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ELASTIC PROPERTIES OF $EuBa_2Cu_3O_{7-\delta}$ CERAMICS AT LOW TEMPERATURES

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ABSTRACT

Ultrasonic velocity measurements on single-phase polycrystalline $EuBa_2Cu_3O_{7-\delta}$ superconducting ($\delta \sim 0.1$) and non-superconducting ($\delta \sim 0.7$) samples have been performed at 9 MHz from 80 K to 280 K in longitudinal mode and from 80 K to 200 K in shear mode. The absolute longitudinal and shear velocities (at 80K) decreased when the oxygen content was reduced from $O_{6.9}$ to $O_{6.3}$. For the superconducting sample, a step-like anomaly was observed around 255 K indicating pronounced lattice stiffening in the longitudinal mode. However, a similar observation was not observed in the shear mode possibly due to the lower temperature limit. In addition, no elastic anomalies were observed for the non-superconducting sample in both longitudinal and shear modes. The elastic anomaly was discussed in terms of a phase transition involving oxygen ordering in Cu-O chains. Elastic moduli values and Debye temperature (θ_D) are also reported.

INTRODUCTION

Superconductors are special materials where their electrical resistance abruptly goes to zero below the critical temperature (T_c). Studies on superconductivity became more interesting when LBCO was discovered as the first high-temperature superconductor (HTSC) with T_c surpassing the conventional 30 K limit [1]. Subsequently, other cuprate superconductors namely the Y-based, RE-based, Tl-based and Hg-based families were discovered [2-11]. Numerous works on characterization of high-temperature superconductors using different techniques to understand their low temperature behaviors were reported. Ultrasonic velocity measurement on superconductors is a useful technique in probing bulk properties of the materials.

Ultrasonic velocity measurements on several superconducting $REBa_2Cu_3O_{7-\delta}$ (RE = Y, Gd, Er) found step-like elastic anomalies around and above 200 K [4, 9, 12]. These step-like elastic anomalies were observed in oxygenated samples but were suppressed when oxygen content of the samples was reduced [13-16]. However, oxygen content may not the primary factor influencing the step-like anomalies. Studies on differently annealed superconducting $REBaSrCu_3O_{7-\delta}$ (RE = Gd and Dy) [17, 18] which is isostructural to $REBa_2Cu_3O_{7-\delta}$ showed step-like elastic anomalies around 200 K only for specially annealed samples. The studies highlight the fact that the step-like elastic anomalies may instead be due to oxygen ordering in CuO chains of oxygenated samples. Previous ultrasonic study on $EuBa_2Cu_3O_{7-\delta}$ between 80 K and 220 K showed a softening tendency near 170 K [19]. However, no step-like anomaly was reported and

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the velocity measurements were limited for the shear mode.

Further investigation on both ultrasonic velocity measurements of $EuBa_2Cu_3O_{7-\delta}$ (RE-based) especially in the longitudinal mode is interesting as Eu^{3+} has an ionic radius larger that Y^{3+}, Gd^{3+} and Er^{3+}. This paper reports the results of velocity measurements on superconducting and non-superconducting polycrystalline $EuBa_2Cu_3O_{7-\delta}$ at 9 MHz. Results of electrical resistance measurements and powder X-ray diffraction analyses are also reported.

EXPERIMENTAL METHOD

The $EuBa_2Cu_3O_{7-\delta}$ samples were prepared by mixing appropriate amounts of Eu_2O_3, $BaCO_3$ and CuO powders with purity ≥ 99.99% using conventional solid state synthesis. The mixed powders were ground in an agate mortar and calcined in air at around 900°C for 48 h with several intermittent grindings before oven cooled. The powders were then pressed into pellets of ≈13 mm diameter and 3 mm thick under a pressure of around 6-7 tons. The pellets were then sintered at around 930°C for 24 h and slow cooled to room temperature at 40°C per hour. The non-superconducting sample was prepared by reheating the $EuBa_2Cu_3O_{7-\delta}$ sample at around 900°C about 2 hours and quenching it immediately in liquid nitrogen. Electrical measurements were carried out using the standard four-point-probe technique with silver paste contacts. The samples were examined by X-ray powder diffraction with $CuK_{\alpha 2}$ radiation (λ = 1.54439 Å) using Rigaku model D/MAX 2000 PC system.

