Chapter 3

Lattice dynamics and Born instability in Yttrium Aluminum Garnet (YAG), \( Y_3\text{Al}_5\text{O}_{12} \) and Rare Earth Doped Aluminum Garnets

3.1 INTRODUCTION

Yttrium Aluminum Garnet (\( Y_3\text{Al}_5\text{O}_{12} \)) is an important solid-state laser host [1,2] material. Nd doped YAG has wide spread use in commercial, medical, military and industrial applications. A combination of ideal spectroscopic properties of the rare-earth ions in YAG crystal, low thermal expansion, high-optical transparency, low acoustic loss, high threshold for optical damage, hardness, stability against chemical and mechanical changes make it the most widely used laser material [3-10]. They are hard, stable, isotropic and their large thermal conductivities permit laser operation at high power levels. Being one of the most creep resistant [9] oxides, it finds application in high-temperature ceramic composites [11]. Various doped YAG materials have been proposed as optical pressure sensors upto very high pressures of the order of 180 GPa [12,13]. Garnets find use as geobarometers [14,15], form a part of mantle transition region in the pressure range between 10-25 GPa [16,17]. Rare earth \( \text{Yb}_3\text{Al}_5\text{O}_{12} \) garnet is a synthetic insulator, plays an important role as host crystals for near-infrared soli-state lasers [36]. \( \text{Lu}_3\text{Al}_5\text{O}_{12} \) doped with \( \text{Ce}^{3+} \) is a promising scintillator material with high density and a fast response time [36].

Owing to its numerous practical applications, a thorough understanding of the vibrational properties and high-temperature, high-pressure behavior becomes vital. Several
studies with the aim of understanding the influence of defects due to doping have already been carried out [18-26]. Better understanding of the parent compound would throw insights into the changes occurring in the solid-state properties of the crystal on doping. This information would further help in improving the usefulness of the doped YAG systems that find varied technological applications. Various workers have reported experimental X-ray and neutron diffraction [27-29], Brillouin scattering and ultrasonic studies [30,31], Raman [32] and infrared spectroscopy [5,30-33], measurements of the specific heat [34] and thermal expansion [35] of YAG. Theoretical studies of the electronic structure of pure garnets [3,8,10], and symmetry based studies on the vibrational properties of several rare-earth garnets [36-41] have also been reported.

The behavior of garnets under pressure has always been a subject of interest. Many garnets like Fe-rich YIG [42], Gallium Garnet (GGG) [28] etc are found to undergo pressure induced amorphization. But experimental studies indicate that YAG based materials are stable under fairly high pressures as high as 180 GPa [12]. It is found to be thermally stable up to high temperatures [34,35] as well. Pressure induced amorphization has been studied in a number of model systems like α-quartz, ice etc and it has been observed that the onset of pressure induced amorphization coincides with zone boundary phonon softening and elastic instabilities [43,44].

A comprehensive lattice dynamics study of pristine YAG, aimed at understanding its vibrational spectra, elasticity and thermodynamical properties at high pressure and temperature has been scarce. This work reports an extensive study on the structure, vibrational and thermodynamic properties of YAG, in detail and elastic stability of rare-earth garnets. The author has calculated the pressure dependence of phonon frequencies in the whole Brillouin Zone. Such extensive calculations of the phonon dispersion relation in the various symmetry directions, phonon density of states and thermodynamic properties of
YAG has not been reported till now. All reported ab initio works [45-56] on various garnet structured materials, including YAG, have mainly been restricted to structural and electronic properties. There are only a few studies [49,53-56] on phonons and due to the complex structures involved, these workers report calculations of only the long wavelength phonons, \textit{i.e.}, at the zone centre. There is no reported high pressure \textit{ab initio} studies on the dynamics and elastic properties of YAG. This work is an effort to understand the basic phonon related properties in pure YAG.

Microscopic understanding of the thermodynamic, high-pressure properties of these garnets is essential for the quantitative understanding of its variety of properties. Accurate characterization of the structural, vibrational and thermodynamic properties is essential for understanding the physics involving these garnets. These studies are fairly involved as these garnets have complex crystal structures with a large number of atoms in the primitive cell. The crystal structure has been calculated along with the elastic constants, and density of states. Thermodynamic properties including the equation of state, specific heat and thermal expansion have also been computed. The aim in the study has been to model the ambient phase, extrapolate the model calculations to high pressure and temperature, search for dynamical instabilities, and understand the changes occurring in the bonding with increasing pressure and temperature. The response of the various Raman active frequencies to pressure has been elucidated.

