Chapter 7
SUMMARY AND CONCLUSIONS

The present thesis is a result of our attempts to probe the elastic properties of selected solid materials by measuring ultrasonic velocity and attenuation in them. Temperature dependence of velocity and attenuation have been measured in all the samples investigated. The materials investigated are the high Tc superconductors Bi-Sr-Ca-Cu-O and Ag-doped Gd-Ba-Cu-O, Y-Ba-Zr-O which is a substrate material for coating 1-2-3 superconductor thin films and the ferroelectric crystal TGS with different levels of phosphate doping. Considerable amount of effort has been put into setup the instrumentation required to undertake these studies. Ultrasonics is an excellent tool to study elastic properties and it is the most effective technique to investigate phase transitions in solids. The results presented in this thesis reconfirm this.

Ultrasonic studies have been carried out in the high temperature superconductors Bi-Sr-Ca-Cu-O and Ag-doped Gd-Ba-Cu-O. In the case of the former a Pb doped sample has been used since addition of Pb stabilizes the Bi2223 phase. Temperature variation of longitudinal velocity of 10MHz wave has been determined. It shows a phase transition like anomaly in the vicinity of Tc which can be attributed to a structural change occurring in the sample prior to the superconductive phase transition. Small velocity maxima are observed in the region above Tc which can be attributed to a second order phase transition occurring in the sample. Ultrasonic velocity and attenuation studies have also been carried out in the superconductor GdBa$_2$(Cu$_{1-x}$Ag$_x$)$_3$O$_{7-\delta}$ with $x = 0$, 0.01, 0.02, 0.03 and 0.05. The temperature dependent velocity curve in the pure sample shows a broad peak at 207K and a sharp slope change at Tc. The peak at 207K in the case of the pure sample gets
shifted to high temperature side with Ag doping. This can be correlated to the oxygen ordering occurring in the one-dimensional Cu-O chain due to the metastability of the 1-2-3 system. Room temperature resistivity and Tc measurements are found to agree with this result. Ultrasonic attenuation curves also show a similar type of behaviour.

Details of the study of ultrasonic as well as thermal properties of a new substrate material YBa2ZrO6 (YBZO) for the preparation of 1-2-3 superconducting thin films and the results obtained form a part of the thesis. From a technological point of view, high Tc superconducting materials prepared in the thin film form are very important and it is necessary to have a suitable material as the substrate to prepare thin films. Since YBCO reacts with almost all materials, conventional substrates are unsuitable for preparing thin films. Moreover, it should have stable elastic and thermal properties while the temperature is varied. The results of the measurement of the temperature dependence of the elastic constants of YBZO is discussed. In addition to the elastic properties, the thermal properties like specific heat and thermal conductivity of this material have also been measured. The specific heat measurements have been carried out by ratio method with a DSC. The thermal conductivity data have been obtained by combining thermal diffusivity data obtained from photoacoustic measurements with the specific heat data. The nonreactivity of the material has been checked by X-ray analysis.

Ultrasonic studies have been carried out on Triglycine Sulphate (TGS) single crystals which is an important ferroelectric material. It is also important from application point of view due to its pyroelectric nature which enables it to be used as IR detectors. Replacement of the sulphate groups in TGS by phosphate groups is very advantageous both from crystallographic and technological points of view. Ultrasonic studies have been carried out in
three samples with different phosphate doping levels. The samples are TGS, TGS\((0.75)P(0.25)\) and TGS\((0.50)P(0.50)\). The samples are prepared by solution growth technique. Results of ultrasonic velocity and attenuation as a function of temperature around the ferroelectric-paraelectric transition point as well as doping levels are discussed in detail.

The overall goal of this thesis work has been to study the elastic properties and phase transitions in selected solids using ultrasonic technique as has been mentioned already. Our studies show that ultrasonics is a sensitive probe to bring out minute variations in the elastic properties of complex systems such as high Tc ceramic superconductors. The effect of doping on oxygen ordering in high Tc superconductors, which is difficult to study using other techniques, clearly show up in the acoustic response of the material. The only thing is that ultrasonic investigations are not so easy to carry out and the experiments are time consuming. The effect of phosphate doping on the phase transition width in TGS is rather small but it clearly shows up in our measurements. One has to undertake very systematic and comprehensive experiments to bring out such minute effects and features. Providing the correct interpretation to the experimental results is another difficult task. Comparison with other experimental results often become necessary to give the correct interpretation to ultrasound results.

There is lot of scope for carrying out further investigations of the above type. It would be very interesting to measure the individual elastic constants of single crystals of high Tc superconductors and their variations through the transition point. Lack of good quality, large size single crystals of these materials has prevented us from doing this. There are a very large number of complex materials whose individual elastic constants are still unknown and ultrasonics can be used to measure them when sample preparation techniques improve to provide good quality, large size single crystals.
Many of these, like high Tc superconductors, have very interesting phase transitions as the temperature is varied and ultrasonics is the ideal tool to bring out changes in elastic properties taking place with changes in temperature.

Eventhough ultrasonics has been a widely used technique to study features of phase transitions near critical points, there is lot of scope for doing a great deal of further work in this direction. Ultrasonics is the most powerful technique to investigate phase transitions in which the order parameter is coupled to the internal strain. Using Landau theory it can be shown that in the case of bilinear coupling between strain and the order parameter there is an elastic instability and the corresponding phonon modes become soft. It gets reflected in ultrasonic measurements with the appropriate elastic constants $C_{ij} \to 0$ at $T_c$ and attenuation tending to infinity. If strain is not directly coupled to the order parameter the anomaly around $T_c$ may not be so prominent but it will be reflected in the measurements. There are a number of solids which undergo phase transitions but have not been explored with ultrasonics.

Only very few systems which undergo incommensurate phase transitions have been studied using ultrasonics. In such modulated or lock-in transitions, the system is characterised by amplitudon and phason modes and ultrasonics is a very powerful technique to investigate the features of such transitions. Due to the difficulties involved in growing large size samples for ultrasonics work, only limited studies have been reported. There is ample scope for doing frontline physics in this area.

Another interesting study one can take up in this line is the measurement of the variations in ultrasonic velocities with external pressure in different samples. Such measurements done for different modes will lead to the determination of higher order elastic constants. So far only third order elastic constants have been measured, that too
only in a few systems belonging to cubic symmetry. Measurement of third order elastic constants is essential to describe nonlinear elastic properties of solids. The variation of third order elastic constants near phase transitions is still unknown in literature. There remain a large number of very interesting problems to be solved in this area. It would be very interesting to pursue work in this direction.