4.1 Introduction

There has been a great deal of interest in understanding the physical properties of high Tc oxide superconductors ever since superconductivity in the 30K range in the multiphase oxide system La-Ba-Cu-O was reported by Bednorz and Müller in 1986 [1]. Among the high Tc cuprates the REBa$_2$Cu$_3$O$_{7-\delta}$ (1-2-3) type systems are the most studied ones where RE stands for rare earth. The first material among them is YBa$_2$Cu$_3$O$_{7-\delta}$ and after this many studies have been made on this material with chemical substitutions at various sites. One of the most interesting results was that Yttrium atom could be replaced almost entirely by any of the rare earths, with the exception of Ce, Pr and Tb without altering the superconducting properties [2,3]. The superconducting properties are not affected by the substitution of Gd for Y despite the fact that the Gd ion carries a large magnetic moment [4].

In 1-2-3 systems both tetragonal and orthorhombic structures occur. For $\delta = 0$ the structure is orthorhombic and contains CuO$_2$ sheets with Cu at the corners of squares and the O atoms at the edge centres. The Cu atoms in these sheets are the plane Cu atoms. Pairs of these sheets are separated by intervening RE layers with the RE atoms located above and below the centres of the CuO$_2$ squares. Above and below this unit there are, first, BaO layers with the O atoms in line with the Cu atoms in the CuO$_2$ squares and the Ba atoms in line with the RE; and, second, CuO layers with the Cu atoms in line with those in the CuO$_2$ layers, but only half of the O sites corresponding to those in the CuO$_2$ layers are filled. The O atoms are ordered along chains in the b-direction, and this
ordering is associated with the orthorhombic structure. The Cu atoms in these layers are the "chain" Cu atoms. \( \delta \) can take values between 1 and 0 and as \( \delta \) increases from zero, O atoms move from the chain sites and ordering of the O atoms in those planes are disrupted. For \( \delta < 0.4 \) the long range order disappears and the structure becomes tetragonal. *In situ* neutron powder diffraction experiments [5-7] have revealed that oxygen vacancy ordering on the CuO basal plane of the 1-2-3 system plays a key role in the tetragonal to orthorhombic phase transition observed in these materials. Thus due to the presence of two chemically inequivalent Cu sites and variable oxygen stoichiometry, these 1-2-3 type systems exhibit many anomalous properties.

Ultrasonics is one of the standard methods of probing superconductivity. Studies of acoustic anomalies in the conventional superconductors have, in the past, been of great importance in probing their elastic properties and measuring the superconducting energy gap. A thorough knowledge of these elastic properties of high Tc materials is necessary to gather information about the different phononic interactions taking place in these samples at Tc and other temperature regions. Since the discovery of high Tc superconductivity in 1-2-3 systems, many researchers have investigated the acoustic properties of these materials [8-24]. Generally the anomalies associated with these superconductors can be divided into two classes. One is the anomaly around Tc and the other is the anomalies occurring above Tc, especially in the 200-250K temperature range. Bhattacharya *et al.* [8,23] have studied the acoustic properties in YBCO and La-Sr-Cu-O systems near the transition point. In an isotropic solid the bulk modulus \( B \) and shear modulus \( G \) are related to the Lamé's constant as

\[
\rho V_s^2 = B + 4/3 \cdot G \\
\rho V_p^2 = G
\] (1)
For polycrystalline materials $G$ represents an average value.
The longitudinal velocity does not yield the bulk modulus alone.
By measuring both $V_l$ and $V_s$, $G$ and $B$ can be separated.
The thermodynamics of a second order phase transition yields
[25-27] the following relations for the bulk and shear moduli and the strain at the transition temperature

\[
\frac{\Delta B}{B} = -\frac{\Delta C_p}{T_c} B \left[ \frac{\partial T_c}{\partial P} \right]^2
\]

\[
\frac{\Delta G}{G} = \frac{T \Delta S}{T_c} G \left[ \frac{\partial^2 T_c}{\partial \sigma_s^2} \right]
\]

