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Elastic behaviour of some Y–Ba–Cu–O high T_c superconducting materials with various oxygen concentrations

K. Ganesh[a], R.J. Topare[b], S.S. Shah[b], P. Venugopal Reddy[a,*]

[a]Department of Physics, Osmania University, Hyderabad 500 007, India
[b]Department of Physics, Dr. B.A. Marathwada University, Aurangabad, India

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Abstract

Y–Ba–Cu–O high T_c superconducting materials with various oxygen concentrations have been prepared by the solid state reaction method. After characterizing the samples X-ray diffraction, iodometry, density etc. measurements, the ultrasonic velocity studies were also undertaken over a temperature range 80–300 K by the pulse transmission technique. It has been observed that the room-temperature Young's and rigidity moduli are found to increase continuously with increasing oxygen concentration of the samples. A suitable explanation for the observed behaviour based on Cu(1)–O(4) bond length, oxygen deficiency, copper valency fluctuations etc. is given. Further, it has also been observed from the velocity vs. temperature plots of all the samples that they are found to behave like normal solids, but for the exhibition of a velocity maximum in the temperature range 160–210 K, signifying the presence of lattice instabilities. A model based on the readjustment of oxygen atoms among Cu–O planes has been used to explain the observed elastic anomalies.

Keywords: Y–Ba–Cu–O, High-T_c superconductors; Ultrasonic velocity

1. Introduction

The role played by the variable oxygen content and the ordering of oxygen vacancies is one of the most interesting and important features of RE–Ba–Cu–O (RE is a rare earth ion) superconducting cuprates. The effect of oxygen stoichiometry on the crystal structure, namely, the orthorhombic-to-tetragonal phase transition [1–3], and on charge transport properties [4] has been studied extensively. In fact, oxygen concentration is considered to be one of the most important factor responsible for symmetry transitions [5] and it has been observed that the oxygen site vacancies become ordered as the crystal becomes a superconductor. It is well known that the oxygen concentration (and hence the porosity of a ceramic superconductor) has tremendous influence on the mechanical properties. Although some scattered information on this particular aspect is available in the literature, no definite conclusion has been arrived at. As such a systematic study of elastic moduli with various oxygen deficiencies of Y–Ba–Cu–O is one of the important motivation for the present investigation.

The present investigation is also designed to understand the phenomenon of lattice instabilities in these materials. It was generally recognized that the phenomenon of lattice and structural instabilities above T_c is a common feature among A15 compounds (Nb_3Sn, V_3Si, Nb_3Ge etc.), generally known as conventional high T_c superconductors. In fact, a close relationship between the high value of T_c and the lattice instabilities among A15-type superconductors [6] was reported. Soon after the discovery of ceramic superconductors, many investigators started to look for a similar type of correlation between high value of T_c and instabilities if any. As the lattice instabilities are manifested well in the elasticity constants of material, a number of studies based on the ultrasonic behaviour of these materials were undertaken with a view to knowing whether the correlation between the high value of T_c and structural instabilities is still valid. 8 years after the discovery of high T_c superconductors there still are several reports both in favour and against the phenomenon of lattice instabilities among

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* Corresponding author.

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these new class of materials. During the last 5 years, few papers published from this laboratory also [7,8] consistently indicate the presence of lattice instabilities among the ceramic superconductors. However, none of the work published either by us or by others so far has given any direct or indirect evidence for a one-to-one relationship between these two parameters. With a view to throwing some more light on this particular aspect, the present investigation uses another set of samples, namely Y–Ba–Cu–O with various oxygen deficiencies. The results of such an investigation are presented here.

2. Experimental details

2.1. Materials

The $YBa_2Cu_3O_{7-\delta}$ samples of the present investigation were prepared by the well-known solid state reaction method using highly pure (99.9%) Y_2O_3, $BaCO_3$ and CuO, in the stoichiometric ratio of 1:2:3. The powders after thorough mixing and grinding were calcined twice at 900 °C for 24 h. The calcined powders then pressed into three pellets, hereafter designated as Y1, Y_2, Y3, of 10 mm diameter and 2–3 mm thickness followed by sintering at 950 °C for 24 h. Later, the sintered samples were annealed for 36 h at 550 °C in different oxygen partial pressures so that samples with different oxygen concentrations could be obtained. All the heat treatments, i.e. heating and cooling, were carried out at a rate of 1 $°C\,min^{-1}$.