3.2. THEORETICAL CALCULATIONS

The general garnet crystal has a chemical formula A$_3$B’$_2$B”$_3$O$_{12}$, space group $Ia3d$ [27] as shown in Fig.3.1. The cubic cell contains eight formula units with the metal ions occupying different symmetry sites. The structure can be viewed as interconnected
dodecahedrons (at the A site), octahedrons (at the B’ site) and tetrahedrons (at the B” site) with shared O atoms at the corners of the polyhedra. Each oxygen atom is a member of two dodecahedra, one octahedron and one tetrahedron. There are three main classes of synthetic garnets based on the atomic species at the B” sites. They are the aluminum garnets, iron garnet and gallium garnets. In case of YAG, the B’ and B” sites are both occupied by the same element (aluminum) in different valence states. These have a complex structure with 80 atoms/primitive cell.

Lattice dynamics calculations of the equation of state and vibrational properties may be undertaken using either a quantum-mechanical *ab initio* approach or an atomistic approach involving semi empirical interatomic potential. Owing to the structural complexity of garnets (80 atoms/primitive cell), the author has used an atomistic approach. The interatomic potential consists of Coulombic and short-ranged Born Mayer type interactions along with a van der Waals interaction term (only between the oxygen atoms) as explained in equation (1.25) in chapter 1. The parameters used in this study have been adjusted to satisfy the conditions of static and dynamical equilibrium. The effective charge and radius parameters used in the calculations are given in Table 3.1.

![Polyhedral representations of the crystal structure of YAG.](image)

**Fig. 3.1.** Polyhedral representations of the crystal structure of YAG.
The van der Waals interaction terms have been introduced only between the oxygen atoms with $C=100$ eVÅ$^6$. The polarizability [60,61] of the oxygen atoms has been introduced in the framework of the shell model with the shell charge $Y(O)=-2.00$ and shell-core force constant $K(O)=110$ eVÅ$^{-2}$.

The equilibrium crystal structure of YAG has been calculated by minimizing the Gibbs free energy at T=0 K with respect to the lattice parameters and the atomic positions. Since the structural energy minimization was done at T=0 K, the vibrational contribution was not included to derive the structure as a function of pressure. A small contribution expected from the quantum mechanical zero-point vibrations has been ignored. The good agreement between calculated and experimental pressure variation of Raman modes up to 20 GPa and equation of state up to 100 GPa (as discussed later) indicates that our model is valid at high pressures.

**Table 3.1:** Model parameters (Al (1) and Al(2) are in the octahedral and tetrahedral positions respectively).

<table>
<thead>
<tr>
<th></th>
<th>Al (1)</th>
<th>Al (2)</th>
<th>O</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>1.7</td>
<td>2.556</td>
<td>-1.5475</td>
<td>2.5</td>
</tr>
<tr>
<td>R(Å)</td>
<td>1.3</td>
<td>1.05</td>
<td>1.89</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 3.3 RESULTS AND DISCUSSIONS

#### 3.3.1 Crystal structure and elastic constants of YAG

The computed garnet crystal structure is found to be in unison with experimental findings [27]. The calculated lattice constant and the fractional coordinates are found to be in good agreement with reported data as can be seen from Table 3.2. The elastic constants
have been calculated from the slopes of the acoustic phonon branches, and bulk modulus has been calculated analytically using the elastic constant values. The pressure derivative $B'$ has been obtained numerically using the values of bulk modulus at different pressures.

Numerical values of elastic constants for a cubic crystal are determined by the values of acoustic mode frequencies near zone center along <100>, <110> crystallographic directions. Along <100> the longitudinal acoustic mode yields $C_{11}$, while the transverse mode gives $C_{44}$. The value $0.5(C_{11}-C_{12})$ is given by the transverse mode along <110> (with polarization along <110> direction). The calculated elastic constants and bulk modulus are found to be comparable with reported values as shown in Table 3.3 [30,31,3,8]. $C_{11}$ is the largest while $C_{12}$ and $C_{44}$ are comparable as is generally found in most cubic crystals. The variation of elastic constants with pressure is plotted in Fig. 3.2. $C_{11}$ and $C_{12}$ vary linearly with pressure while $C_{44}$ remains almost unchanged. Bulk modulus at 100 GPa is 556 GPa, which is about thrice its value at ambient pressure, so it becomes very hard compared to the ambient phase.

