The second-order elastic constants, third-order elastic constants, pressure derivatives of the second-order elastic constants and the anisotropic low temperature thermal expansion of the trigonal crystals; CaCO$_3$, Bi and LiNbO$_3$ are studied in this thesis.

General expressions for the strain energy density derived using the deformation theory have been compared with the strain dependent lattice energy from continuum model approximation to obtain the expressions for the second-order as well as the third-order elastic constants for the trigonal crystals; CaCO$_3$, Bi and LiNbO$_3$. We have taken into account the two-body interactions up to third neighbours and the three-body interactions up to second neighbours for each atom in the unit cell for the evaluation of the strain energy density. The complete set of second-order elastic constants and third-order elastic constants of the trigonal crystals; CaCO$_3$, Bi and LiNbO$_3$ have been determined and are compared with the available experimental results.
The pressure derivatives of the second-order elastic constants of the trigonal crystals; CaCO₃, Bi and LiNbO₃ have also been determined. The low temperature limits of the lattice thermal expansion of the trigonal crystals; CaCO₃, Bi and LiNbO₃ are calculated using the generalized Gruneisen functions. The low temperature behaviour of the lattice thermal expansion is governed by the generalized Gruneisen functions $\gamma'_j(\theta, \phi)$ and $\gamma''_j(\theta, \phi)$ for the acoustic modes propagating in the crystal. These generalized Gruneisen functions have been evaluated from the second and third-order elastic constants of these crystals. The procedure for the evaluation has also been given. The low temperature limits of the effective Gruneisen functions $\gamma'_\perp(0)$ and $\gamma'_\parallel(0)$ for the three trigonal crystals; CaCO₃, Bi and LiNbO₃ have also been obtained. The variations of mode gammas $\gamma'_j(\theta)$ and $\gamma''_j(\theta)$ as a function of $\theta$ are studied. The low temperature limits of the volume of Gruneisen function $\gamma_L$ have been obtained for the trigonal crystals; CaCO₃, Bi and LiNbO₃.

The second-order elastic constants of the CaCO₃ crystal are in reasonable agreement with the available experimental values. Also it is found that $C_{33}$ is less than $C_{11}$, which corresponds to the binding forces along the basal plane of the crystal. Therefore, in CaCO₃ the bonding between the atoms along the basal plane is
stronger than that between the atoms along the unique axis. Measurements of elastic constants except those along the crystallographic axes may lead to imprecise results due to the uncertainty in the orientation of single crystals.

The third-order elastic constants evaluated in the present work are compared with those of Kaga [1]. $C_{333}$ is smaller than $C_{111}$ and $C_{222}$, which means that the anisotropy along the basal plane is more pronounced than that along the unique axis. All the third-order elastic constants are negative except $C_{114}$, $C_{124}$ and $C_{134}$ for CaCO$_3$.

The pressure derivatives of the second-order elastic constants of CaCO$_3$ obtained in the present work are compared with those of the other workers [1, 2]. It is found that the pressure derivative $dC_{33}/dp$ is the largest, which indicates that the compressibility along the unique axis is higher than that along the other planes.

The mode Gruneisen parameters of CaCO$_3$ for different acoustic wave propagation directions are calculated. These results give evidence for thermal expansion anisotropy of the material for various acoustic modes. $\gamma''$, which corresponds to the change in frequencies due to a uniform longitudinal strain along the unique axis of CaCO$_3$, is found to be more anisotropic than $\gamma'$, which refers to the change in frequencies due to a uniform areal strain perpendicular to the unique axis. Hence the vibrational
anharmonicity along the unique axis is more pronounced than that along the basal plane in CaCO$_3$. The anisotropy in all the graphs of $\gamma'_1$ and $\gamma'_2$ vs. $\theta$ accounts for the pronounced anharmonicity of the solid in these directions. The low temperature limit of the lattice thermal expansion $\gamma_L$ is calculated from mode Gruneisen gammas and is found to have a value $\gamma_L = 0.85$. The low temperature limit $\gamma_L$ is positive and hence we expect the volume lattice thermal expansion to be positive down to 0K for CaCO$_3$.