Ultrasonic velocity was measured using a Matec 7700 system which utilizes the pulse-echo-overlap technique. Nonaq stopcock grease was used to bond the polished sample surface with the quartz transducer. Sound velocity was propagated along the direction of pressing using X-cut (longitudinal) or Y-cut (shear) transducer with the carrier frequency of 9 MHz. The velocity measurement was performed in a Janis Cryostat model VNF-100T and the temperature was changed at rate of about 1 K/min during heating.

For polycrystalline ceramic material, the elastic moduli for longitudinal and shear modulus can be approximated by an isotropic-elastic medium. In this approximation, the longitudinal and shear modulus are given by $C_L = \rho v_l^2$ and $\mu = \rho v_s^2$, respectively, where ρ is the mass density, v_l is the longitudinal velocity, v_s is the shear velocity, C_L is the longitudinal modulus and μ is the shear modulus. The Debye temperature (θ_D) can be estimated using the standard formula

$$\theta_D = \left(\frac{h}{k}\right)\left(\frac{3N}{4\pi V}\right)^{1/3} v_m \qquad \text{eq (1)}$$

where

$$\frac{3}{v_m^3} = \frac{1}{v_l^3} + \frac{2}{v_s^3}, \qquad \text{eq (2)}$$

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h is the Planck constant, k is the Boltzmann constant, N is the number of mass point, V is the atomic volume, v_m is the mean velocity, v_l is the longitudinal velocity and v_s is the shear velocity.

RESULT AND DISCUSSION

Powder X-ray diffraction pattern (figure not shown), showed both samples to be single-phase with space group Pmmm (orthorhombic) and P4/mmm (tetragonal). The superconducting sample has the orthorhombic structure with lattice parameters a = 3.860 Å, b = 3.908 Å and c = 11.727 Å, while the quenched sample has a tetragonal structure with $a \approx b$ = 3.902 Å and c = 11.769 Å. Measurement of temperature dependence of electrical resistance (Figure.1) showed superconducting $EuBa_2Cu_3O_{7-\delta}$ exhibits metallic normal state behavior with zero-resistance temperature ($T_{c\ zero}$) of 87.5 K. The quenched $EuBa_2Cu_3O_{7-\delta}$ sample was non-superconducting down to 40 K (Table 1).

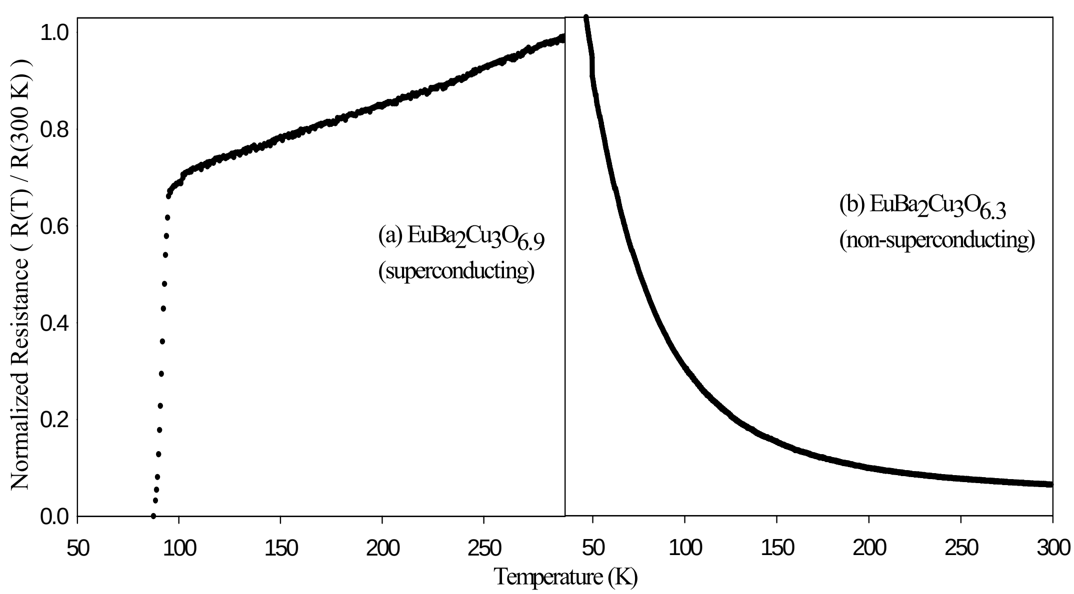

Figure.1: Normalized resistance versus temperature for (a) superconducting $EuBa_2Cu_3O_{6.9}$ and (b) non-superconducting $EuBa_2Cu_3O_{6.3}$