2.2. Methods

With the aim of determining the superconducting transition temperature (T_c), the D.C. resistance measurements were carried out over the temperature range 80–300 K, using the standard four-probe method. The X-ray diffraction studies have also been undertaken with Cu Kα radiation in the scanning range $2\theta = 4$–60°, and it has been observed that the diffractograms contain a major orthorhombic phase with the characteristic defect perovskite structure.

The surface morphology and grain size of a solid material are important surface properties, and they were measured by a scanning electron microscope (JSM-35CF model). The oxygen concentration and copper valency of cuprate superconductors in general and Y–Ba–Cu–O samples in particular are expected to vary from sample to sample; both the parameters were also determined by the standard iodometric titration method [9]. Later, bulk density measurements were also carried out by the immersion method. Finally, the longitudinal and shear wave velocities were measured over the temperature range 80–300 K by the pulse transmission technique, details of which have been given elsewhere [10]. The velocity measurements were carried out while both cooling and warming at the rate of 1 K min^{-1} and the process was repeated three times. The overall accuracy of the longitudinal velocity is found to be 1%.

3. Results

3.1. Electrical resistance vs. temperature

The electrical resistance with temperature is carried out in the range 80–300 K. All the samples are found to exhibit a single-step superconducting transition with $T_{c(onset)}$ in the range 86–89 K and a transition width of around 4 K. The room-temperature resistance $R_{300\,K}$, $T_{c(onset)}$, $T_{c(0)}$ and ΔT for all the samples are given in Table 1. As expected, $R_{300\,K}$ is found to decrease, while $T_{c(0)}$ to increasing continuously with increasing oxygen concentration.

3.2. X-ray diffraction

It has been observed from the X-ray diffractograms that almost all the samples of the present investigation are found to have a single orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$. Although some traces of second phase (CuO and Y_2BaCuO_5) could be seen, they were not within the limits of detectability. Further, by indexing the X-ray patterns of all the three samples with respect to an appropriate unit cell, the values of the *d* spacings and the cell parameters have been calculated and are given in Table 2. It can be seen from the table that the cell parameters *a* and *c* are found to decrease, while the *b* parameter increases with the increasing oxygen content and the behaviour is in conformity with that reported in [11]. All the lattice parameters are found to be comparable, within the limitations of the experimental error [12].

3.3. Oxygen content

The oxygen content present in Y–Ba–Cu–O samples is a very important physical parameter and knowledge of its value for each of the samples is essential. In general, its value can be calculated either

Table 1
$R_{300\,K}$, $T_{c(onset)}$ and $T_{c(0)}$ for $YBa_2Cu^3O_{7-\delta}$ samples

Sample	$R_{300\,K}$ (mΩ)	$T_{c(onset)}$ (K)	$T_{c(0)}$ (K)	ΔT (K)
Y1	7.72	92	89	3
Y2	6.69	93	90	3
Y3	5.60	95	91	4

Table 2
X-ray diffraction and other experimental data

Sample	Lattice parameters			Ratio $(b-a)/a$ $(\times 10^{-2})$	Oxygen content		Copper valency
	a (Å)	b (Å)	c (Å)		Experimental	Theoretical	
Y1	3.839	3.881	11.713	1.09	6.69	6.69	2.13
Y2	3.834	3.883	11.694	1.28	6.80	6.82	2.20
Y3	3.823	3.885	11.683	1.62	6.89	6.91	2.26
Literature	3.823	3.886	11.684				

by titration or by a theoretical method. The experimental method is simple and straightforward, while the theoretical method requires knowledge of the lattice parameter data and the details are outlined below.

The oxygen content together with the copper valency determined by the iodometric titration method are given in Table 2. Jung et al. [13] while discussing the influence of silver on various physical properties of $YBa_2Cu_3O_{7-\delta}$–Ag composites, observed that there is a correlation between the lattice parameter c and the oxygen deficiency δ and derived a relationship between them:

$$\frac{dc}{d\delta}=0.047 \tag{1}$$

Using Eq. (1), the values of oxygen content have been calculated for all the samples of the present investigation and are given in Table 2 together with those by the titration method. It can be seen from the table that the values obtained by the two methods are in good agreement, thereby indicating that both are good.

3.4. Elastic moduli at room temperature

The experimental values of longitudinal wave velocity V_l and shear wave velocity V_s altogether with those of computed Young's modulus E and rigidity modulus G are given in Table 3. Both the elastic moduli are found to increase continuously.

3.5. Porosity correction

As the porosity values are found to vary from 20 to 33%, the measured elastic moduli do not have much significance unless they are corrected to a void-free state. As such, the non-porous values of all the moduli have been arrived at by using MacKenzie's [14] formulae.

$$\frac{B_0-B}{B_0}=\frac{P(3B_0+4G_0)}{4G_0(1-P)}+O(P)^3 \tag{2}$$

$$\frac{G_0-G}{G_0}=\frac{5P(3B_0+4G_0)}{(9B_0+8G_0)}+O(P)^3 \tag{3}$$

where B_0 and G_0 are the bulk and rigidity moduli respectively of a non-porous matrix, while B and G are the real quantities of the same parameters and P is the porosity of the material. The corrected values of the moduli, i.e. E_0 and G_0, are given in Table 4.

3.6. Scanning electron microscopy

The scanning electron micrographs of all the samples of the present investigation on fractured surface are shown in Fig. 1. The grains of the samples are randomly oriented with 10 μm size. Further, the grain size is found to decrease with increasing oxygen concentration and the behaviour is in conformity with the observation variation in elastic moduli with increasing oxygen concentration. This is quite possible

Table 4
Elastic moduli corrected to zero porosity

Sample	E_0 (GPa)	G_0 (GPa)	Θ_D (K)	σ_0
Y1	96	39.7	311	0.21
Y2	103	40.5	315	0.27
Y3	118	47.5	341	0.24
Literature [16]	126	50.5	–	–

Table 3
Experimental data of $YBa_2Cu_3O_{7-\delta}$

Sample	Bulk density (kg m^3)	Porosity (%)	V_l (m s^{-1})	V_s (m s^{-1})	E (GPa)	G (GPa)
Y1	4.258	33.3	3086	1.773	40.3	13.4
Y2	4.673	26.8	3564	2044	58.9	19.5
Y3	5.021	21.2	3957	2352	80.7	27.7

