Elasticity studies of aluminium-substituted high T_c superconducting materials

P VENUGOPAL REDDY[†], S SHEKAR and Y V RAMANA*

Department of Physics, Osmania University, Hyderabad 500 007, India

*National Geophysical Research Institute, Hyderabad 500 007, India

Abstract. Longitudinal and shear wave velocities of Al-substituted Bi–Sr–Ca–Cu–O superconducting materials prepared by the ceramic technique were measured by the pulse transmission technique. Using the data, several elasticity parameters like Young's modulus, rigidity modulus, Poisson's ratio, Debye temperature etc were evaluated. Variation of elasticity parameters with composition has been explained in terms of binding forces between various atoms of the superconducting materials. Temperature variation of longitudinal wave velocity has also been measured and attempts have been made to explain the anomalies at 200 K.

Keywords. Elasticity; Al-substituted HTSC; Young's modulus; rigidity; Poisson's ratio.

1. Introduction

A knowledge of elasticity in solids and more particularly in high T_c superconductors is important as it helps us to understand the possible application of the materials. Also, it helps to know how the interatomic forces change when a particular dopant like aluminium is added. As such, a study of elasticity parameters as a function of aluminium content and temperature has been undertaken and the results are presented in this paper.

2. Experimental

The samples with nominal composition (1112) $\text{Bi}_{1-x}\text{Al}_x\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$ (where $x = 0.0, 0.5, 0.10, 0.15, 0.20$) were prepared by the solid-state reaction method using high purity oxides of bismuth, copper and aluminium and carbonates of strontium and calcium in stoichiometric proportions. The samples were sintered at 850°C for 45 h. After characterizing the samples by X-ray powder diffraction method, bulk density and porosity were measured by immersion method. The ultrasonic longitudinal and shear velocity were measured by the pulse transmission technique (Ramana 1979), using 1 MHz PZT transducers. The error in velocity measurements was $\pm 0.5\%$.

3. Results and discussion

Electrical resistivity measured from 77 to 300 K by the standard four-probe method, is reported in table 1. X-ray diffraction patterns show that none of the samples are

[†]For correspondence.

Table 1. Data on electrical behaviour of Bi–Al–Sr–Ca–Cu–O samples.

Composition	Specimen no.	Electrical behaviour	Superconducting transition temperature (T_c)
$\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$	BiAl ₁	Superconducting	79
$\text{Bi}_{0.95}\text{Al}_{0.05}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$	BiAl ₂	Superconducting	77 K
$\text{Bi}_{0.9}\text{Al}_{0.1}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$	BiAl ₃	Metallic	—
$\text{Bi}_{0.85}\text{Al}_{0.15}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$	BiAl ₄	Metallic	—
$\text{Bi}_{0.8}\text{Al}_{0.2}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_y$	BiAl ₅	Metallic	—

Figure 1. Cell parameters a and c vs composition. **Figure 2.** Plots of cell parameter b and cell volume v vs composition.

single phase. However, the major phase is found to have an orthorhombic crystallographic structure when indexed. Using the calculated values of d spacings, lattice parameters a , b and c have been obtained for each composition. The variation of lattice parameters as a function of composition (figure 1) reveals that the lattice parameter a decreases initially when 0.05 mol of Al is added. However, on further addition of Al, the cell parameters remain almost constant. On the other hand the cell parameter c behaves in an opposite manner. Similarly the variation of b parameter and cell volume v with composition are shown in figure 2.

3.1 Elastic moduli versus composition

From the experimental values of longitudinal (V_L) and shear (V_s) velocities, the values of Young's modulus (E) and rigidity modulus (n) have been computed (table 2). As the porosity of the samples determined by the immersion method ranges from 3.0 to 36.9%, the values at E and n have been corrected to zero porosity using McKenzie's (1950) formula. The corrected values of elastic moduli (table 3) show that the values

Table 2. Elasticity data (uncorrected) on Bi-Al-Sr-Ca-Cu-O samples at room temperature.