\[
\Delta \varepsilon_{\alpha} = \frac{T \Delta S}{T_c} B \frac{\partial T_c}{\partial \sigma_{\alpha}}
\]

where $\Delta C_p$ refers to the discontinuity in the specific heat and
$\Delta S$ is the entropy change at $T_c$; $\sigma_s$ is the shear stress, $\varepsilon_{\alpha}$ is the generalized strain and $\sigma_{\alpha}$ is the conjugate stress. For a mean field transition a discontinuity occurs at $T_c$ in the bulk modulus itself (or any modulus involving a volume preserving distortion) and in the temperature derivatives of $G$ and $\varepsilon_{\alpha}$ i.e., $G$ and $\varepsilon_{\alpha}$ are expected to show kinks at $T_c$ since $\Delta S$ is continuous at $T_c$ [28]. Bhattacharya et al. [23] have obtained a hardening in elastic modulus at $T_c$. They report the existence of another anomaly above $T_c$ at $T_s = 95K$ in La-Sr-Cu-O system and at $\approx 120K$ in Y-Ba-Cu-O system suggesting that the state between $T_s$ and $T_c$ is the "normal" state preceding superconductivity. The anomalous elastic behaviour at and below $T_c$ is dominated by the shear modulus and not by the bulk modulus, implying an unusually strong coupling of the order parameter to shear distortions. Hardening of elastic modulus below $T_c$ has been reported by other workers also [9-12]. The behaviour is identical for shear as well as longitudinal waves except for the fact that anomaly is larger in the case of shear waves. Sun et al. [12] report a small dip in velocity at $T_c$ on the velocity versus temperature curve and
a faster velocity change in the superconducting state compared to the normal state. Horn et al. [29] have reported the temperature variation of lattice constants of 123 systems as there is an orthorhombic distortion occurring at temperatures between 60 and 140K and showed a maximum difference between b and a appearing around the superconducting transition. This does not change the volume of the unit cell and area of a unit basal plane. The softening at Tc may be due to this structural instability. The transition occurring above Tc i.e., at Ts is also important since it suggests that the state between Ts and Tc is the true normal state from which the bulk superconducting condensation occurs and it is suggested that the rotation of the Cu-O complex in the a-b plane can be responsible for this [23]. It is also suggested that the pronounced hardening of the shear modulus below Tc may be due to the depletion of an excitation that cocondenses with the carriers and that also couples strongly to transverse acoustic phonons. Increase in attenuation has also been reported by several authors at the transition point [8,12,23,24]. For this, phonon-phonon interactions provide a satisfactory explanation [8,23]. The sound damping is given by the Mason-Bateman formula (for the $\omega \tau < 1$ regime) [30]

$$\alpha \approx \frac{D(\gamma) C_p T}{\rho V^3} \omega^2 \tau$$

where $D(\gamma)$ is a measure of anharmonicity $\gamma$ and $\tau$ is the thermal relaxation time. If $\tau$ is limited by the scattering of phonons by the carriers in the normal state, then the condensation of carriers below Tc enhances $\tau$ and thereby increases $\alpha$. At lower temperatures the effect of $\tau$ saturates and the decrease in $\alpha$ is dominated by $C_p(T)$. Temperature dependence of thermal conductivity is a straight test of this since $K \sim \alpha/T$. Xu et al. [24] suggest that fluctuations contributed by the one dimensional nature of the CuO network also can account for this anomalous attenuation.