Trigonal Bi possesses seven second-order elastic constants. The results obtained in the present work are in good agreement with other reported values [3, 4] except the value of $C_{14}$. The elastic constant $C_{33}$, which corresponds to the wave propagation along the unique axis of the crystal, is in reasonable agreement with the available experimental values. Also it is found that $C_{33}$ is less than $C_{11}$, which corresponds to the binding forces along the basal plane of the crystal. Therefore, in Bi the bonding between the atoms along the basal plane is stronger than that between the atoms along the unique axis.

The third-order elastic constants evaluated in the present work are compared with the reported values [4]. The pressure derivatives $dC_{ij}/dp$ obtained in the present work indicate that trigonal Bi is not easily compressible.
The mode Gruneisen parameters of Bi for different acoustic wave propagation directions are calculated. This data gives evidence for thermal expansion anisotropy of the material for various acoustic modes. $\gamma_j''$ which corresponds to the change in frequencies due to a uniform longitudinal strain along the unique axis of Bi is found to be more anisotropic than $\gamma_j'$ which refers to the change in frequencies due to a uniform areal strain perpendicular to the unique axis. Hence the vibrational anharmonicity along the unique axis is more pronounced than that along the basal plane in Bi. The anisotropy in all the graphs of $\gamma_j'$ and $\gamma_j''$ vs. $\theta$ accounts for the pronounced anharmonicity of the solid in certain specific directions. The average Gruneisen functions suggest that the thermal expansion of Bi is markedly anisotropic.

The low temperature limit of the lattice thermal expansion $\gamma_L$ for Bi calculated from its mode Gruneisen gammas is found to have a value $\gamma_L = -1.09$.

The values of second-order elastic constants of LiNbO$_3$ obtained in the present work $C_{ij}$, which corresponds to the wave propagation along the different axes of the crystal are in reasonable agreement with the available experimental values.[5-9] except for $C_{44}$. Also it is found that $C_{33}$ is greater than $C_{11}$ which corresponds to the binding forces along the basal plane of the crystal. Therefore, in
LiNbO\(_3\) the bonding between the atoms along the unique axis is stronger than that between the atoms along the basal plane. All the third-order elastic constants of LiNbO\(_3\) evaluated in the present work are negative except \(C_{444}\). The pressure derivatives of the second-order elastic constants of LiNbO\(_3\) \(dC_{ij}/dp\) obtained in the present work indicate that trigonal LiNbO\(_3\) is compressible.

The mode Gruneisen parameters of LiNbO\(_3\) for different acoustic wave propagation directions are also calculated. These results give evidence for thermal expansion anisotropy of the material for various acoustic modes. \(\gamma^\prime\), which corresponds to the change in frequencies due to a uniform longitudinal strain along the unique axis of LiNbO\(_3\), is found to be more anisotropic than \(\gamma_1\), which refers to the change in frequencies due to a uniform areal strain perpendicular to the unique axis. Hence the vibrational anharmonicity along the unique axis is more pronounced than that along the basal plane in LiNbO\(_3\). The anisotropy in all the graphs of \(\gamma_1\) and \(\gamma^\prime\) vs. \(\theta\) accounts for the pronounced anharmonicity of the solid in certain directions. The average Gruneisen functions suggest that the anisotropy in the thermal expansion along the unique axis is more pronounced than that along the basal plane.

The low temperature limit of the lattice thermal expansion \(\gamma_L\) is calculated for LiNbO\(_3\) from its mode Gruneisen gammas and is
found to have a value $\gamma_l = 2.37$. The low temperature limit $\gamma_l$ is positive and hence we expect the volume lattice thermal expansion to be positive down to 0K for LiNbO$_3$.

The scheme worked out in this thesis can be extended to other trigonal crystals also to determine their higher order elastic constants and the low temperature thermal expansion.

References