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Ultrasonic studies of aluminium-substituted Bi(Pb)-2223 superconductors

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Abstract. The compositional dependence of elastic properties of Al^{3+}-substituted Bi(Pb)-2223 superconducting system with the general formula $Bi_{1.7-x}Al_xPb_{0.3}Sr_2Ca_2Cu_3O_y$ (x = 0.0, 0.1, 0.2 and 0.3) have been studied by means of ultrasonic pulse transmission (UPT) technique at 1 MHz (300 K). The elastic moduli of the specimens are computed and corrected to zero porosity. The observed variation of elastic constants with aluminium substitution has been explained on the basis of the strength of interatomic bonding. The applicability of heterogeneous metal mixture rule for estimating elastic constants and transition temperature has been tested.

Keywords. Superconductor; ultrasonic pulse transmission technique; elastic constants.

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1. Introduction

Sound is the strain wave propagating through a solid. The velocity of longitudinal and transverse elastic waves thus produced is a characteristic feature of a solid. The basic idea is that if there is any distortion of the solid from its equilibrium shape, the average separation of the atoms within the solid is no longer optimal. Some atoms will be too close to their neighbours, and some too far apart. In either case there will be a restoring force, which will act to return the atoms to their equilibrium separations. The dynamics of the elastic wave will be affected by the way the solid responds to the restoring force. The two factors most critical in determining this response are the restoring force per unit displacement (the natural 'springiness' of the substance), and the density of the substance. The restoring force on a small region of a solid depends on the type of distortion (strain) that has taken place during synthesis process. The parameters that describe the restoring force per unit strain are known as the elastic moduli of a substance. In the present work we have

employed the ultrasonic pulse transmission technique as a tool to get an idea about such stress/strain ratio.

After the discovery of high T_c superconductivity [1], several investigations were started almost simultaneously to understand the mechanism responsible for the phenomenon. A number of researchers [2–8] reported the existence of elastic anomalies in the temperature range from room temperature to the superconducting transition temperature (T_c), signifying the presence of lattice instabilities. As the lattice instabilities are manifest well in the elastic studies, a number of investigations were undertaken with a view to know the correlation between high value of T_c and structural instabilities.

When ceramic superconductors are subjected to high magnetic field, large stresses developed in the material. It is always desirable to have a general idea of elastic moduli values that represent mechanical strength, fracture toughness and thermal shock resistance. From fundamental research points of view the knowledge of elastic moduli of any polycrystalline material elucidate the nature of binding forces and also help to understand thermal properties of the solids when we think about the application of any polycrystalline material. Besides the knowledge of its magnetic and electric responses, the elastic properties help to decide the suitability of the material for a specific application.

The Young's modulus of a superconductor is an important parameter in determining critical grain sizes above which microcracking will occur due to anisotropic thermal stresses that arise during processing. This phenomenon of microcracking has been determined to cause a decrease in the attainable critical current density in bulk superconductors. The bulk modulus of a solid influences the speed of sound and other mechanical waves in the material. On the other hand, the Debye temperature of a superconducting material may provide information about the role of phonons in its superconducting mechanism.

In the present work an attempt is made to see the effect of Al^{3+} substitution for Bi^{3+} on the elastic behaviour of $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ superconducting system at 3 00 K. The composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ was chosen as a starting composition because it has the highest T_c and Pb plays a very important role in stabilizing the phase. The substitution of Al at Bi-site is expected to provide stability to the structure and improve the conductivity value with nominal reduction in critical temperature. From the point of view of the microstructural and elastic properties, substitution of Al enhances grain growth and grain alignment along with reduction in porosity. Sound velocity, density and as a result the strength of the material is expected to increase with decreasing porosity.

2. Experimental details

A series of samples having stoichiometric compositions $Bi_{1.7-x}Al_xPb_{0.3}Sr_2Ca_2Cu_3O_y$ (Bi(Pb)-Al(2223) (x = 0.0, 0.1, 0.2 and 0.3) were synthesized by the solid state route using highly pure (99.99%) Bi_2O_3, $CaCO_3$, CuO, Sr_2CO_3, Al_2O_3 and $PbCO_3$. The powders after thorough mixing and grinding, was then heated to about 800°C for 24 h followed by two more similar treatment with intermediate grinding. The calcinated powders after pressing into disc were sintered at 810°C for

Table 1. Molecular weight (M), X-ray density (ρ_X), bulk density (ρ), pore fraction (f), longitudinal velocity (V_l), shear velocity (V_s) and mean sound velocity (V_m) for Bi(Pb)-Al(2223) system.

Al content (x)	M (kg) $\times 10^{-3}$	ρ_X (kg/m^3) $\times 10^{-3}$	ρ	f	V_l (m/s)	V_s (m/s)	V_m (m/s)
0.0	1023.433	4.78	4.28	0.101	3181	2028	2229.09
0.1	1005.233	4.74	4.42	0.067	3218	2165	2363.95
0.2	987.033	5.04	4.87	0.033	3338	2175	2384.52
0.3	968.833	5.74	4.65	0.020	3426	2158	2375.22

24 h and slowly cooled to room temperature at the rate of 1°C/min. The structural characterization of all the samples was carried out at 300 K by X-ray diffraction technique using CuKα radiation. The X-ray diffraction pattern consists mostly of the high T_c (2223) phase with characteristic peaks 0012, 1011, 200, 2012 with a small amount of the low T_c (2212) phase. The X-ray density (ρ_X) values calculated from the corresponding lattice constant values are summarized in table 1. The DC electrical resistance was measured with the four-probe technique from 300–80 K on rectangular specimens with silver paste contacts on conjunction with a Cryoline-91. Fine enameled copper wires were used to pass the constant current through the outer leads using constant current source (Keitheley Model no. 224), while the voltage developed across the two inner leads was measured using nano-voltmeter (Keitheley model no. 18). The temperature of the sample was measured using Pt-100 thermocouple.

In general, sintered ceramic samples have large number of closed and open pores inside and on their surface and hence the ordinary method of determining the bulk density (ρ) and porosity by hydrostatic method is found to give spurious results. In such cases immersion method gives fairly good and reliable values. In the present investigation, the values of bulk density (ρ) of Bi(Pb)-Al(2223) samples were determined by the immersion method and the values of pore fraction ($f = 1-\rho/\rho_X$) thus obtained are presented in table 1.

The ultrasonic pulse transmission technique [9] was used for the measurement of longitudinal wave velocity (V_l) and shear wave velocity (V_s) at 1 MHz. The RF pulse generated by a pulse oscillator was applied to quartz transducer. The acoustic pulses were converted into electrical signals by the receiving transducer. The output signal was displayed on a digital taxtronic 2230 oscilloscope. The difference in time (Δt) between two overlapping received pulse train was noted with the help of the timer. The sound velocity was measured using the equation $V = L/\Delta t$ where V is the sound velocity, L is the length of the superconducting specimen, and t is the time. The accuracy of the sound velocity measurement was $\pm 0.5\%$.

A number of research reports is available in the literature describing various aspects of the elastic behaviour of different superconducting systems [2–10]. To our knowledge no work has been reported on the elastic properties of aluminium-substituted Pb-containing Bi-2223 superconducting series.

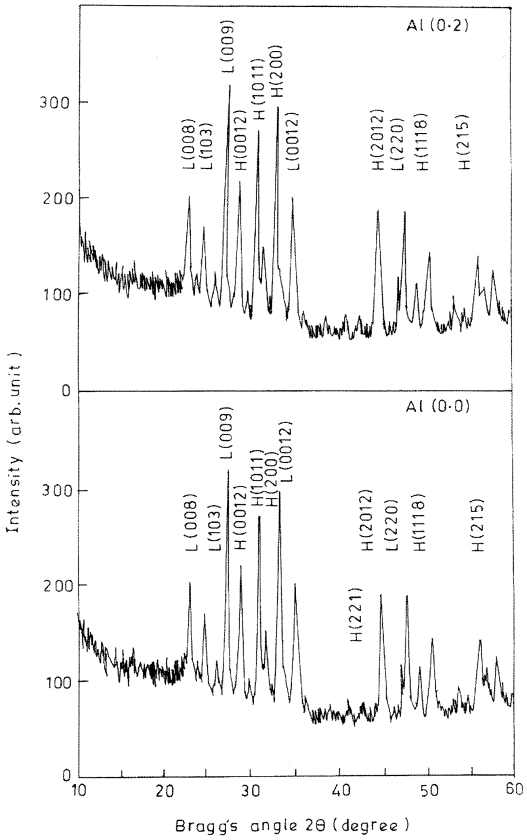

Figure 1. X-ray diffraction pattern for Bi(Pb)-Al(2223) system at 300 K. (H) - high T_c phase, (L) - low T_c phase.