Since the 200K temperature range is an important
region in the case of high Tc superconductors, there are several reports which show anomalous changes in sound velocity and attenuation in the 123 system above 200K [8,14,24]. There is a considerable interest in the properties of high Tc materials in this range since several reports show anomalies in $C_p$ at 220K in several samples and correlate them with the specific heat jump at Tc [31-33]. According to Laegreid [32] the $C_p$ anomaly at 220K is largest in the samples with the largest jump in $C_p$ at 90K. In YBCO Calemzuk [34] has observed a large peak at 220K in $C_p$ measurement. It is correlated to a large and hysteretic change of the Young’s modulus and a small resistance anomaly. Laegreid et al. [35] have reported that such an anomaly is observed only upon heating and attributed it to annealing of a metastable state. Ultrasonic velocity and attenuation measurements show that a structural instability does occur in YBCO below room temperature. On the connection between the 90K and 220K $C_p$ anomalies, Laegreid et al. [32] suggest that ordering in the oxygen system may be responsible for the 220K anomaly. Xu et al. [24] have observed an attenuation peak at 252K and suggest that the maxima are produced by a relaxation mechanism. He Yusheng et al. [14] report about anomalies in velocity and attenuation peaks around 250K and 160K as there is some kind of lattice instability or structural phase transition. Thus in YBCO system the lattice instability near 160K and 250K have been investigated and attributed to the oxygen ordering readjustments along the one dimensional Cu-O chain [14,15,32].

In spite of all these results, the mechanisms are still unclear and yet to be explored. In order to obtain a clear understanding about this metastability and to gain an insight into some of the possible reasons for the existing controversies in experimental results, we have undertaken ultrasonic velocity and attenuation measurements in Ag doped $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Gd123) system. As Ag is a noble metal with a stable charge state, doping it in 123 systems has been
reported before [36-40]. At low and moderate concentrations, Ag is believed to substitute Cu at the chain site and influence oxygen-vacancy ordering in these chains. Since anomalous ultrasonic velocity change above \( T_c \) has been reported to be arising due to oxygen order-disorder phase transitions, Ag doping is expected to influence such anomalies and throw light on the mechanism of superconductivity in these materials.

4.2 Experimental

Samples studied here have a general formula \( \text{GdBa}_2(\text{Cu}_{1-x}\text{Ag}_x)_3\text{O}_{7-\delta} \) with \( x = 0, 0.01, 0.02, 0.03 \) and 0.05. These are prepared by the standard solid state reaction method. Stoichiometric mixtures of \( \text{Gd}_2\text{O}_3, \text{BaCO}_3, \text{CuO} \) and \( \text{Ag}_2\text{O} \) powders are thoroughly mixed and calcined in the form of loosely packed pellets for about 80 hours with three intermediate grindings. Samples are then powdered and pelletised under a pressure of nearly 100 Kg cm\(^{-2}\) and sintered at 900°C for 24 hours and then furnace cooled to room temperature.

DC resistivity from 77K to room temperature (300K) has been measured using a four probe setup. Oxygen contents of the samples are determined by iodometric titration.

Ultrasonic measurements at 10 MHz have been carried out in the temperature range 85-300K. Pelletised samples of diameter \( \approx 10\text{mm} \) and thickness \( \approx 4.5\text{mm} \) have been used for the measurements. The faces of the samples have been well polished so that they are plane and parallel to each other. 10 MHz X-cut quartz transducer has been mounted on the sample with silicone grease as the bond. The velocity as well as attenuation have been measured as a function of temperature using the experimental setup described in chapter 2. Reasonably good echoes are obtained in four of the samples. The quality of the echoes obtained from sample with \( x = 0.05 \)
is found to be poor for the PEO method employed here. So the ultrasonic measurements have been restricted to first four samples with \( x = 0, 0.01, 0.02 \) and 0.03. The cooling rate was kept \( \leq 1 \text{K/min} \).

4.3 Results and discussions

The variation of the ratio of the change in longitudinal velocity to the room temperature velocity (\( \Delta V / V_{300} \)) with temperature for all the four samples is shown in Fig.4.1. All the curves show a small softening near \( T_c \) and below \( T_c \) there is a marked change in slope \( \text{i.e.,} \) the velocity increase becomes faster compared to the normal state. Another striking feature of the graph is that there is a broad peak around 207K in the case of pure sample \( \text{i.e.,} \) sample with \( x = 0 \). This peak is found to shift to the high temperature side with Ag doping. In the case of sample with \( x = 0.01 \) it is at about 245K. For the sample with \( x = 0.02 \) the peak is not so pronounced as in the case of other samples but the temperature at which the peak occurs is clear. The variation of this temperature at which the broad peak occurs (\( T_{vp} \)) with Ag doping concentrations is shown in Fig.4.2. At low concentrations of Ag (\( x \approx 0.01 \)) the peak shifts to higher temperatures. Further increase in Ag concentration does not shift the peak significantly as shown in the Fig.4.2.