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Table 1: Zero-resistance transition temperature ($T_{c\ zero}$), onset-transition temperature ($T_{c\ onset}$), electrical resistivity (300 K), lattice parameters and unit cell volume for (a) superconducting $EuBa_2Cu_3O_{6.9}$ and (b) non-superconducting $EuBa_2Cu_3O_{6.3}$

Sample	$T_{c\ zero}$ (K) ±0.1	$T_{c\ onset}$ (K) ±0.1	Resistivity (mΩ cm) ±0.1	Lattice parameters 123 phase a (Å)	b (Å)	c (Å)	Volume V(Å^3)
(a) $EuBa_2Cu_3O_{6.9}$ (superconducting)	87.5	94.9	14.0	3.860 ± 0.002	3.908 ± 0.006	11.728 ± 0.004	176.9 ± 0.4
(b) $EuBa_2Cu_3O_{6.3}$ (non-superconducting)	-	-	48.6 x 10^2	3.899 ±0.003	3.902 ±0.011	11.767 ±0.013	179.0 ± 0.8

Absolute velocity measurements at 80 K showed both absolute values of v_l and v_s and related elastic moduli decreased as the oxygen content of the sample was reduced (Table 2). The calculated Debye temperature for superconducting $EuBa_2Cu_3O_{6.9}$ is also larger than the quenched $EuBa_2Cu_3O_{6.3}$ sample (Table 2). The decrease in the absolute velocity values is probably related to reduction in the oxygen content which caused increase in ionic radius of Cu ions and subsequent changes in interatomic distances and bonding length [14].

Table 2: Density, 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 for (a) superconducting $EuBa_2Cu_3O_{6.9}$ and (b) non-superconducting $EuBa_2Cu_3O_{6.3}$. All the values were corrected for porosity.

Sample	Density (g/cm^3)	v_l (kms^{-1})	v_s (kms^{-1})	C_L (GPa)	μ (GPa)	B (GPa)	Y (GPa)	θ_D (K)
(a) $EuBa_2Cu_3O_{6.9}$ (superconducting)	5.89 ±0.04	5.59 ±0.08	3.10 ±0.04	213.2 ±1.6	65.6 ±0.5	125.7 ±1.8	167.2 ±5.6	430 ±1
(b) $EuBa_2Cu_3O_{6.3}$ (non-superconducting)	5.77 ±0.04	4.71 ±0.07	2.67 ±0.04	148.8 ±1.1	47.8 ±0.4	85.1 ±1.3	120.8 ±4.2	369 ±2

Longitudinal and shear velocity measurements on superconducting $EuBa_2Cu_3O_{6.9}$ showed percentage changes of 1.9% (Figure. 2a) and 1.6% (Figure. 3a), respectively. The dotted lines in Figure. 2a represents the change in slope where a step-like anomaly indicating pronounced lattice stiffening was observed around 255 K for the longitudinal mode. A similar step-like anomaly was not observed in the shear mode probably due to the lower temperature limit for shear measurements. However, contrary to previous report of a shear velocity anomaly around 170 K [19], no softening tendency in the shear mode was observed in this work. For non-superconducting $EuBa_2Cu_3O_{7-\delta}$, the longitudinal and shear velocity measurements showed percentage change of 2.7% (Figure. 2b) and 1.7% (Figure. 3b), respectively. No velocity anomaly was observed for

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both the longitudinal and shear modes.

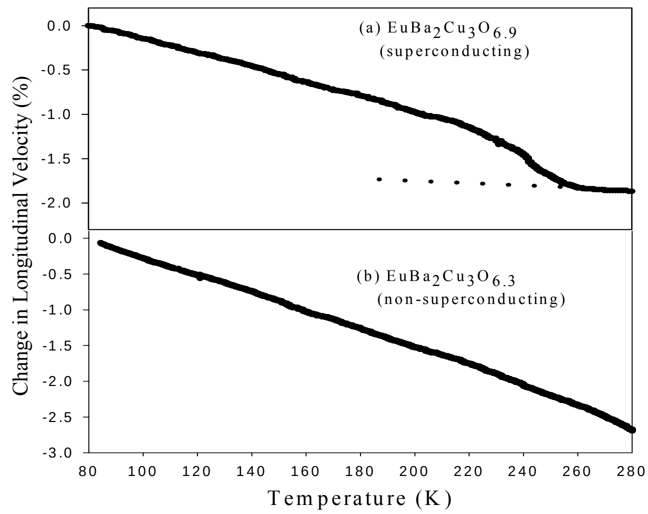

Figure 2: Temperature dependence of longitudinal velocity at 9 MHz for (a) superconducting $EuBa_2Cu_3O_{6.9}$ and (b) non-superconducting $EuBa_2Cu_3O_{6.3}$ samples. The dotted line is a guide to the eye to illustrate the change in slope at around 255 K.