Stability of a lattice is central to understanding its structural response to change in physical conditions. Born criteria deals with systematic study of crystal stability in the unstressed conditions. The criteria are namely, $C_{11}+2C_{12}>0$; $C_{44}>0$ and $C_{11}-C_{12}>0$, where $C_{ij}$ are the conventional elastic constants [62a,b,c,]. There are several definitions for elastic constants at high pressure. For cubic crystals the relevant elastic constants under hydrostatic pressure that define the Born stability criteria are $c_{11} = C_{11} - P$, $c_{12} = C_{12} + P$ and $c_{44} = C_{44} - P$, where $C_{11}$, $C_{12}$ and $C_{44}$ are the elastic constant values derived from the slopes of the acoustic phonon branches. For cubic crystals, under hydrostatic loading, the mechanical Born stability criteria [62] leads to $c_{11}+2c_{12}>0$, $c_{11}-c_{12}>0$ and $c_{44}>0$. For the system to be mechanically stable, all these three conditions given above must be
simultaneously satisfied. The Born stability criteria that is violated in the present case is that the parameter $c_{44} = C_{44} - P$ should be positive. This implies that the crystal loses its resistance to shear deformation. This violation is found in the calculation at $P$ above 108 GPa. Although $C_{44}$ itself remains positive, the value of the pressure derivative of the elastic constant $C_{44}$ is less than 1 as per our calculations; as a result the parameter $c_{44} = C_{44} - P$, is very close to zero at 100 GPa and becomes negative beyond 108 GPa. Fig. 3.2 gives $c_{11}$, $c_{12}$ and $c_{44}$ for YAG under pressure; it can be see that $c_{44}$ becomes negative around 108 GPa. Reported experimental [12] energy dispersive X-ray diffraction data suggests that long range crystalline order is lost beyond 100 GPa in Sm-doped YAG.

The pressure derivatives of the computed elastic constants have been compared in Table 3.4 with those reported by Saunders [29] (calculated using a atomistic model) et al and with experimental (ultrasonic wave velocity measurements up to 0.15 GPa) results of Yogurtcu [31] et al. Our calculations are in good agreement with experimental values as well as with the previous calculations by Saunders et al (those obtained with 90% ionicity).

### 3.3.2 Long wavelength phonon frequencies of YAG

Corresponding to the 80 atoms in the garnet primitive cell, a total of 240 phonon modes occur at every wave vector. Group theoretical symmetry analysis was undertaken to classify the phonon modes belonging to various representations. Because of the selection rules only phonon modes belonging to certain group theoretical representations are active in typical single crystal Raman, infrared and inelastic neutron scattering measurements. These selection rules are governed by the symmetry of the system and the scattering geometry employed. The theoretical scheme for the derivation of the symmetry vectors is based on Irreducible Multiplier Representations [63-65] involving construction
of symmetry adapted vectors, which are used for block diagonalizing the dynamical matrix. This enables the assignment of the phonon modes belonging to various representations, and direct comparison with observed single crystal Raman and infrared data.

Table 3.2: Comparison of calculated (ambient as well as high pressure) structural parameters and average bond lengths with reported experimental and ab initio data under ambient conditions. For the space group $Ia\bar{3}d$, the Y, Al(1), Al(2), and O atoms are located at Wyckoff positions $24(c)(0, 0.25, 0.125)$, $24(d)$ $(0, 0, 0)$, $16(a)$ $(0.375, 0, 0.25)$ and $96(h)$ $(u,v,w)$ respectively.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>Experimental [27] (ambient)</th>
<th>0 (ab-initio [3,8,9])</th>
<th>0</th>
<th>50</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter, $a$ (Å)</td>
<td>12.0</td>
<td>11.904</td>
<td>11.96</td>
<td>11.24</td>
<td>10.78</td>
</tr>
<tr>
<td>$u$</td>
<td>0.9694</td>
<td>0.96</td>
<td>0.959</td>
<td>0.959</td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>0.0512</td>
<td>0.047</td>
<td>0.054</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>$w$</td>
<td>0.15</td>
<td>0.16</td>
<td>0.159</td>
<td>0.157</td>
<td></td>
</tr>
<tr>
<td>Y-O (Å)</td>
<td>2.3675</td>
<td>2.37</td>
<td>2.36</td>
<td>2.24</td>
<td>2.15</td>
</tr>
<tr>
<td>Al(1)-O, Al(2)-O (Å)</td>
<td>1.937, 1.761</td>
<td>1.94, 1.76</td>
<td>1.94, 1.76</td>
<td>1.94, 1.52</td>
<td>1.85, 1.48</td>
</tr>
</tbody>
</table>
Table 3.3: Comparison of elastic and Gruneisen parameter data. $B$ and $B'$ are the bulk modulus and its pressure derivative respectively.

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Calculated (This work)</th>
<th>Calculated (ab initio [3,8])</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>328 [a], 339 [b]</td>
<td>329</td>
<td></td>
</tr>
<tr>
<td>$C_{12}$ (GPa)</td>
<td>106 [a], 114 [b]</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>114 [a], 116 [b]</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>$B$ (GPa)</td>
<td>185 [b], 189 [c], 220 [d]</td>
<td>178</td>
<td>220.7</td>
</tr>
<tr>
<td>$B'$</td>
<td>-</td>
<td>4.1</td>
<td>4.12</td>
</tr>
<tr>
<td>$\gamma^\text{th}$</td>
<td>1.43 [a]</td>
<td>1.45</td>
<td></td>
</tr>
</tbody>
</table>

[a]: Reference 31; [b]: Reference 30; [c]: Reference 33; [d]: Reference 5.

Table 3.4: Comparison of our results with those of Saunders [29] et al and with reported experiment [31]. (a: 90% ionicity; b: 100% ionicity)

<table>
<thead>
<tr>
<th>Lattice Parameter (Å)</th>
<th>C$_{11}$ (GPa)</th>
<th>C$_{12}$ (GPa)</th>
<th>C$_{44}$ (GPa)</th>
<th>B (GPa)</th>
<th>$\gamma^\text{th}$</th>
<th>$\gamma^\text{el}$</th>
<th>$\partial C_{11}/\partial P$</th>
<th>$\partial C_{12}/\partial P$</th>
<th>$\partial C_{44}/\partial P$</th>
<th>$\partial B/\partial P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saunders [a] et al</td>
<td>11.93</td>
<td>325</td>
<td>102.7</td>
<td>103</td>
<td>0.9</td>
<td>0.73</td>
<td>6.3</td>
<td>2.5</td>
<td>0.19</td>
<td>3.76</td>
</tr>
<tr>
<td>Saunders [b] et al</td>
<td>11.93</td>
<td>401</td>
<td>127</td>
<td>127</td>
<td>0.9</td>
<td>0.73</td>
<td>6.3</td>
<td>2.5</td>
<td>0.19</td>
<td>3.75</td>
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<tr>
<td>Yogurtçu [31] et al</td>
<td>12.0</td>
<td>328</td>
<td>106</td>
<td>114</td>
<td>1.43</td>
<td>0.727</td>
<td>6.31</td>
<td>3.51</td>
<td>0.62</td>
<td>4.42</td>
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<tr>
<td>This work</td>
<td>11.96</td>
<td>329</td>
<td>103</td>
<td>90</td>
<td>1.45</td>
<td>1.1</td>
<td>4.6</td>
<td>3.4</td>
<td>0.16</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Fig. 3.2. Pressure dependence of elastic constants and bulk modulus of YAG. For cubic crystals the relevant elastic constants under hydrostatic pressure that define the Born stability criteria are \(c_{11} = C_{11} - P\), \(c_{12} = C_{12} + P\) and \(c_{44} = C_{44} - P\), where \(C_{11}\), \(C_{12}\) and \(C_{44}\) are the elastic constant values derived from the slopes of the acoustic phonon branches.

At the zone center, the phonon modes are classified into the following irreducible representations:
The $3A_{1g}$, $8E_g$ and $14T_{2g}$ modes are Raman active while $18T_{1u}$ modes are infrared active. The $E$ modes are doubly degenerate while the $T$ modes are triply degenerate. These modes have been experimentally [5,32] measured and they compare (Table 3.5) very well with our calculated values. However, there are no $ab$ initio calculations of the long-wavelength phonons for comparison. The calculated phonon frequencies with mode assignments are compared with the available Raman and infrared data [5,32] in Fig. 3.3. Hurrell [32] et al have measured 15 of the IR modes using near-normal reflection method. Hofmeister [5] et al have measured all the modes through a combination of reflection and absorption spectroscopy. The static $\varepsilon_\infty$, and high-frequency $\varepsilon_\infty$, dielectric constants are related to the infrared frequencies through the Lyddane Sachs-Teller (LST) relation:

$$\prod \left( \frac{v_i(LO)}{v_i(TO)} \right)^2 = \frac{\varepsilon_\infty}{\varepsilon_\infty}$$

(1)

The experimental value for YAG is 3.2 (Ref [5] and references therein); value calculated by Hurrell [32] et al using their measured frequencies is 3.96, while the one calculated by Hofmeister is 3.27. Our calculated value is 3.46. There appears to be no band gaps in the frequency spectrum. Both the experimental studies as well as the calculations support this observation. This is against the general trend found in aluminosilicate garnets [14,15], which show a band gap in the 650-800 cm$^{-1}$ frequency range. The low energy modes are in very good agreement with experimental data. However, at the higher frequency region, the calculated values seem to be slightly different from experimental data. