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ELASTIC PROPERTIES AND INFLUENCE OF Ba-SITE SUBSTITUTION ON SUPERCONDUCTIVITY OF $HoBa_2Cu_3O_{7-\delta}$

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ABSTRACT

The ultrasonic velocities of 10 MHz longitudinal and shear waves have been measured on $HoBa_2Cu_3O_{7-\delta}$ using the pulsed-echo-overlap method. Superconducting $HoBa_2Cu_3O_{7-\delta}$ ($T_{c\ zero}$~89 K) showed a longitudinal velocity change of 2.3 % between 80 K to 270 K and an anomalous change in slope around 230 K indicating a pronounced lattice stiffening. A similar velocity anomaly was not observed for non-superconducting $HoBa_2Cu_3O_{7-\delta}$. Absolute longitudinal and shear velocity measurements on superconducting and non-superconducting $HoBa_2Cu_3O_{7-\delta}$ at 80 K showed strong influence of oxygen content on elastic properties. In addition, ultrasonic velocity measurements was performed on $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$ ($T_{c\ zero}$~70 K). $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$ showed a change in longitudinal velocity of 2.0 % between 80 K - 270 K and a change in shear velocity of around 1.5 % between 80 K - 195 K. A longitudinal velocity anomaly around 230 K, similar to superconducting $HoBa_2Cu_3O_{7-\delta}$, was also observed. The velocity anomalies are explained in terms of possible oxygen-related processes and effects of Ba-site substitution.

INTRODUCTION

Ultrasonic investigations at low temperatures are useful in providing valuable information on various dynamic properties of materials and are sensitive to changes in elastic properties. Studies on $REBa_2Cu_3O_{7-\delta}$ (RE-rare earth) and other high-temperature superconductors showed several elastic anomalies near T_c [1,2] and above 200 K [3,4]. The elastic anomalies above 200 K are related to the oxygen content and are interpreted to be due to some form of oxygen ordering in the materials. The studies confirm the major role played by oxygen not only on superconductivity of high-temperature superconductors but also on its elastic properties. Nevertheless, the nature of the mechanisms that control the elastic anomalies remains an open question.

On the other hand, the effects of chemical substitutions on the physical and superconducting properties of $REBa_2Cu_3O_{7-\delta}$ have been extensively reported. Reasonable interest was focussed on occupancy of RE^{3+} at Ba-site of $REBa_2Cu_3O_{7-\delta}$ to investigate the importance of the atomic-site in the 123 structure [5-7]. It was also predicted that Pr123 would be a superconductor if it is synthesized without the magnetic Pr ion going into

the Ba-site [8]. However, the question still remains whether the magnetic RE^{3+} ions at the Ba-sites really have fatal effects on superconductivity. Very few ultrasonic studies have reported the effect of chemical substitutions on absolute velocity values and temperature dependent velocity profiles of high-temperature superconductors [9-13]. Thus, an ultrasonic study on $RE(Ba_{2-x}RE_x)Cu_3O_{7-\delta}$ would be of particular interest to provide further understanding on the importance and role played by the Ba-site.

This paper reports on the longitudinal and shear ultrasonic wave velocity measurements in superconducting $Ho(Ba_{2-x}Ho_x)Cu_3O_{7-\delta}$ (x= 0 and 0.15) and non-superconducting $HoBa_2Cu_3O_{7-\delta}$ with the aim of investigating the effect of oxygen content and Ba-site substitution on the elastic properties of these materials. Powder X-ray diffraction was performed to determine structure of the samples.

SAMPLES PREPARATION AND EXPERIMENTAL DETAILS

The $HoBa_{2-x}Ho_xCu_3O_{7-\delta}$ (x=0 and 0.15) samples were prepared by mixing appropriate amounts of Ho_2O_3, $BaCO_3$ and CuO powders with purity ≥ 99.99%. The materials were ground in a mortar then calcined in air at around 900 °C for 48 hours with several intermittent grindings and oven cooled. The powders were then pressed into pellets of ~12.5 mm diameter and 2-3 mm thickness under a load of 8 to 9 tons. The pellets were sintered at the same temperature for 24 hours and slow cooled to room temperature at 40 °C per hour. The non-superconducting sample was prepared by reheating the $HoBa_2Cu_3O_{7-\delta}$ sample at around 900 °C for 30 minutes and quenching it immediately in liquid nitrogen.