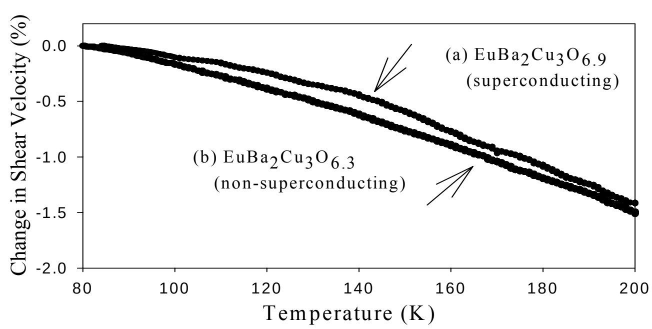

Figure 3: Temperature dependence of shear velocity at 9 MHz for (a) superconducting $EuBa_2Cu_3O_{6.9}$ and (b) non-superconducting $EuBa_2Cu_3O_{6.3}$ samples.

A comparison between superconducting and quenched $EuBa_2Cu_3O_{7-\delta}$ samples in Figure. 2(a) and (b), clearly shows that the 255 K step-like anomaly is oxygen content related. Similar observations of step-like anomalies were previously reported around and above 200 K for superconducting $YBa_2Cu_3O_{7-\delta}$ (around 200 K), $GdBa_2Cu_3O_{7-\delta}$ (around 240 K) and $ErBa_2Cu_3O_{7-\delta}$ (around 230 K) which disappeared after oxygen content reduction [9,10,12,16]. However, studies on differently annealed RE1113 (RE = Gd and Dy) which are isostructural to $REBa_2Cu_3O_{7-\delta}$ indicates that although the step-like anomaly is oxygen content related the actual factor is oxygen ordering in the materials. Velocity measurements on some $YBa_2Cu_3O_{7-\delta}$ [5] and high-temperature annealed RE1113 [17,18] samples did not reveal any step-like elastic anomaly probably due to the lack of oxygen ordering. Ceder et al [20] proposed that a first-order phase transition involving oxygen ordering in Cu-O chains takes place in $REBa_2Cu_3O_{7-\delta}$ materials around 200 K.

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The phase transition corresponds to the crossing of the phase boundary between different orthorhombic superstructure regions namely ortho-I and mixed ortho-I and ortho-III regions [5,14] and its temperature range is sensitive to oxygen content of the materials. As such, based on the above, the 255 K step-like anomaly observed for $EuBa_2Cu_3O_{7-\delta}$ in this work is possibly due to some kind of oxygen ordering taking place in Cu-O chains. It is interesting to highlight that the temperature of the step-like anomaly observed for $EuBa_2Cu_3O_{7-\delta}$ in this study is higher than those reported for $YBa_2Cu_3O_{7-\delta}$ [4], $GdBa_2Cu_3O_{7-\delta}$ [9], and $ErBa_2Cu_3O_{7-\delta}$ [12]. The higher temperature for the anomaly compared to 200-240 K for other $REBa_2Cu_3O_{7-\delta}$ superconductors previously reported [4,9,12,16] may be related to its larger ionic radius which caused higher internal chemical pressure in the $REBa_2Cu_3O_{7-\delta}$ unit cell [21]. The increase in internal pressure may have influenced nucleation of different oxygen superstructures causing the phase transition to occur at a higher temperature.

CONCLUSION

Longitudinal and shear velocity measurements on superconducting and non-superconducting $EuBa_2Cu_3O_{7-\delta}$ have been performed. Absolute velocity at 80 K for both modes decreased with reduction in oxygen content. Temperature dependent velocity measurements revealed a step-like anomaly indicating pronounced lattice stiffening in superconducting $EuBa_2Cu_3O_{7-\delta}$ around 255 K for the longitudinal mode. No elastic anomaly was observed for non-superconducting $EuBa_2Cu_3O_{7-\delta}$. The longitudinal velocity anomaly is suggested to correspond to some kind of oxygen ordering in Cu-O chains.

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