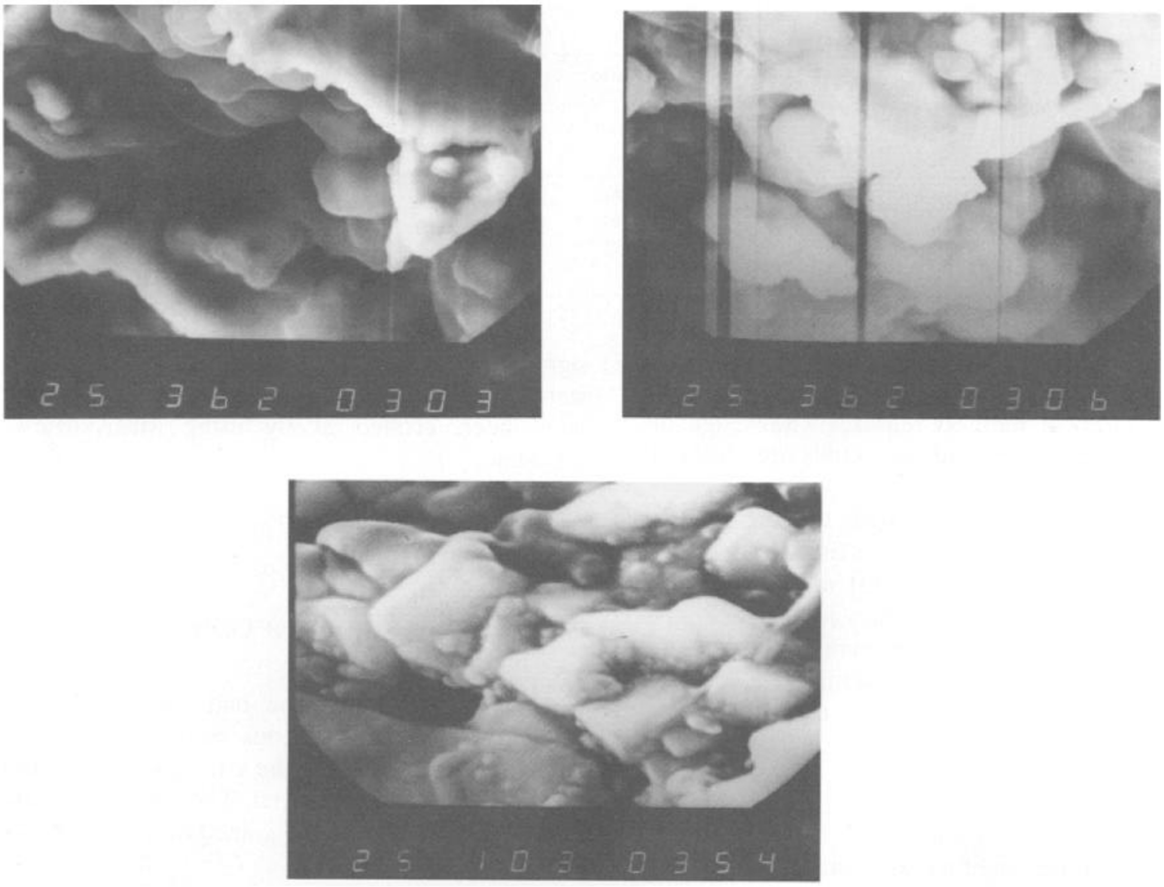

Fig. 1. Scanning electron micrographs: (a) Y1; (b) Y2; (c) Y3.

because finer grains are supposed to be mechanically stiffer than coarser grains.

3.7. Acoustic Debye temperature

The Debye temperature $\Theta_{\rm D}$ provides useful information about the thermal properties of solids in general and superconductors in particular. As such, the values $\Theta_{\rm D}$ have also been calculated using Anderson's [15] formula:

$$\Theta_{\rm D} = V_{\rm m} \frac{h}{k} \left(\frac{3qN_0\rho}{4\pi M} \right)^{1/3} \tag{4}$$

where h is Planck's constant, k Boltzmann's constant, N Avogadro's number, M the molecular weight of the specimen, q the number of atoms in a molecule, ρ the density of the specimen, and $V_{\rm m}$ the average sound velocity. Here $V_{\rm m} = \frac{1}{3}(2/V_{\rm s}^{0^3} + 1/V_{\rm l}^{0^3})^{-1/3}$ and the $V_{\rm m}$ values are included in Table 4. The longitudinal and shear wave velocities corrected to zero porosity ($V_{\rm l}^0$ and $V_{\rm s}^0$ respectively) used here have been obtained from the corresponding non-porous elastic moduli by

$$V_{\rm s}^0 = \left(\frac{G_0}{\rho} \right)^{1/2} \tag{5}$$

$$V_{\rm l}^0 = \left(\frac{2V_{\rm s}^{0^2}}{(1-2\sigma_0) + V_{\rm s}^{0^2}} \right)^{1/2} \tag{6}$$

It can be seen from the table that all the elastic moduli including $\Theta_{\rm D}$ are found to increase with increasing oxygen content.

3.8. Comparison with literature

Ledbetter [16], while discussing the variation in elastic moduli with oxygen content of a series of Y–Ba–Cu–O polycrystalline samples, observed that they do not vary systematically. In contrast with this, although the number of samples studied in the present investigation are only three, a definite conclusion that both the moduli increase with increasing oxygen concentration, has been arrived at. Further, the value of 118 GPa obtained for Young's modulus of a sample in the present investigation (with an oxygen concentration of 6.89) is comparable with that reported by Ledbetter for a sample having almost the same oxygen content. Even the slight difference in the value could be attributed to the variations in the microstructure of the samples.

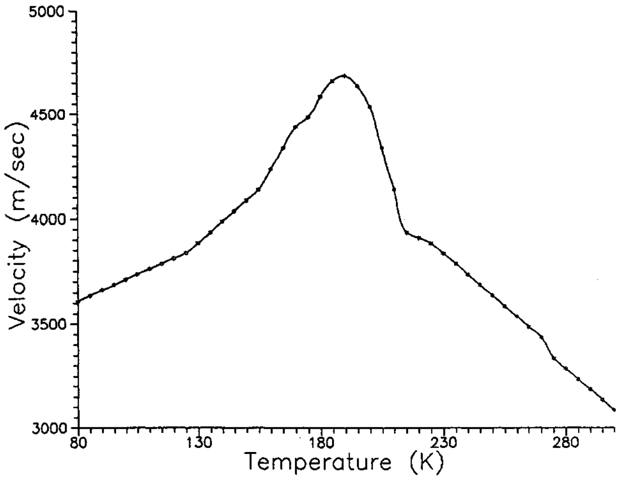

Fig. 2. Temperature variation of longitudinal velocity in Y1.