Specimen no.	Bulk density 10^3 kg/m^3	Percentage porosity	V_1	V_s	E	N	(Poisson's ratio) σ
			m/s		10^{10} Pa		
BiAl ₁	5.53	20.30	2734	1205	2.215	0.803	0.379
BiAl ₂	4.23	6.93	1720	1040	1.108	0.458	0.212
BiAl ₃	3.28	35.91	1788	1020	0.859	0.341	0.259
BiAl ₄	4.56	2.96	2411	1497	2.425	1.022	0.186
BiAl ₅	3.46	24.20	2622	1546	2.039	0.827	0.234

Table 3. Elasticity data (corrected to zero porosity) at room temperature.

	E_0	n_0	K_0		
Composition	10^{10} Pa			σ_0	θ_D (K)
BiAl ₁	2.937	1.70	2.00	0.255	168.03
BiAl ₂	1.263	0.52	0.73	0.213	131.45
BiAl ₃	1.520	0.58	1.36	0.313	119.54
BiAl ₄	2.278	0.96	1.21	0.187	195.26
BiAl ₅	2.740	1.22	1.21	0.122	186.25

of E_0 and n_0 decrease initially when 0.05 mol of Al is added. However, on further increase of Al content, both E_0 and n_0 increase.

3.2 Debye temperature

From the corrected values of elastic moduli, the compressional (V_1) and shear velocities and Debye temperature (θ_D) for all the compositions have been computed using Anderson's (1965) formula. The calculated θ_D values vary from 119 to 195 K. Following Wooster (1953), it can be understood that the atomic bonding between various atoms of Al-doped Bi-based superconducting materials initially decreases when 0.05 mol of Al is added. However, further addition of aluminium increases atomic bonding.

3.3 Mean atomic weight and velocities

From the measured values of V_1 and V_s , the values of V_1/ρ and V_s/ρ are evaluated and given in table 4 along with the mean atomic weight (M/q) for each composition. It is seen that as the mean atomic weight decreases, the V_1/ρ and V_s/ρ values increase. A similar relationship was obtained by Anderson (1965) using the results of Birch (1961) on some oxide minerals like garnet, TiO_2 , Fe_2O_3 and ZnO . Reddy (1988) and Reddy *et al* (1985) also obtained a similar relationship for Mn-Mg and Li-Ni magnetic ceramic oxides (ferrites).

Table 4. Relationship between mean atomic weight and velocities.

Superconducting material	M/q	V_1	V_s	V_m	V_1/ρ	V_s/ρ
		m/sec				
BiAl ₁	45.52	2734	1205	1350.46	494.75	218.66
BiAl ₂	44.82	1220	1040	1148.80	406.62	245.80
BiAl ₃	44.12	1788	1022	1133.56	545.12	311.60
BiAl ₄	43.42	2411	1497	1650.25	528.72	328.30
BiAl ₅	42.72	2722	1546	1713.09	757.80	446.80

Figure 3. $\Delta V/V$ vs temperature T for the sample Bi₁Ca₁Sr₁-Cu₂-O_x.

3.4 Temperature variation of longitudinal velocity

Figure 3 shows the temperature variation of relative change in longitudinal ultrasonic velocity ($\Delta V/V$) for the sample BiAl₁, over a temperature range 80 to 300 K. $\Delta V/V$ decreases continuously with decreasing temperature showing a minimum at 200 K. However, on further decrease of temperature, $\Delta V/V$ increases rapidly and even becomes positive at about 180 K. When the temperature is further decreased, it shows a decreasing trend up to 80 K. Once the sample attains the superconducting phase at 79 K, $\Delta V/V$ almost remains constant. A similar change in velocity with temperature has been observed for BiAl₂ and BiAl₃ samples also, with minima at 210 and 215 K. The minimum observed in the present investigation for the specimens BiAl₁, BiAl₂ and BiAl₃ may be attributed to softening of the lattice. A similar softening around 200 K was also reported for La-Sr-Ca-CuO (Bourne *et al* 1987) and Y-Ba-Cu-O samples (Ewert *et al* 1987; Srinivasan *et al* 1987). Further studies are in progress to determine whether the so-called softening of the lattice in superconductors, and particularly in Bi-Ca-Sr-Cu-O samples, is a precursor to the phenomenon of superconductivity.

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