The variation of velocity near \( T_c \) indicates a dip and a hardening of elastic modulus at temperatures below \( T_c \). This suggests that a structural instability is occurring at the transition point and a hardening of modulus below \( T_c \) which may be due to the depletion of an excitation that cocondenses with the carriers, which couples strongly to the transverse acoustic phonons. The anomalies are not so pronounced due to the fact that it is the longitudinal wave and not the transverse wave used here. The order parameter has a stronger coupling with shear distortions than with compressive distortions, since the superconducting transition is
Fig. 4.1 Temperature dependence of the relative change in longitudinal velocity ($\Delta V/V_{300}$) for GdBa$_2$(Cu$_{1-x}$Ag$_x$)$_3$O$_{7-\delta}$ with different $x$ values.

- (O) for $x = 0$
- (•) for $x = 0.01$
- (△) for $x = 0.02$
- (▲) for $x = 0.03$
Fig. 4.2 Variation of $T_{vp}$ as a function of Ag doping concentration in GdBa$_2$(Cu$_{1-x}$Ag$_x$)$_3$O$_{7-\delta}$. 
associated with a volume preserving shear lattice distortion. Similarly the anomaly above $T_c$ at $T_s$ which is reported by Bhattacharya et al. [23] is also not visible in all the measurements which also can be attributed to the same reason.

In order to understand the mechanisms that cause a variation in $T_{vp}$ as shown in Fig.4.2, we have carried out resistivity measurements in all these samples as a function of temperature. The variation of $T_c$ as a function of Ag concentration is shown in Fig.4.3. $T_c$ decreases with increasing Ag concentrations upto 2 at. wt.% (i.e., $x = 0.02$). On further increase in the Ag concentrations, $T_c$ increases. At still higher Ag concentration, however, $T_c$ once again starts falling. Fig. 4.3 also reveals that the variation of room temperature resistivity ($\rho_{300}$) with Ag concentration is well correlated to the corresponding $T_c$ variation.

To understand the dependence of $T_c$ on Ag concentration in these samples, we investigated the dependence of oxygen stoichiometry on Ag concentration. As shown in Fig.4.4 the oxygen content decreases with increase in Ag concentration. Thus in the low Ag concentration regime the decrease in $T_c$ and the increase in the room temperature resistivity can be understood if Ag substitutes Cu(1) in the lattice decreasing the oxygen stoichiometry and affects oxygen ordering. For Ag concentration beyond 2 at. wt. % the increase in $T_c$ and the fall in resistivity indicate that at higher concentrations, Ag mostly goes into the grain boundaries. Presence of Ag as pure metal in the grain boundaries is responsible for this fall in room temperature resistivity.

At still higher concentrations of Ag, i.e., with $x = 0.05$ the samples show semiconducting behaviour and do not show superconductivity down to 77K. To understand this behaviour we note that in this concentration range, while most of the Ag go into the grain boundaries, higher Cu deficiency results in the formation of other insulating phases like $\text{Gd}_2\text{BaCuO}_5$, BaO,
Fig. 4.3 Variation of transition temperature $T_c$ (○) and room temperature resistivity $\rho_{300}$ (●) as a function of Ag doping concentration $x$ in GdBa$_2$(Cu$_{1-x}$Ag$_x$)$_3$O$_{7-\delta}$.
Fig. 4.4 Dependence of oxygen stoichiometry on Ag concentration in $\text{GdBa}_2(\text{Cu}_{1-x}\text{Ag}_x)_3\text{O}_{7-\delta}$.
$\text{Gd}_2\text{O}_3$, $\text{BaCuO}_2$ etc. making the sample a mixed phase one. Those insulating phases also occupy the grain boundaries increasing the normal state resistivity by an order and suppressing the $T_c$ value. The difficulty in making ultrasonic measurements in this sample is due to the occurrence of such a mixed phase in the sample.

