Ultrasonics is one of the most widely used techniques to investigate phase transition in crystals. It is also the most established technique to determine the elastic moduli of both static and dynamic properties that can be measured simultaneously. Measurements of the elastic constants of a crystal as a function of temperature enable one to locate phase transition points. Second order elastic constants can be measured by measuring the velocity of the ultrasonic pulses of different polarization along different symmetry directions. Different techniques have been developed for precise measurement of velocity. Of these Pulse Echo Overlap (PEO) technique is the most accurate and precise one.

In this thesis the results of ultrasonic investigation of the elastic properties of five crystals, namely, Lithium Sodium Sulphate (LSS), Sulphamic Acid (SA) and Potassium Sulphamate (PS), Sodium doped Lithium Potassium Sulphate (LiNa_{0.5}K_{0.9}SO_{4}), Potassium Lithium Hydrogen Sulphate (KLHS) are presented. The Pulse Echo Overlap technique has been used for the velocity measurements. The thesis is presented in 8 chapters.

Chapter 1 contains a brief introduction to the theory of elastic wave propagation through anisotropic media. Expressions for the velocity of propagation of ultrasonic waves along different symmetry directions are derived from Christoffel equation for crystals of orthorhombic, tetragonal, trigonal and hexagonal symmetries. The necessary theory and details of investigation of phase transition using ultrasonic technique are outlined. Various other elastic constants such as Young's modulus, Linear compressibility, Bulk modulus, Volume compressibility and Poisson's ratio are also discussed briefly. The significance of these selected sulphate and sulphamate crystals are also given in this Chapter.

Second chapter talks about the various techniques to measure ultrasonic velocity, especially Pulse echo overlap technique, which is discussed in detail.
The MATEC model 7700 Pulse modulation and Receiver with necessary subsystem has been used for accurate measurement of ultrasonic velocity using the PEO technique. All the crystals under study were grown in our laboratory by the slow evaporation technique. The necessary constant temperature bath for the crystal growth is successfully fabricated. The McSkimin $\Delta t$ correction procedure is also included with necessary theoretical support.

The third chapter describes in detail the synthesis of Lithium sodium sulphate single crystal (LSS), purification, crystal growth, identification of the morphology of the grown crystal and preparation of the specimen. The elastic properties of the crystal have not been investigated so far. Hence the entire six independent elastic stiffness constants, compliance constants and Poisson's ratios of LSS are reported for the first time. The surface plots for phase velocity, slowness, young's modulus and linear compressibility for this crystal are also presented. In trigonal type I structure there were only 6 elastic constants $C_{11} = C_{22}$, $C_{33}$, $C_{44} = C_{55}$, $C_{12}$, $C_{13}$, $C_{14}$. If the elastic stiffness constant $C_{14}$ is zero in the measurement, the structure will be hexagonal. From various studies it is evident that ultrasonic velocity in [100] and [010] crystallographic directions are equal for hexagonal crystal and not equal for trigonal crystal. This result also can be used as a confirmation test for the structural studies. Thus the controversy which existed in the structure of $\beta$-LSS crystal raised by NMR studies has been resolved with the measurement of elastic constants. Investigation on the temperature variation of elastic constants of LSS, above room temperature using ultrasonics is undertaken since no reports on the temperature variation of elastic constant were found in the literature. An earlier pyro-luminescent study conducted by some other researchers on $\beta$-LSS crystal proposed a weak phase transition at 365 K and this study investigated it by ultrasonic technique for the first time. Ultrasonic technique is a very sensitive and precise tool for probing the phase transition in a crystal. Temperature variations of elastic constants have showed elastic anomalies for the constants $C_{11}$, $C_{12}$, $C_{33}$ and $C_{44}$ at 320 K and 350 K. These elastic anomalies are attributed to the phase transition of the crystal at 320 K and 350 K. The investigation of phase transition in $\beta$-LSS by the Differential Scanning
Calorimetric measurements at a very slow heating rate are presented. DSC measurements also indicated weak anomalies for LSS near 310 K.

The elastic properties of orthorhombic Sulphamic acid crystal have been presented in the fourth chapter. Even though elastic constants of this crystal have been reported under resonant ultrasound technique, temperature variation studies of elastic constants have not been reported so far. In this chapter the results of the measurements of elastic constants by ultrasonic PEO technique and temperature variation of elastic constants over a range of 300-400 K have been undertaken for the first time. All the nine elastic constants were measured using PEO technique by measuring velocity in different symmetry directions. Surface plots of phase velocity, slowness, Young's modulus, linear compressibility have been made and they reveal the anisotropy in elastic properties. The elastic constants show clear anomalies near 335 K. This transition is weak because the observed anomalies are very small compared to what one expects in a usual structural phase transition in a crystal. DSC measurements have also shown weak anomalies at 331 K.