3. Results and discussion

The powder X-ray diffraction patterns for typical compositions $x = 0.0$ and 0.2 are shown in figure 1. The reflections due to the low and high T_c phase were identified and marked separately in figure 1. The Bragg's reflection peaks were indexed using DEBYE & INDEX computer program. The prominent high T_c phase reflections are found to increase gradually with Al-substitution. Figure 2 shows the resistance vs. temperature curve for all the compositions. All these samples exhibit a linear decrease in resistance with decrease in temperature up to their onset temperature indicating metallic behaviour in normal state. The values of T_c (zero), T_c (onset), transition bandwidth (ΔT_c) and resistance at 300 K for different compositions are given in table 2. The detailed analysis on structural and superconducting properties of Bi(Pb)-Al(2223) system will be given elsewhere.

The values of longitudinal wave velocity (V_l), transverse wave velocity (V_s) determined through UPT technique and bulk density (ρ) for different compositions are used to calculate Young's modulus (E), bulk modulus (B), rigidity modulus (G),

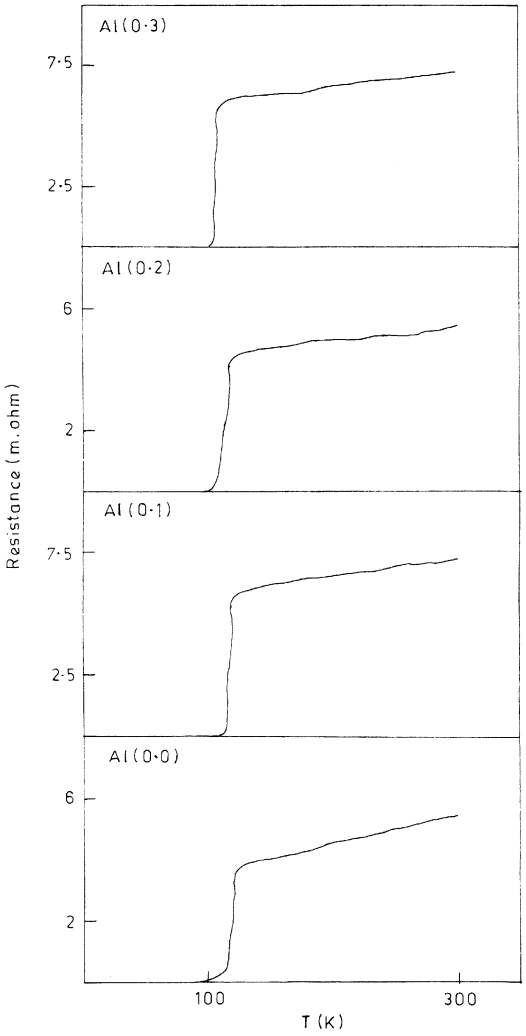

Figure 2. Thermal variation of resistance for Bi(Pb)-Al(2223) system.

Poisson's ratio (σ), mean sound velocity (V_{m}) and Debye temperature (θ) using the following formulae [11,12]:

Longitudinal modulus $(L) = \rho(V_{\mathrm{l}})^2$,
Rigidity modulus $(G) = \rho(V_{\mathrm{s}})^2$,
Bulk modulus $(B) = L - (4/3)G$,
Poisson's ratio $(\sigma) = (3B - 2G)/6B + 2G$,
Young's modulus $(E) = (1 + \sigma)2G$.

Table 2. Critical temperature (T_c), transition bandwidth (ΔT_c) and resistance at 300 K (R) for Bi(Pb)-Al(2223) system.

Al content (x)	T_c (onset) (K)	T_c (zero) (K)	ΔT_c (K)	R (mΩ)
0.0	120	115	5	5.5
0.1	119	112	7	7.4
0.2	118	110	8	5.4
0.3	109	107	2	7.3

Table 3. Elastic moduli, Poisson's ratio and Debye temperature for Bi(Pb)-Al(2223) system.

Al content (x)	B (GPa)	E (GPa)	G (GPa)	σ	θ (K)
0.0	19.88	40.87	17.64	0.158	240.82
0.1	20.64	43.34	18.84	0.150	251.61
0.2	23.54	52.12	23.04	0.131	272.21
0.3	25.71	50.72	21.65	0.171	268.67

$$\text{Mean sound velocity, } V_m = \left[3\left(\frac{V_l^3 \cdot V_s^3}{V_s^3 + 2V_l^3}\right)\right]^{1/3}$$

and

$$\text{Debye temperature, } \theta = \frac{h}{k_B}\left[\frac{3N_A}{4\pi V_A}\right]^{1/3} \cdot V_m,$$

where h and k_B are the Planck's and Boltzmann's constants, respectively, N_A is the Avogadro's number and V_A is the mean atomic volume given by $(M/q)/\rho$, where M is the molecular weight (table 1) and q is the number of atoms (i.e. 19) in the formula unit.