The peak in the velocity curve at 207K in the case of pure sample may be due to the reordering of $\text{O}$ ions in the one dimensional Cu-O chain. This is because the 123 system generally remains in a metastable state. With increasing Ag concentration the increase in $T_{vp}$ is due to the fact that the oxygens are locked to Ag and so a higher temperature is necessary for the reordering to occur. On further increasing the Ag content, some of the Ag goes into the grain boundaries as pure metal. The sample seems to go into a relatively stable state and consequently there is no significant shift in $T_{vp}$ at higher Ag concentrations, compared to the initial sharp increase. Addition of Ag in excess of 2 at.wt. % results in silver cluster formation but this is again in the same condition and hence $T_{vp}$ does not shift significantly. The variation in $T_c$ and $\rho_{300}$ with Ag doping concentrations substantiate these arguments. Thus it is reasonable to conclude that Ag doping do influence the metastability of the 123 system at low Ag doping levels. Increase in $T_{vp}$ with Ag concentration in the low concentration regime indicates that the oxygen reordering occurs at a higher temperature than in the case of undoped Gd 123.

$\rho_{300}$ and $T_c$ data (Fig. 4.3) indicate that Ag goes into the lattice of Gd 123 at low concentrations. Ag is known to have a stable $1^+$ charge state unlike Cu which can have charge states $1^+$, $2^+$or $3^+$depending on oxygen coordination. The oxygen atoms around Ag are tightly bound providing it a fixed oxygen coordination. The oxygen reordering in such case requires higher activation energy and can occur at high
temperatures. Therefore $T_{vp}$ is expected to increase with Ag doping at low concentrations as observed. At higher Ag doping levels, the excess Ag goes into the grain boundaries or form clusters but these do not influence the oxygen reordering in the Cu-O chain and hence the sample is in a relatively higher stable state and hence $T_{vp}$ does not shift significantly at higher Ag doping levels.

Ultrasonic attenuation also shows a similar type of behaviour. The temperature dependence of attenuation shows a dip at the temperature at which a peak in the velocity occurs. The variation of attenuation ($\alpha$) vs. temperature is shown in Fig. 4.5. Upon cooling, below this dip attenuation again shows a peak at temperature at which the velocity curve shows a minimum. Near $T_c$ attenuation again increases from its usual trend of decrease. This increase in attenuation may be due to the increase in thermal relaxation time and the hardening of the lattice due to the superconducting transition as explained before. Sample with $x = 0.03$ has an attenuation curve with a number of irregular peaks and it is not shown in the figure. This can be attributed to the presence of additional phases in the grain boundary, such as pure Ag.

### 4.4 Conclusions

The temperature dependence of ultrasonic velocity in Gd 123 shows anomalies around $T_c$ as well as on the higher temperature side around 207K. The anomaly around $T_c$ can be due to the superconducting transition. The 207K anomaly is attributed to the reordering occurring in the one dimensional Cu-O chain in the superconductor. Since the Ag doped in the Gd 123 is found to go to the lattice site it is found that the peak observed in the velocity curve at 207K in the case of undoped Gd 123 shifts to high temperature side with Ag doping. The Cu-O reorientation occurring in the sample can be due to the metastability of the system and upon Ag doping a higher temperature is required for this reorientation transition to
Fig. 4.5 Variation of ultrasonic attenuation with temperature for GdBa$_2$(Cu$_{1-x}$Ag$_x$)$_3$O$_{7-δ}$ with different x value.

( O ) for x = 0 , ( ■ ) for x = 0.01 and ( △ ) for x = 0.02
occur. In the lower Ag concentration regime this shift remains almost the same and after a particular level of Ag doping the sample quality becomes poor and the sample does not show any superconducting property due to the presence of different constituent phases in the sample. Thus with low concentrations of Ag the temperature at which Cu-O ordering occurs can be shifted to high temperature significantly.
References