The studies carried out on the elastic properties of orthorhombic Potassium Sulphamate (PS) crystal are described in chapter 5. The synthesis of the material, purification, crystal growth, identification of the morphology of the grown crystal and preparation of the specimen are described. All the nine independent second order elastic stiffness constants, compliance constant, Poisson's ratios are estimated. These results are well correlated with earlier studies using resonant ultrasound technique. There exists no previous investigation on the temperature variation of elastic constants. Hence a thorough study of the temperature variation of elastic constants over a range of 300K-400 K has been undertaken. The elastic constants \( C_{44}, C_{55} \) and \( C_{66} \) exhibit substantial anomalies at 350 K. Other elastic constants also show small anomalies in the range 330K-340 K. For the substantiation of the ultrasonic study, differential scanning calorimetry study at a very slow heating rate is also conducted and presented. DSC measurements also exhibit small feature around 340 K.
Chapter 6 outlines the phase transition study of doped Lithium Potassium Sulphate. Lithium potassium sulphate (LKS) is a very extensively studied crystal because it presents an interesting sequence of phase transitions. In a Brillouin scattering study by Drozdowki et al. a new phase transition was suggested near 333 K, but the anomaly failed to show up in a later Brillouin study by another group. In another ultrasonic investigation on this crystal by Godfrey et al. such anomalies were not observed. The present investigation was carried out to see the effect of doping the crystal with sodium or the temperature variation of elastic constants and also to see whether this doping has any connection with phase transition. Earlier reports indicated that doping would enhance the anomalies near Phase transition. The constants $C_{44}$, $C_{33}$ and $C_{66}$ exhibited anomalies in the range 313K-345K. Clear anomalies observed might be an indication of phase transition. DSC measurements have also shown no anomalies. The results of Drozdowki et al. may be due to the presence of impurities like sodium. Elastic properties of the doped crystal are studied for the first time. All the five elastic constants have been presented. There exists a controversy regarding the symmetry of the crystal while growth is performed at 35°C with equimolecular fraction of $Li_2SO_4H_2O$, $K_2SO_4$ and $Na_2SO_4$. This checking is performed using the measurement of interfacial angles, X-ray diffraction study, density and measurement of elastic constants using ultrasonics. From the present study the misconception about the structure of the crystal has been solved. Surface plots of phase velocity, slowness, Young's modulus, linear compressibility have been made and they revealed the anisotropy in elastic properties.

In Chapter 7 the elastic properties of Potassium Lithium Hydrogen Sulphate (KLHS) crystal by using ultrasonic PEO technique have been detailed since no such study is reported in the literature. Thermal studies on this crystal by earlier workers have shown three weak phase transition points at 411, 437 and 442 K. Elastic properties of the crystal were investigated by Brillouin studies and no temperature variation studies on elastic constants are reported so far. Hence the temperature dependence of elastic stiffness constants in the temperature range 300K-420 K have been examined and such studies on this crystal are presented.
for the first time. The only indication of a phase transition in KLHS is a slight change in the slope of the curves for modes $C_{44}$, $C_{66}$ at 340K. Where as no anomalies have been found near 400K as reported by Piskunowicz. All the 7 independent second order elastic stiffness constants, compliance constants, Poisson's ratios are presented.

Chapter 8 discusses the general aspects of the five single crystals. It also reviews the scope for future studies in these types of investigations.

The following papers have been published / presented / communicated for publication in different journals / conferences during the course of this work.


4. Elastic properties of potassium sulphamate single crystal-an ultrasonic study. p.57 (Presented at the 12th National Seminar on ferroelectrics and dielectrics-NSFD-XII held during Dec.16-18, 2002 at IISc Bangalore).

5. Growth and Micro hardness study of Lithium sodium sulphate p.94 (Presented at the National Seminar on current trends in material science held during 23-24 March, 2001 at M.G.University, Kottayam).

6. Phase transition at 350K for Potassium Sulphamate (KNH$_2$SO$_3$) crystal-An ultrasonic study. (Communicated to Physical Review B).

7. Ultrasonic investigation of Phase transition at 333 K in Li K$_{0.9}$Na$_{0.1}$SO$_4$ Single crystal. (Communicated to J. Appl. Physics).