It can be seen from table 3 that, B, E and G increase with increasing Al-content (x) up to $x = 0.2$. Following Wooster's work [13], the variation of B, E and G with increasing Al-content (x) for Bi in Bi(Pb)-Al(2223) superconducting system may be interpreted in terms of the interatomic bonding. Thus, it can be inferred from the increase in elastic moduli with concentration (x) that the interatomic bonding between various atoms is being strengthened continuously. The observed increase in θ with aluminium concentration (x) suggested that lattice vibrations are hindered due to aluminium substitution. This may be due to the fact that strength of interatomic bonding increases as supported by our results on the variation of elastic moduli with concentration (x). The magnitude of elastic moduli and Debye temperature are consistent with other Bi-2223 and Bi-2212 superconducting systems [10]. The values of Poisson's ratio are found in the range of 0.13–0.17 for all the compositions. These values lie in the range from −1 to 0.5 which are in conformity with the theory of isotropic elasticity.

In general, the samples prepared by solid-state reaction method are found to be porous. The interconnected pores of a sintered material provide an opportunity for free movement of oxygen into the bulk of a sample. So oxygen is distributed throughout the volume of the sample. Furthermore, it also relieves the internal stresses resulting in obtaining less constrained polycrystalline materials. Therefore, porosity plays an important role in governing certain important physical properties. In order to improve the mechanical properties of ceramic materials it is essential to understand the relationship between porosity and its elastic behaviour. The measured elastic moduli do not have much significance unless they are corrected to zero porosity. In engineering practice, the elastic constants often used are the Young's modulus, rigidity modulus, and Poisson's ratio. As the superconducting specimens under study are porous ($f \approx 0.02$–0.10), the values of elastic moduli have been corrected to zero porosity using Ledbetter and Datta formula [14] and are given by

$$\frac{1}{E_0} = \frac{1}{E}\left[1 - \frac{3f(1-\sigma)(9+5\sigma)}{2(7-5\sigma)}\right],$$
$$\frac{1}{G_0} = \frac{1}{G}\left[1 - \frac{15f(1-\sigma)}{(7-5\sigma)}\right],$$
$$\sigma_0 = (E_0/2G_0) - 1.$$

The corrected values of Young's modulus (E_0), rigidity modulus (G_0) and Poisson's ratio (σ_0) are given in table 4.

It is always desirable to have a general idea of the elastic moduli values before synthesis and characterization of the material, in order to tailor the properties. Recently, we have developed and successfully implemented heterogeneous-metal-mixture rule (MMMR) to estimate elastic constants of various spinel ferrites [15], garnets [16] and La-based perovskites [17]. The aim of the present work is to test the validity of this model for estimating elastic moduli of various Bi(Pb)-Al(2223) superconducting compositions and to compare the results with experimentally obtained values. The basic idea behind this model is that the density, longitudinal and transverse wave velocities and thus elastic moduli and Debye characteristic temperature of such polycrystalline oxide compositions, depend up on the density and elastic wave velocity of individual metallic cation present in the system.

Table 4. Corrected values of elastic moduli and Poisson's ratio for Bi(Pb)-Al(2223) system.

Al content (x)	UPT			(MMMR)		
	E_0 (GPa)	G_0 (GPa)	σ_0	E^* (GPa)	G^* (GPa)	θ^* (K)
0.0	51.15	21.93	0.166	51.16	21.45	224.08
0.1	50.00	21.82	0.146	51.58	21.61	227.52
0.2	55.77	24.71	0.128	52.00	21.76	230.95
0.3	52.82	22.56	0.171	52.43	21.92	234.39

According to this model 'the elastic constant and Debye temperature value of polycrystalline oxide material ($K^*_{\rm pm}$) is equal to the average stoichiometric compositional addition of elastic constant values of metallic elements present in the material'. The elastic moduli such as Young's modulus, rigidity modulus and Debye temperature values of various metallic elements are taken from [18,19] and are used to estimate $K^*_{\rm pm}$. The elastic constant value, to be estimated, for a given superconducting system can be given as

$$K^*_{\rm pm} = \frac{1}{n} \sum_{\substack{i>0 \\ n=1}}^{\infty} C_{in} K_n,$$

where $K^*_{\rm pm}$ is either Young's modulus, rigidity modulus or Debye temperature of the composition to be estimated, n is the total concentration of metallic cations involved in the chemical formula of the polycrystalline material ($n = 9$ in the present case), C_{in} is the concentration of the nth cation in the formula unit while K_n is the corresponding modulus of the metallic element.