4. Temperature variation in longitudinal velocity

The temperature variation in longitudinal velocity for the three samples over the temperature range 80–300 K is shown in Figs. 2–4. It can be seen from the figures that the velocity of all the samples is found to increase continuously with decreasing temperature, reaching a maximum value at a particular temperature, hereafter designated T_m. Later, the velocity surprisingly is found to decrease continuously and more rapidly. However, in the vicinity of superconducting transition temperature T_c, the decrease in the velocity slows down considerably. A close examination of the all the three figures indicates that it appears as though, but for the occurrence of a hump in the temperature range 160–210 K, the longitudinal velocity of all the three samples, after showing an initial increase over a small temperature region, remains almost constant exhibiting a normal solid behaviour, whose velocity is likely to increase with decreasing temperature. As such it may be concluded that all the samples exhibited well-defined velocity peaks, signifying anomalous behaviour in that temperature region.

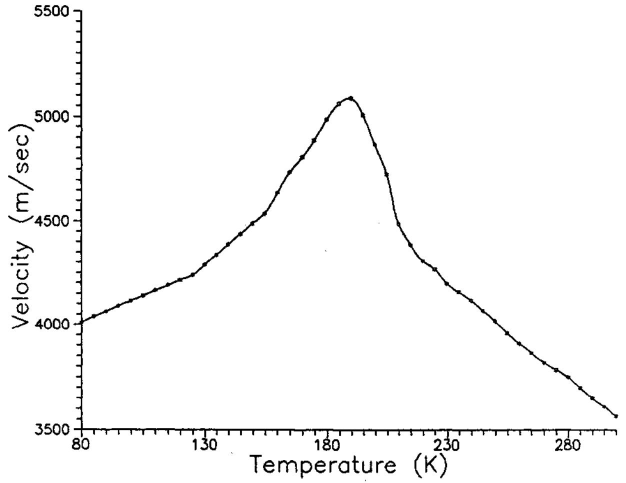

Fig. 3. Temperature variation of longitudinal velocity in Y2.

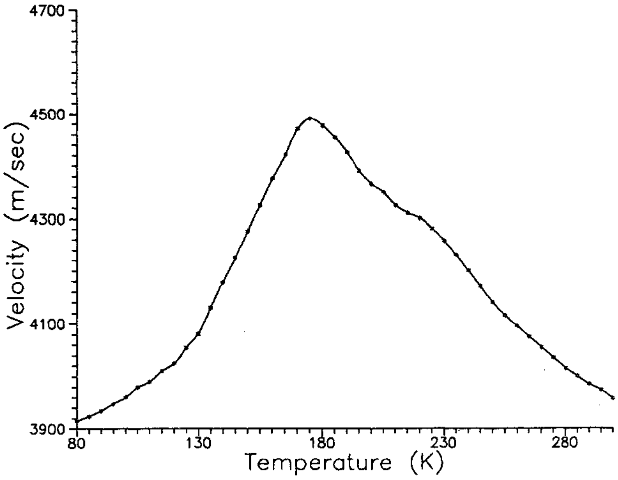

Fig. 4. Temperature variation of longitudinal velocity in Y3.

5. Discussion

5.1. Room-temperature elastic behaviour

It is known [17] that the perovskites are oxides having the general formula ABO_3. By triplicating the elementary cell along the *c* axis, with A = RE and Ba and B = Cu, $REBa_2Cu_3O_{7-\delta}$-type high temperature superconductors are obtained. In $REBa_2Cu_3O_{7-\delta}$ samples, since the number of oxygen atoms are $O_{7-\delta}$ rather than O_7, these compounds are known to be oxygen deficient and the phenomenon usually occurs owing to the elimination of O from RE plane and partially from one of the CuO_2 planes. It is also known that the compounds with vacant sites are known to be elastically softer [18,19] than those with compounds with filled sites. In the samples of the present investigation since there are number of oxygen vacant sites for the reasons explained above, their presence must have given rise to a lower elastic moduli than otherwise. With decreasing oxygen deficiency, since the number of vacant sites decreases considerably, an observed increase in elastic moduli is expected.

