Effect of Ag⁺-addition on elastic behaviour of Bi-2212 superconductors

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Ultrasonic pulse transmission technique at 1 MHz (300 K) has been employed to study the elastic properties of Ag⁺-added Bi₂Sr₂Ca₁Cu₂O₉ superconducting system. The longitudinal and transverse wave velocities are used to compute elastic constants corrected to zero porosity. The observed enhancement of elastic moduli may be due to hindrance of dislocation motion with Ag-addition.

Keywords: Superconductors, Ultrasonic pulse transmission technique, Elastic properties
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1 Introduction

Ultrasonic waves are important in research and applications. By employing coherent ultrasonic phonons of carefully controlled frequency and polarization, several basic properties of solids have been investigated.

In high Tc superconducting materials, ultrasonic study plays a major role in the investigation of phase transition. Ultrasonic attenuation and velocity measurements have been useful to identify large anisotropy in the sintered forged samples of the superconducting material. The Young’s modulus of a superconductor is an important parameter in determining critical grain size above which micro cracking will occur due to anisotropic thermal stresses that arise during processing. This phenomenon of micro cracking 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 superconducting material may provide information about the role of phonons in its superconducting mechanism.

Recently, we have studied elastic behaviour of Al substituted Bi(Pb)-Al (2223) and Ga-substituted Bi(Pb)-Ga(2212) superconducting systems. In the present paper, the effect of Ag⁺-addition on the elastic properties of Bi₂Sr₂Ca₁Cu₂O₉ [Bi-(2212)] superconducting system at 300K has been studied. When Ag₂O is added, it is expected to remove the micro structural defects and thereby reduction in porosity of the ceramic superconductors. Silver remains an additive material and improves the superconducting properties and mechanical strength of the superconducting compounds. The X-ray diffraction patterns of all these compositions confirm the formation of 2212 phase.

2 Experimental Details

Six samples with nominal composition Bi₂Sr₂Ca₁Cu₂O₉ + x weight % Ag₂O (x = 0-5% in the interval of 1) were prepared by the usual shake and bake method. The starting materials were of high purity (99.9%) Bi₂O₃, SrCO₃, CaCO₃, CuO and Ag₂O. The powders in stoichiometric proportion after thorough mixing and grinding heated at about 800°C for 24 h followed by two more similar heat treatments. The calcinated powders after pressing into disc were sintered at 810°C for 24 h and slowly cooled to room temperature at the rate of 1°C/min. The single 2212 phase formation of the compositions was confirmed by X-ray diffraction patterns analysis. The value of lattice parameters was determined and X-ray density values (ρ) thus, calculated is given in Table 1. In the present investigation, the value of bulk density (ρ) were determined by the immersion method and the values of pore fraction (f = 1-ρ/ρx) thus, obtained are presented in Table 1.

The ultrasonic pulse transmission technique (UPT) was used for the measurements of longitudinal wave
velocity ($V_l$) and shear wave velocity ($V_s$) at 1 MHz. The radio frequency pulse generated by pulse oscillator was applied to quartz transducer. The output signal was displayed on a digital taxtronic oscilloscope. The difference in time ($\Delta t$) between two overlapping received pulse trains was noted with the help of timer. The sound velocity was measured using the equation $V = d/\Delta t$ where $V$ is the sound velocity, $d$ is the length of the superconducting specimen. The accuracy of the sound velocity measurement was ±0.5%.

### 3 Results and Discussion

The values of longitudinal wave velocity ($V_l$), transverse wave velocity ($V_t$) determined through UPT technique and bulk density ($\rho$) for different compositions are used to calculate Young’s modulus ($E$), bulk modulus ($B$) rigidity modulus ($G$), Poisson’s ratio ($\sigma$), mean sound velocity ($V_m$) and Debye temperature ($\theta$) using the following formulae:

- Longitudinal modulus ($L$) = $\rho (V_l)^2$
- Rigidity modulus ($G$) = $\rho (V_l)^2$
- Bulk modulus ($B$) = $L - (4/3)G$
- Poisson’s ratio ($\sigma$) = $(3B-2G)/(6B+2G)$
- Young’s modulus ($E$) = $(1+\sigma) 2G$
- Mean sound velocity, $V_m = 3(V_l^3 V_t^3)/(V_s^3 + 2V_t^3)^{1/3}$
- and Debye temperature, $\theta = h/\kappa_B [3N_A/4\pi V_A]^{1/3} V_m$

where $h$ and $\kappa_B$ are the Planck’s and Boltzmann’s constants, respectively, $N_A$ is Avogadro’s number and $V_A$ is the mean atomic volume given by $(M/\rho)/q$, where $M$ is the molecular weight and $q$ is the number of atoms (i.e. 15) in the formula unit.

The high temperature superconducting materials are ceramic in nature. Therefore, porosity is the single most important parameter, which determines the overall strength of the superconductors. 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. As the superconducting specimens under study are porous ($f = 0.07-0.13$), the values of elastic moduli have been corrected to zero porosity using Hasselman and Fulrath formula and are given by:

\[
\frac{1}{E_o} = \frac{1}{E} \left[1 - \frac{3f(1-\sigma)(9+5\sigma)}{2(7-5\sigma)}\right]
\]

\[
\frac{1}{G_o} = \frac{1}{G} \left[1 - \frac{15f(1-\sigma)}{7-5\sigma}\right]
\]

