinghua University in April 1989. The nominal composition of the sample is $BiSrCaCu_3O_z$ and it was quenched in liquid nitrogen after sintering; however, x-ray diffraction and resistivity measurements showed that it contains both (2212) and (2223) phases with transition temperatures at 87 K and 120 K respectively.

Matec 7700 series equipment was used for both longitudinal and transverse ultrasonic wave measurements with 5–15 MHz $LiNbO_3$ or quartz transducers. The transducers

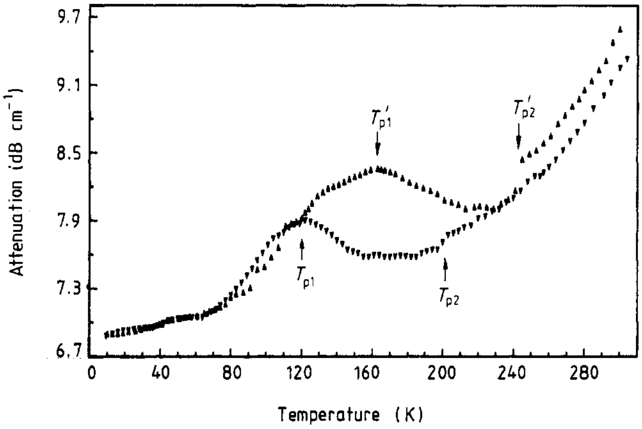

Figure 2. The temperature dependence of the changes in attenuation of 10 MHz longitudinal sound waves propagating in sample BW0701 ($Bi_2Sr_2CaCu_2O_{8+y}$) both when cooling (▼) and when heating (▲) the sample: ↑ ↓, temperatures of anomalous changes.

were bonded to the sample by water-free Nonaq stopcock grease in the usual way. The sound velocity was measured by the standard pulse-echo overlap method and the change in attenuation was measured by the double-echo method. For each measurement, at least two (for the transverse wave) or six (for the longitudinal wave) echoes can be clearly observed at room temperature. The experiments were carried out in a closed cycling refrigerator (Air Products) with a vacuum of better than 5×10^{-3} Torr. The temperature range was from 300 to 10 K with an accuracy of ± 0.1 K. The rate of temperature change was controlled within 0.3–0.5 K min^{-1} or slower to ensure that thermal equilibrium was achieved. Some of the above measurements were repeated in a conventional Dewar (300–78 K) with nitrogen gas for heat exchange. The reproducibility of the results is excellent.

3. Results

The first successful measurement of ultrasonic anomalies was performed in July 1988 on a $Bi_2Sr_2CaCu_2O_{8+y}$ sample with a comparatively lower T_c (74 K). The temperature dependences of the changes in longitudinal sound attenuation at 10 MHz for both cooling and heating the sample are shown in figure 2. It can be seen that in the cooling curve a remarkable broad attenuation peak appears near 120 K denoted as T_{p1}. Another anomalous change in attenuation step near 200 K denoted as T_{p2} is also noticeable. The same anomalies are observed in the heating curve, except that the anomalous temperatures in the heating curve are about 40 K higher than those in the cooling curve—clear evidence of thermal hysteresis. Correspondingly the curves of the longitudinal velocity of sound also reveal two anomalous changes (figure 3). The slope change of the cooling curve in figure 3, for example, is so remarkable near 80 K that the velocity stops its increasing trend and starts to decrease as the temperature is lowered. The anomalous change near 200 K is quite different, as the slope change of the curve (from 0.23 to 0.08 m s^{-1} K^{-1}) is accompanied by a sudden jump in velocity. Figure 4 shows the temperature dependence of the changes in the transverse velocity of sound and attenuation at 15 MHz when the same sample was cooled. The velocity curve reveals exactly the same anomalous behaviour as that shown in figure 3, whereas the attenuation curve