The values of elastic moduli (E^*, G^*) and Debye temperature (θ^*) obtained from MMM rule are summarized in table 4. The results of our calculations are in conformity with the elastic constant and Debye temperature values obtained from ultrasonic pulse transmission technique with adequate accuracy (table 4). This finding is interesting in the sense that the elastic moduli of such oxide compositions can be estimated from the elastic constants of metallic elements present in the system and surprisingly the oxygen does not seem to play significant role for assigning elastic constants of these oxide compositions. Further investigation in this direction is in progress.

We have extended the use of Debye temperature values calculated from MMM rule for estimating superconducting transition temperature ($T_{\rm c}$) for Bi(Pb)-Al(2223) system and compared the values with those deduced experimentally from thermal variation of DC resistivity measurements (figure 2). The formulation is based on Debye temperature values for pristine, $\theta(0.0)$, substituted compositions, $\theta(x)$, obtained from MMM rule and transition temperature found experimentally for un-substituted composition $T_{\rm c}(0.0)$. It is given by

$$\left| \frac{T_{\rm c}(x) - T_{\rm c}(0.0)}{\theta(x) - \theta(0.0)} \right| = K = \text{const.},$$

where $T_{\rm c}(x)$ is the transition temperature to be estimated for substituted composition. The value of K is determined from the ratio of $T_{\rm c}(0.0)$ and $\theta(0.0)$. In the present case it is found to be 0.51321. The values of $T_{\rm c}(x)$ for $x = 0.1$, 0.2 and 0.3 estimated from the above equation are listed in table 5. This formula is analogous to the known relation for superconducting materials, $(T_{\rm c}/\theta) =$ constant [19]. For the sake of comparison the values of $T_{\rm c}(x)$ ($x = 0.1$, 0.2 and 0.3) deduced from resistivity measurements, are also given in table 5 to facilitate the discussion. It is seen that there is quite reasonable agreement between the two. When no such simple formulation is available in the literature for theoretical estimation of superconducting transition temperature ($T_{\rm c}$), this will provide great tool for the same.

Table 5. Superconducting transition temperature (T_c) for Bi(Pb)-Al(2223) system.

Al content (x)	T_c (zero) (K) (Resistivity)	T_c (K) (MMMR)	Error (%)
0.0	115	–	–
0.1	112	113.23	1.09
0.2	110	111.47	1.32
0.3	107	109.71	2.47

4. Conclusions

Summing up the elastic moduli determination through ultrasonic pulse transmission technique for Bi(Pb)-Al(2223) superconducting system, it is suggested that:

(i) the observed increase of elastic constants with aluminium substitution suggest strengthening of interatomic bonding,

(ii) the elastic moduli corrected to zero porosity are in good agreement with those determined through metal-mixture rule, confirming the validity of the method,

(iii) in polycrystalline oxide compositions oxygen anions play important role for structure formation but less decisive to the elastic constant values,

(iv) the superconducting transition temperature for substituted compositions $T_c(x)$ can be estimated theoretically from the corresponding Debye temperature values and T_c of the pristine composition $T_c(0.0)$.

Appendix

Illustrative calculations for Young's modulus and Debye temperature determination through MMM rule

(i) $Bi_{1.6}Al_{0.1}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ ($x = 0.1$)

$$\begin{aligned} E^*_{\rm pm} &= 1/9[(1.6)32\ \text{GPa} + (0.1)70\ \text{GPa} + (0.3)16\ \text{GPa} \\ &\quad +(2)15.62\ \text{GPa} + (2)20\ \text{GPa} + (3)110\ \text{GPa}] \\ &= 51.58\ \text{GPa} \quad \text{(MMMR) ref. [18]} \\ E_0 &= 50.00\ \text{GPa (UPT)}. \end{aligned}$$

(ii) $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y$ ($x = 0.0$)

$$\begin{aligned} \theta^*_{\rm pm} &= 1/9[(1.7)119\ \text{K} + (0.3)105\ \text{K} + (2)147\ \text{K} + (2)230\ \text{K} + (3)343\ \text{K}] \\ &= 224.08\ \text{K} \quad \text{(MMMR) ref. [19]} \\ \theta &= 240.82\ \text{K (UPT)}. \end{aligned}$$

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