The valence fluctuations of the copper ions play an important role in the mechanism of superconductivity in Y–Ba–Cu–O and other related compounds. There are two different copper sites in the unit cell of Y–Ba–Cu–O structure: these are designated as Cu(1) chain sites and Cu(2) sites. It is known that [20,21] the valence of Cu(1) fluctuates between Cu^+ and Cu^{3+}, while that of Cu(2) varies from Cu^+ and Cu^{2+}. These fluctuations appear to be one of important characteristics of the high T_c superconductors formed with copper oxides. It is also known that, since the higher valence ions are smaller than the lower valence ions, coupling to the lattice is generally stronger for longitudinal modes. The increase in elastic moduli with increasing copper valencies observed in the present investigation is in conformity with the above observation.

In fact, this observation is in conformity with the findings of Kim et al. [22] who have studied the valence fluctuation aspects of high T_c superconductors. These workers observed that, because of the valence fluctuations in copper oxide compounds, the softening in the bulk modulus and Poisson's ratio competes with the force constant effects, resulting in a high value of bulk modulus and a positive Poisson's ratio.

Further, it was reported [23] that a continuous increase in the oxygen deficiency of the $REBa_2Cu_3O_{7-\delta}$ samples results in a continuous decrease in the Cu(1)–O(4) bond length and lattice parameter ratio $(b-a)/a$. In fact, it was observed that the tetragonal Gd–Ba–Cu–O which has only six oxygen atoms exhibits elastically softer behaviour than the orthorhombic compound having 7–δ oxygen atoms [24]. Therefore it may presumably be assumed that the observed variation in Young's modulus with decreasing oxygen deficiency may be due to increase in the Cu(1)–O(4) bond length. In fact the observed continuous decrease in the lattice parameter ratio $(b-a)/a$ with increasing oxygen deficiency clearly confirms the above conclusion.

5.2. Temperature variation in elastic moduli

Velocity maxima are not totally uncommon to high T_c superconducting materials, as several researchers have reported earlier [25–29] almost similar values. According to these workers, the elastic instabilities in solids are generally manifested either by a downward cusp or by a step. Cusps are usually observed near phase transitions mainly owing to the weakening of certain force constants, such as softening of phonon modes, while the velocity maxima are observed near order–disorder transitions resulting from the reorientation or ordering of oxygen ions in the copper–oxygen planes. It was also observed that the lattice instabilities above T_c are a type of precursor to the superconducting phenomenon. In view of this, it may be speculated that the velocity maxima observed among the samples in the present investigation could be due to ordering readjustments of the oxygen atoms among the Cu–O planes.

Further, the lattice instabilities are observed not only in the form of velocity maxima among the samples of the present investigation but also in other forms such as softening etc.; as observed by others earlier [7,8], no definite relationship between the high value of T_c and lattice instabilities could be arrived at.

In fact, it was reported by Levy [30] and Fossheim et al. [31] that there is a correlation between the anomalous temperature dependence and hysteresis effect in the case of oxide superconductors. Strong hysteresis effects are in turn closely related to the grain size of the sintered oxide superconductors. According to Levy [30], coarse-grained samples of grain diameter 50 μm and thickness 10 μm always exhibit hysteresis. This is possible because, in a sample with large crystallites, there probably exists two phases: a high T_c phase that is stiffer and a low T_c phase that is softer, resulting in a hysteresis in the ultrasonic velocity (because two thermally different phases always exhibit a hysteresis effect). It was also reported that [32,33] the anomalous temperature difference of elastic constants may not occur in a sample with fine grains (less than 5 μm) and a high density (above 90%). It was also observed that the elastic anomalies are possible only when the grains of the sintered sample have grown to a sufficient size. It was also concluded that [34,35] the microstructure of the oxide superconductors is the main controlling factor for the generally observed elastic anomalies. In the present investigation, since the grain size is of the order of 10 μm and the samples to a large extent are single phase, a hysteresis effect in the ultrasonic velocities has not been observed.

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