Electrical resistance (dc) measurements of the samples were carried out using the four-point-probe technique with silver paint contacts. The samples were also examined by X-ray powder diffraction with CuK radiation using Siemens D 5000 diffractometer.

The ultrasonic velocity was measured at 10 MHz using a Matec 7700 system which utilizes the pulse-echo-overlap technique. The transducer was bonded on polished sample surface using Nonaq stopcock grease. Sound velocity was propagated along the direction of pressing using X-cut (longitudinal) or Y-cut (shear) transducer with a carrier frequency of 10 MHz. The velocity measurements were performed in an Oxford Instrument liquid nitrogen cryostat model DN 1711 and the temperature was changed at a rate of around 1 K/min. during warming and cooling. No thermal expansion correction was made.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns (Fig. 1) showed all samples to be generally single phased 123 structure. Minor impurity peaks can be observed for $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$. Electrical resistance versus temperature measurements for $HoBaCu_3O_{7-\delta}$ and $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$ (Fig. 2) showed metallic normal state behaviors with $T_{c\,zero}$ of 89 K and 70 K, respectively. Quenched $HoBa_2Cu_3O_{7-\delta}$ is non-superconducting down to

80 K and it not expected to superconduct because of high resistivity value at room temperature. Table 1 shows the $T_{c\,zero}$, $T_{c\,onset}$, resistivity at 300 K, density and lattice parameters of all samples. The absolute values of longitudinal and shear velocities at 80 K are tabulated in Table 2.

Table 1. $T_{c\,zero}$, $T_{c\,onset}$, resistivity (at 300 K), density and lattice parameters of a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$

Sample	T_c zero (K)	T_c onset (K)	Resistivity (mΩ.cm)	Density (gcm^{-3})	Lattice Parameters		
					a(Å)	b(Å)	c(Å)
$HoBa_2Cu_3O_{7-\delta}$[a]	89	93	0.8	5.6	3.83	3.88	11.68
$HoBa_2Cu_3O_{7-\delta}$[b]	-	-	2.9×10^{4}	5.4	3.87	3.87	11.82
$HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$[c]	70	77	6.4×10^{1}	5.3	3.87	3.88	11.68

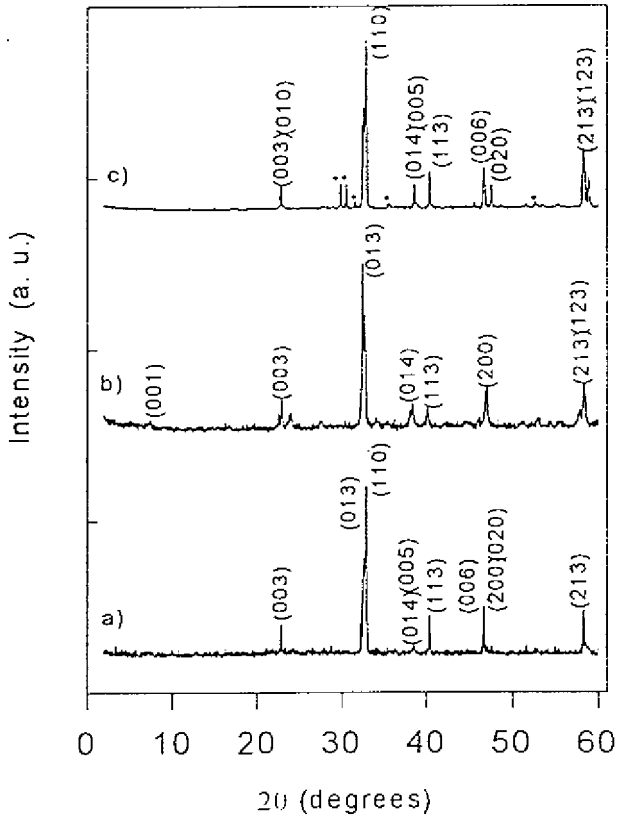


Figure 1. X ray powder diffractograms of a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$