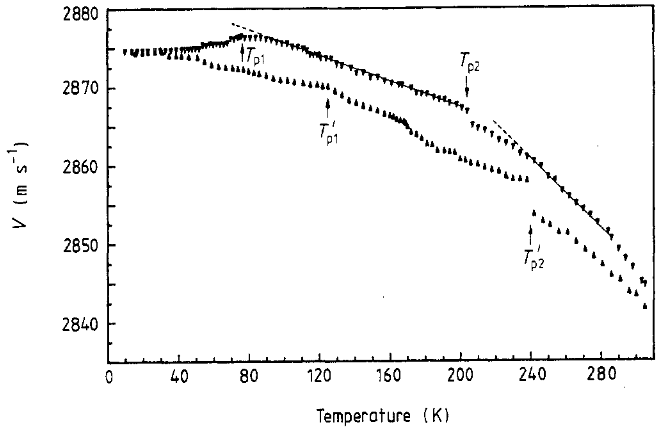

Figure 3. The temperature dependence of the velocity of 10 MHz longitudinal ultrasonic waves propagating in sample BW0701 both when cooling (▼) and when heating (▲) the sample: ↑ ↓, temperatures of anomalous changes; - - -, fitted linearly increasing trend.

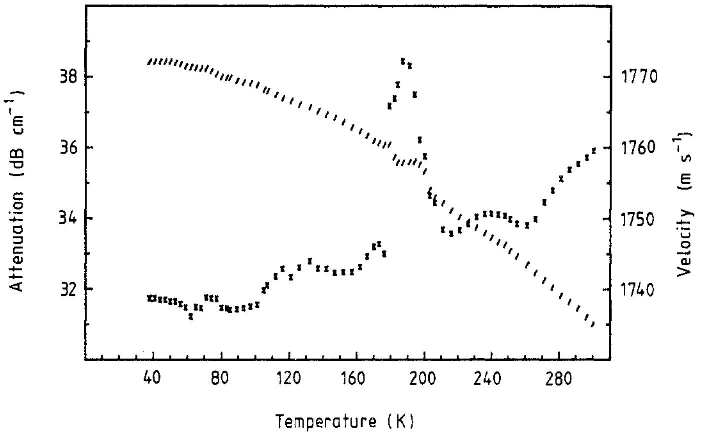

Figure 4. The temperature dependence of the changes in transverse velocity of sound (/) and attenuation (×) at 15 MHz for sample BW0701.

shows a striking peak at 200 K, manifesting unambiguous evidence for the existence of an attenuation anomaly.

In order to confirm the reproducibility of the above anomalies and to understand their physical meaning, measurements on the other six samples were performed to ensure that the results are real and reproducible. Typical results of the anomalous temperatures T_{p1}, T_{p2} (during cooling runs), T'_{p1} and T'_{p2} (during heating runs) and the corresponding attenuation changes $\Delta\alpha$ and $\Delta\alpha'$ and velocity changes ΔV and $\Delta V'$ as well as the ultrasound modes and frequencies F are summarised in table 1.

It can be seen that all of the samples show remarkable anomalies near 200–209 K (when cooling the sample) or 234–243 K (when heating the sample). If the rate of temperature change was slow enough, a striking sudden rise in both velocity and attenuation appears near 208–209 or 234–243 K and is followed by a noticeable sudden drop (see the insets of figure 5). A detailed study revealed that such a sudden rise in attenuation and velocity is actually an isothermal-like process. As the step in the temperature change

Table 1. Summary of the main results of ultrasonic anomalies in $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ samples. L denotes longitudinal mode and T transverse mode. Sample BW0701 was quenched in air after sintering. For sample BW1211, the same results were obtained after 3 months. For sample BP1214, measurements of three successive cooling–heating cycles in 48 h gave consistent results. Sample BK0401 was quenched in liquid nitrogen after sintering.

Sample	Phase	T_c (K)	F^* (MHz)	T_{p1} (K)	T'_{p1} (K)	T_{p2} (K)	$\Delta\alpha$ (dB cm^{-1})	ΔV (m s^{-1})	T'_{p2} (K)	$\Delta\alpha'$ (dB cm^{-1})	$\Delta V'$ (m s^{-1})
BW0701	(2212)	74	L10	120	160	200	0.2	2	240	0.4	5
	($x = 0$)		T15	120		200	6	4	240		
BP1210	(2212)	85	L10			208	1	6			
	($x = 0.15$)										
BP0311	(2212)	80	L10			208	1	7	234	0.6	3
	($x = 0.17$)		T10			208	5	5		7	11
BW1211	(2223)	107	L10			208	10	16	234	8.5	2
	($x = 0.15$)		L5			208	5	9	234	3	4
			T10			209	6	7	236	4	8
BP1214	(2223)	112	L10			209	5–7	7–9	243.5	7–8	3–4
	($x = 0.15$)										
BP0317	(2223)	110	L5			208	2	2			
	($x = 0.17$)										
BK0401	(2212) and	87	L5		120				243	1.5	
	(2213)		L10		120				243	2.5	
	($x = 0$)		T5						243	6	