$\sigma_o = (E_o/2G_o) - 1$

$B_o = (E_oG_o)/3(3G_o - E_o)$

The magnitude of elastic constants $E_o$, $G_o$ and $B_o$ increases with increasing Ag-content ($x$) in Bi (2212) superconducting system which suggests that the corresponding deformation of the solid is difficult and the solid has strong tendency to spring (analogous to planes within a solid held to gather by atomic bond) back to its equilibrium position (Table 2). Following Wooster’s work, the observed variation of elastic constants may be interpreted in terms of change in the strength of interatomic bonding. The strength of interatomic bonding is expected to change (i) if interatomic distances get changed by the substitution of larger or smaller cation in the system, (ii) change in electronic configuration as a result of nature of bond formation between cations and cation-anion by cationic substitution in the structure. It is known that Ag-ion goes along grain boundaries and not occupying the interstitial structural position. This is further supported by very small change in unit cell volume of the present system and Pb-containing Bi-2212 and Bi-2223 superconducting systems. Thus, the observed variation of elastic moduli with Ag-content cannot be explained on the basis of change in strength of inter-atomic bonding. This can be explained as follows: The size of the grains or grain

### Table 1 — X-ray density ($\rho_x$), ($\rho$) pore fraction ($f$), wave velocity ($V_l$, $V_s$, $V_m$), and Debye temperature ($\theta$) for Ag-added Bi (2212) superconducting system

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\rho_x$ (kg/m$^3$) $\times 10^9$</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$f$</th>
<th>$V_l$ (m/s)</th>
<th>$V_s$ (m/s)</th>
<th>$V_m$ (m/s)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi – 2212 + 0%Ag</td>
<td>6.379</td>
<td>5.562</td>
<td>0.128</td>
<td>2831</td>
<td>1814</td>
<td>1992</td>
<td>311</td>
</tr>
<tr>
<td>Bi – 2212 + 1%Ag</td>
<td>6.412</td>
<td>5.694</td>
<td>0.112</td>
<td>2972</td>
<td>1865</td>
<td>2054</td>
<td>314</td>
</tr>
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<td>Bi – 2212 + 2%Ag</td>
<td>6.371</td>
<td>5.683</td>
<td>0.108</td>
<td>3093</td>
<td>1935</td>
<td>2131</td>
<td>323</td>
</tr>
<tr>
<td>Bi – 2212 + 3%Ag</td>
<td>6.369</td>
<td>5.777</td>
<td>0.093</td>
<td>3146</td>
<td>2024</td>
<td>2222</td>
<td>327</td>
</tr>
<tr>
<td>Bi – 2212 + 4%Ag</td>
<td>6.368</td>
<td>5.801</td>
<td>0.089</td>
<td>3204</td>
<td>2068</td>
<td>2270</td>
<td>334</td>
</tr>
<tr>
<td>Bi – 2212 + 5%Ag</td>
<td>6.435</td>
<td>5.972</td>
<td>0.072</td>
<td>3324</td>
<td>2185</td>
<td>2393</td>
<td>331</td>
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</table>
structure of a polycrystalline powder influences the mechanical properties. Adjacent grains normally have different crystallographic orientation and of course a common grain boundary. The grain boundary acts as a barrier to strain motion. In the present case, added Ag-ions reside at grain boundaries and likely to impede dislocation motion (strain). This enhances the magnitude of elastic constants with Ag-addition. This effect is more pronounced as compared to Al- and Ga-substitution in Bi-based superconducting systems\textsuperscript{1,2}. The observed increase in $\theta$ with Ag-addition suggested that lattice vibrations are hindered. This may be due to the fact that the strength of the material increases as supported by the variation of elastic moduli with Ag-concentration (Table 2). The value of Poisson’s ratio is found in the range 0.11-0.19 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.

4 Conclusions

The results of ultrasonic measurements on Ag-added Bi (2212) superconducting system at 300K have been summarized. It is suggested that Ag-addition in Bi (2212) results in increase in magnitude of elastic moduli there by increase the strength of the materials. This may be due to the fact that added Ag-ions reside at grain boundaries and likely to impede dislocation motion. Cationic addition has some beneficial effect on mechanical properties as compared to cationic substitution.

Acknowledgement

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References


<table>
<thead>
<tr>
<th>Composition</th>
<th>$B_o$</th>
<th>$E_o$</th>
<th>$G_o$</th>
<th>$\sigma_o$</th>
<th>$L$</th>
<th>$B_o$</th>
<th>$E_o$</th>
<th>$G_o$</th>
<th>$\sigma_o$</th>
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<tbody>
<tr>
<td>Bi – 2212 + 0%Ag</td>
<td>20.18</td>
<td>42.16</td>
<td>18.30</td>
<td>0.152</td>
<td>44.58</td>
<td>26.34</td>
<td>56.56</td>
<td>24.76</td>
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<tr>
<td>Bi – 2212 + 1%Ag</td>
<td>23.89</td>
<td>46.53</td>
<td>19.80</td>
<td>0.175</td>
<td>50.29</td>
<td>30.33</td>
<td>59.92</td>
<td>25.59</td>
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<td>26.00</td>
<td>50.13</td>
<td>21.28</td>
<td>0.178</td>
<td>54.37</td>
<td>32.69</td>
<td>63.90</td>
<td>27.21</td>
<td>0.174</td>
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<tr>
<td>Bi – 2212 + 3%Ag</td>
<td>25.62</td>
<td>54.25</td>
<td>23.67</td>
<td>0.147</td>
<td>57.18</td>
<td>36.66</td>
<td>69.26</td>
<td>29.22</td>
<td>0.185</td>
</tr>
<tr>
<td>Bi – 2212 + 4%Ag</td>
<td>26.47</td>
<td>56.67</td>
<td>24.81</td>
<td>0.142</td>
<td>59.55</td>
<td>31.42</td>
<td>68.84</td>
<td>30.33</td>
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<tr>
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<td>27.97</td>
<td>63.80</td>
<td>28.51</td>
<td>0.119</td>
<td>65.98</td>
<td>31.88</td>
<td>74.80</td>
<td>33.48</td>
<td>0.111</td>
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