Table 2. Longitudinal velocity (v_l) , shear velocity (v_s), longitudinal modulus (C_L), shear modulus (μ) , bulk modulus (B), Young's modulus (Y) and Debye temperature (θ_D) measured at 80 K of a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$

Sample	V_l (kms^{-1})	V_s (kms^{-1})	C_L (GPa)	μ (GPa)	B (GPa)	Y (GPa)	θ_D (K)
$HoBa_2Cu_3O_{7-\delta}$[(a)]	4.15	2.52	95.7	35.3	48.7	85.3	348
$HoBa_2Cu_3O_{7-\delta}$[(b)]	3.95	2.33	84.6	29.5	45.2	72.8	322
$HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$[(c)]	4.55	2.49	109	32.8	65.8	84.4	347

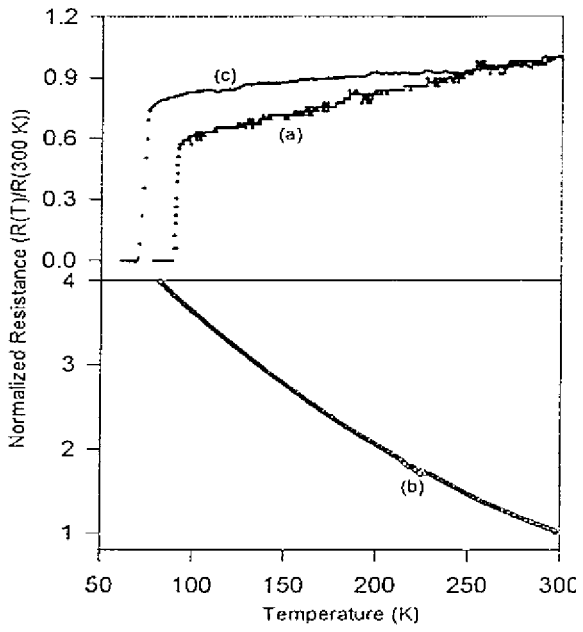


Figure 2.Normalized resistance versus temperature curve of a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$ samples.

The Debye temperature (θ_D) of the superconducting $HoBa_2Cu_3O_{7-\delta}$ evaluated at 80 K is 348 K and is comparable to $REBa_2Cu_3O_{7-\delta}$ (RE= Y, Gd) superconductors (Dominec, 1993). Substitution of Ho^{3+} for Ba^{2+} in $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$ which suppressed T_c did not cause significant change in θ_D. The reduction of oxygen content of $HoBa_2Cu_3O_{7-\delta}$ by quenching caused a decrease in both the v_l, v_s, related elastic moduli and θ_D (Table 2). The decrease in v_l, and v_s, may not be due to differences in porosity because the same pellet was used for the preparation of superconducting and non-superconducting $HoBa_2Cu_3O_{7-\delta}$. As such, it is

possible that the decrease in the longitudinal velocity observed for non-superconducting $HoBa_2Cu_3O_{7-\delta}$ is caused by a volume dependent mechanism which involves reduction in the mean copper valency as a result of oxygen O(4) removal from the Cu-O chains during quenching. The reduction of average Cu valence caused an increase in ionic radius of Cu ions which acts to change some interatomic distances and bonding length. A reduction in the absolute values of ultrasonic velocities due to similar removal of oxygen have also been observed for $REBa_2Cu_3O_{7-\delta}$ (RE= Y, Er, Gd) [14,15]. On the other hand, the Ba-site substitution in $HoBa_{1.85}Ho_{1.5}Cu_3O_{7-\delta}$ caused an increase in v_l, C_L and B (Table 2). The substitution also caused a small decrease in v_s, μ and Y. The increase in longitudinal velocity may be due to cell volume change as a result of substitution of the smaller Ho^{3+} (ionic radius 0.894 Å) for Ba^{2+} (ionic radius 1.34 Å). The substitution may also have altered some interatomic distances and bonding lengths in $HoBa_2Cu_3O_{7-\delta}$ and this volume change is detected by the longitudinal phonons which are strongly coupled to the lattice as it acts to alter the unit cell volume [16].