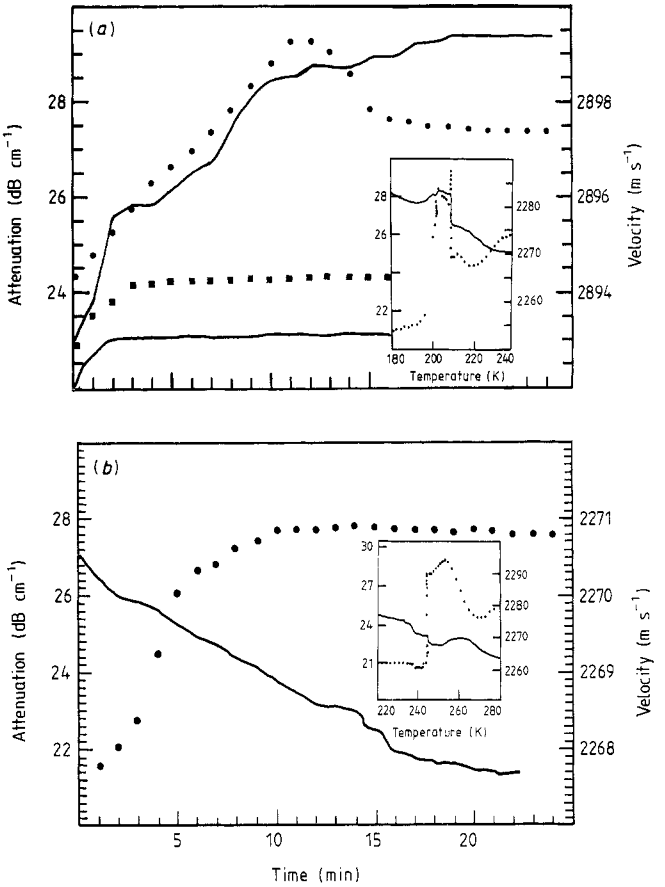

Figure 5. The time dependence of the changes in velocity (—) and attenuation (●) of 10 MHz longitudinal ultrasound waves propagating in sample BW1211 ($(Bi_{0.85}Pb_{0.15})_2Sr_2Ca_2Cu_3O_{10+y}$) in (*a*) cooling and (*b*) heating runs. The temperatures are 109.0 ± 0.1 K (the upper curves in (*a*)), 110.0 ± 0.1 K (the lower curves in (*a*)) and 243.5 ± 0.1 K (the curves in (*b*)). The corresponding temperature-dependent curves are also shown in the insets of both (*a*) and (*b*).

was only 1–3 K each time that this occurred, it usually took only a few minutes to achieve thermal equilibrium and hence to show stable values of sound attenuation and velocity, as shown in the lower curves of figure 5(*a*), whereas at the anomalous temperature, e.g. 209.0 ± 0.1 K (the accuracy of the temperature controller is ±0.1 K), the continuous changes in sound attenuation and velocity could even last for more than 20 min (the upper curves in figure 5(*a*)). The same isothermal-like process can be also seen in figure 5(*b*), during heating the sample. Both longitudinal and transverse sound waves showed similar anomalies at the same temperatures. Frequency-dependent measurements indicated no detectable shift of the anomalous temperatures, although the height of the anomalies did increase with increasing frequency (figure 6). It can also be seen from table 1 that the reproducibility of the anomalies is excellent. For example, results from three successive cooling–heating cycles, which lasted for 48 h, were consistent with each other (sample BP1214). The same results were obtained after an interval of 3 months (sample BW1211). The only exception, however, is the first sample (BW0701). The difference between the first sample (BW0701) and the others in attenuation anomalies

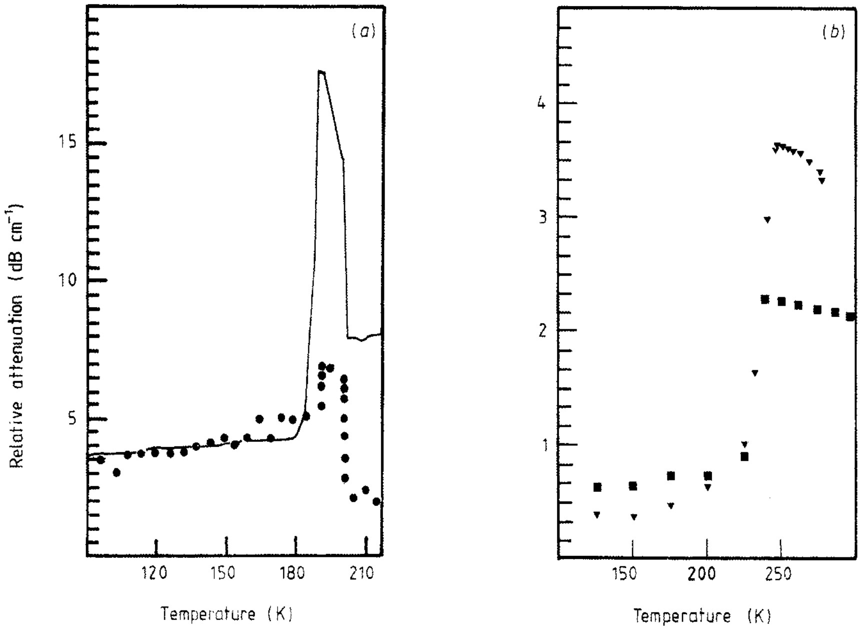

Figure 6. Frequency dependence of the changes in attenuation of (*a*) sample BW1211 during cooling runs (—, 10 MHz; ●, 5 MHz) and (*b*) sample BW0401 during heating runs (▼, 10 MHz; ■, 5 MHz).

may be attributed to the rather faster changing rate in temperature especially near T_{p2}, where 20–40 mins were needed to ensure that stable values of attenuation and velocity were obtained. Unfortunately we did not realise that there is an isothermal-like process until the second sample was examined (October 1988). The above anomalies cannot be due to the effects of transducers or bonding materials since, using the same transducers (quartz and $LiNbO_3$) and bonding agent (Nonaq grease), systematic examinations on quartz crystals, Ti–Ni–Fe alloys, and La–Sr–Cu–O and Y–Ba–Cu–O superconducting ceramics have been carried out and no similar anomalies were found. It is worth mentioning that the seven samples were made by three different laboratories (i.e. six of them were made by Tsinghua University and Peking University and one sample was offered to us by the University of Science and Technology of China and examined here (in April 1989) and the nominal compositions and sintering processes, etc, were considerably different. The excellent reproducibility of the anomalies near 200–209 or 234–243 K indicates that such anomalies are sample (or technological process) independent.

On the contrary, the situation for the attenuation anomaly near T_{p1} is completely different. It can be seen from figure 7(*a*) that, for all the Pb-doped samples which had been slowly cooled after sintering, the attenuation curves are quite flat near this temperature region whereas for samples BW0701 and BK0401, which was quenched in air and in liquid nitrogen, respectively, a broad attenuation peak appears near 160 or 120 K (for heating runs). It is thus suggested that this attenuation peak seems to relate to some kind of relaxation process and does depend on the sample composition and heat treatments. From figure 7(*b*), however, it seems that a small velocity hump always appears very close to the critical temperature T_c (or about 10 K higher than the zero-resistance temperature T_{c0}). It is very likely that there are some close correlations

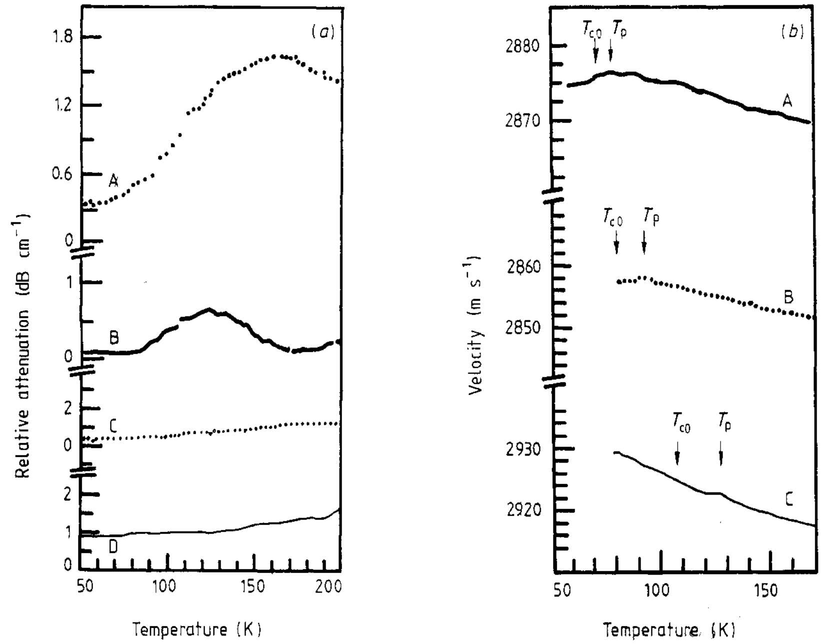

Figure 7. (*a*) The temperature-dependent ultrasonic attenuations below 200 K during heating runs: curve A, sample BW0701; curve B, sample BK0401; curve C, sample BP0311; curve D, sample BP1214. (*b*) The temperature-dependent ultrasonic velocities below 200 K during cooling runs: ↓, zero-resistance temperature T_{c0} and the anomalous hump T_p; curve A, sample BW0701; curve B, sample BP0311; curve C, sample BW1211.

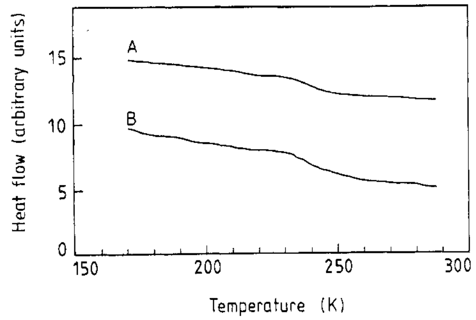

Figure 8. DTA results for sample BW1202 (curve A), and DSC results for sample BP1211 (curve B).

between them. Therefore it will be very interesting to continue this study using more precise techniques.

In order to investigate the physical origin of the above anomalies, 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 Du Pont 990 type differential thermal analyser (for sample BW1202, obtained in the same batch as BW1211) and a Du Pont 1090 type differential scanning calorimeter (for sample BP1211 obtained in the same batch as BP1210). It can be seen from figure 8 that both curves show similar specific heat changes between 230 and 245 K during the heating runs, implying that a phase transition had occurred. This was confirmed by our recent

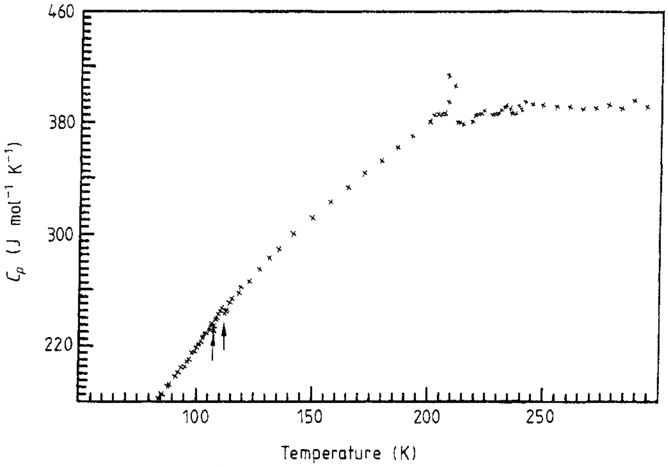

Figure 9. Specific heat of $(Bi_{0.85}Pb_{0.15})_2Sr_2Ca_2Cu_3O_{10+y}$ in which a clear anomaly near 210 K can be seen: ↑, superconducting transition temperatures of the samples.