Superconducting $HoBa_2Cu_3O_{7-\delta}$ showed a change in longitudinal velocity of 2.3 % (Fig. 3) between 80 K - 270 K and a change in shear velocity of around 1.5 % (Fig. 4) between 80 K - 205 K. Longitudinal velocity showed a change in slope around 230 K, below which, the velocity showed large increase indicating pronounced lattice stiffening tendency. A small longitudinal velocity hysteresis was observed between 140 K and 210 K.

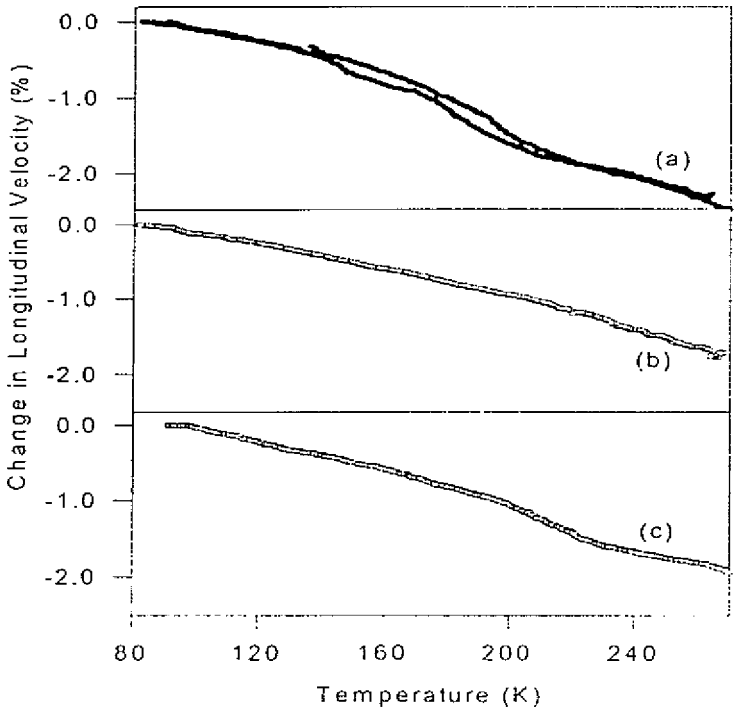


Figure 3. Temperature dependence of longitudinal velocity for a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$

After quenching to reduce the oxygen content, non-superconducting $HoBa_2Cu_3O_{7-\delta}$ showed a change in longitudinal velocity of 1.8 % (Fig. 3) between 80 K - 270 K and a change in shear velocity of around 1.2 % (Fig. 4) between 80 K - 205 K. No velocity anomaly was observed for non-superconducting $HoBa_2Cu_3O_{7-\delta}$ for both modes. A comparison of the velocity profiles for superconducting and non-superconducting $HoBa_2Cu_3O_{7-\delta}$ showed strong influence of oxygen content above 140 K for both modes.

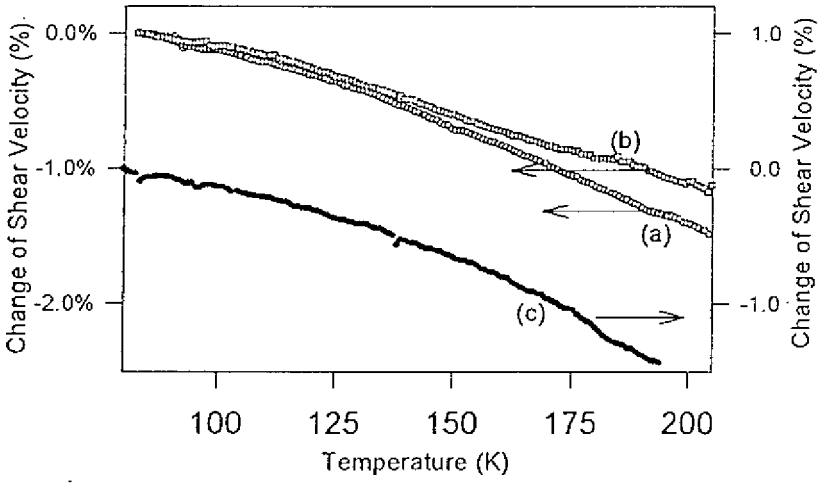


Figure 4. Temperature dependence of shear velocity for a) superconducting $HoBa_2Cu_3O_{7-\delta}$ b) non-superconducting $HoBa_2Cu_3O_{7-\delta}$ and c) $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$

$HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$ showed a change in longitudinal velocity of 2.0 % between 80 K - 270 K (Fig. 3) and a change in shear velocity of around 1.5 % between 80 K - 195 K (Fig. 4). Longitudinal velocity showed an anomalous change in slope around 230 K indicating pronounced lattice stiffening tendency. No longitudinal velocity hysteresis was observed.

The 230 K longitudinal velocity anomaly in superconducting $HoBa_2Cu_3O_{7-\delta}$ could not be due to a structural transition since no structural anomaly is reported around 200 K. A possible explanation to the 230 K anomaly could be due to oxygen ordering in the sample. The temperature dependence of longitudinal velocity is dominated by vibrational anharmonicity at low temperatures but above 180 K an oxygen-related mechanism dominates causing the 230 K anomaly. A similar velocity anomaly observed in $YBa_2Cu_3O_{7-\delta}$ around 200 K was suggested to be a first order phase transition between the Ortho-I and mixed Ortho-I and Ortho-III phases in the temperature range of 200 K - 230 K [17-19]. Ortho-I is a structure with filled Cu-O chains along the a-direction, Ortho-II is a cell-doubling superstructure along the a-direction with alternately filled and empty Cu-O chains and Ortho-III is a cell tripling superstructure with two filled chains and a third empty chain along the a-direction. A similar oxygen ordering mechanism may also cause the 230 K anomaly in $HoBa_2Cu_3O_{7-\delta}$ as orthorhombic

superstructures has been observed in high resolution electron microscopy studies of $REBa_2Cu_3O_{7-\delta}$ [20]. The absence of a similar velocity anomaly in non-superconducting $HoBa_2Cu_3O_{7-\delta}$ confirms its oxygen-related feature. It also shows a clear role of oxygen in the acoustic anomaly in agreement with previous reports for $REBa_2Cu_3O_{7-\delta}$ [10, 21,22]. However, in-line with the observation for Gd1113, the absence of the anomaly in non-superconducting $HoBa_2Cu_3O_{7-\delta}$ may not simply be due to reduced oxygen content but the lack of oxygen ordering [23]. Observation of a similar longitudinal velocity anomaly for $HoBa_{1.85}Ho_{0.15}Cu_3O_{7-\delta}$ indicates that the Ba-site substitution does not significantly affect the oxygen ordering process suggested above. The suppression of $T_{c\ zero}$ by 19 K and the large increase in room-temperature resistivity due to Ho^{3+} substitution for Ba^{2+} strongly indicate lowering of charge carrier concentration. However our study shows that although Ho^{3+} substitution at Ba-sites has fatal effects on superconductivity, the step-like acoustic anomaly is not affected by the lower charge carrier concentration. As such, there may be is no direct relationship between the anomaly and charge carrier concentration. In addition, if the longitudinal velocity anomaly is due to existence of some kind of oxygen ordering then it can be suggested that the Ba-site substitution may not affect the ordering process.

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