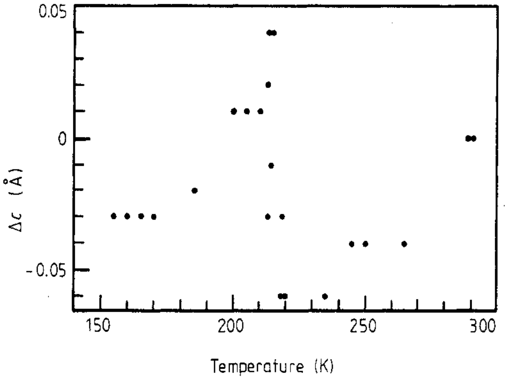

Figure 10. Temperature dependence of the relative change Δc in lattice constant of sample BW1202, obtained from x-ray diffraction experiments.

specific heat measurements. The measurements were conducted in the Chinese National Institute of Metrology with an accuracy of better than 1%. The total masses of the samples used were 8 g; these samples came from two batches with superconducting transition temperatures T_c of 107 K and 112 K, respectively. A clear anomalous peak with ΔC_p near 20 J mol^{-1} K^{-1} can be observed near 210 K (figure 9). X-ray diffraction experiments also showed a sudden anomalous increase in lattice constant near this temperature (figure 10), although 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 could occur.

4. Discussion

All the above experimental results seem to be consistent with each other, suggesting that a certain physical process takes place near these anomalous temperature regions

(T_{p2} or T'_{p2}). It is well known that ultrasonic measurement is a very sensitive volume probe for subtle structure changes. The above attenuation and velocity anomalies near T_{p2} or T'_{p2} indicate that some kind of structure change occurred. It was also found (He *et al* 1989b) that the bulk modulus derived from the above data, which reflects dilatational modes, decreases as the temperature is lowered in this region, and the derived Poisson ratio, which reflects changes in the inter-atomic bonding, shows irregularities near this temperature. The existence of the soft mode and the change in inter-atomic bonding forces are usually directly related to a displacive structural phase transition. The thermal analysis and specific heat results of the same samples provided unambiguous evidence of the existence of such possible phase transitions. The x-ray diffraction experiments confirmed that the fine structure (e.g. the lattice constants) does change during these phase transitions, although the average symmetry or the framework of the whole lattice does not alter. Such fine-structure changes could be the changes in bonding length or bonding configurations. For example, the possible tilt or stretch of Cu–O or Bi–O bonds or displacements of Bi and O atoms will result in an anomalous increase in lattice constants, leading to a structural phase transition. To determine the details of the phase transition, however, more powerful experiments (e.g. temperature-dependent neutron diffraction investigations) and theoretical calculations and modelling are necessary and are now being conducted in this group.

At the present stage, it is worth mentioning the interesting work of Dmowksi *et al* (1989). From their neutron scattering results on $Tl_2Ba_2CaCu_2O_{8+y}$ at 17 K, Dmowksi *et al* proposed a model of short-range ordering due to displacements of thallium and oxygen atoms. It is suggested that, at low temperatures, both Tl (or Bi in our case) and O atoms are displaced along the $\langle 1\,1\,0 \rangle$ direction, resulting in locally orthorhombic order. The ordering, however, remains very much short range and does not alter the average symmetry, resulting in no distinct change in diffraction pattern, which is consistent with our x-ray diffraction results. Similar displacements could occur for Bi and O atoms near 200 K, leading to a displacive structural phase transition. As mentioned by Dmowksi *et al*, such local ordering has many implications with respect to the ordering of superconductivity in these oxides. Recent band-structure calculations (Hybersten and Mattheiss 1988) also indicate that the Bi–O octahedra are important for superconductivity.

As mentioned in § 1, in our early investigations we found that there are ultrasonic anomalies near 160 and 250 K for $YBa_2Cu_3O_{7-y}$ superconductors, which are accompanied by anomalous changes in specific heat (Laegreid *et al* 1987) and lattice constants (He *et al* 1989a). Now similar anomalies near 200–209 K for the Bi(Pb)–Sr–Ca–Cu–O superconductors are also observed. The nature, however, of the attenuation anomaly in $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ is different from that of $YBa_2Cu_3O_{7-y}$. The latter showed a very broad peak with its central position about 20 K higher than that of the corresponding velocity anomaly (He *et al* 1987, Laegreid and Fossheim 1988), whereas the former showed a sudden change (or quite a narrow peak) at the same temperature as the velocity anomaly. Such a striking difference has a physical origin. $YBa_2Cu_3O_{7-y}$ has both a layer structure and a chain structure and many believe that the Cu–O ordered array along the *b* axis accounts for the strong superconductivity. The ordering readjustments of oxygen vacancies on approaching T_c from room temperature was suggested as a possible explanation for the observed ultrasonic, specific heat and other anomalies (He *et al* 1987, 1988, Laegreid *et al* 1987, Laegreid and Fossheim 1988). Such ordering readjustment process must depend on the ability of oxygen atoms to make diffusion movements and could take place in a rather wide temperature range, corresponding to a 'broad diffuse phase transition' (Kurtz *et al* 1989). For the Bi(Pb)–Sr–Ca–Cu–O superconductor systems, their tetragonal structure consists of a packing of two crystallographically shared $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ ($n = 1, 2$) slabs with no Cu–O chain but 10 or 12 weakly interacting layers (four or six ABO_3 layers plus six AO layers). Like La–Sr–Cu–O, the small displacements of atoms, e.g. the displacements of Bi and O atoms (as suggested in the model of Dmowksi *et al*) might break the symmetry and result in a slight difference between the *a* and *b* axes and a change in the *c* axis. Such a small lattice distortion could be completed within a very short temperature range, as a sudden change.

It is interesting to point out that the lattice instability or structural readjustment seems to be a common feature of all the layered superconducting perovskite ceramics discovered so far. Although the driving forces might be quite different from one another, the lattice instability seems very likely to appear at temperatures near $T = 2T_c$, which is surprisingly similar to that of A15 compounds. It is suggested that such structural instability may, as seems to be the case in A15 compounds, be important for the understanding of the extraordinary superconducting properties of these perovskite ceramics and may have some close relation to their high T_c.

5. Conclusions

(i) Ultrasound anomalies near the range 200–209 K in single-phase $(Bi_{1-x}Pb_x)_2Sr_2Ca_nCu_{n+1}O_{2n+6+y}$ ($x = 0$–0.2, $n = 1, 2$) superconducting systems were observed during cooling of the samples by velocity and attenuation measurements. The results were consistent for both longitudinal and transverse sound waves with a frequency range of 5–15 MHz and are reproducible for seven samples made in three different laboratories. Detailed investigations revealed that such anomalous changes were actually isothermal-like processes. On heating the samples, the anomalous temperatures shifted to 234–243 K, indicating thermal hysteresis.

(ii) The anomalous attenuation peak near 120–160 K observed for some samples proved to be related to some kind of relaxation process and does depend on the sample composition and heat treatments. The small velocity hump, however, appearing very close to the superconducting transition temperature T_c might have some close correlation with its high T_c.

(iii) Thermal analysis and specific heat measurements, x-ray diffraction experiments and the derived elastic constants of the same samples showed anomalous changes near the same temperature regions in which the ultrasonic anomalies appear. The consistency of all the above experimental results suggests strongly that a structural phase transition takes place near these temperature regions. The changes, however, remain very much short range or of fine structure and do not alter the average symmetry or the framework of the whole lattice as indicated by the x-ray diffraction pattern. The possible tilt or stretch of Bi–O bonds or even displacements of Bi and O atoms (as suggested in the model of Dmowksi *et al*) could result in the observed anomalies and may have correlations with its high-T_c superconductivity.

(iv) It is suggested that the lattice instability or structural readjustment appearing at temperatures near $T = 2T_c$ seems to be a common feature of the existing layered superconducting perovskite ceramics. The driving forces, however, and the characteristics of the anomalies observed are quite different for different superconducting perovskite systems owing to the difference in their structures. Such a lattice instability might have a close relation with their high T_c as the case of A15 compounds.

Acknowledgments

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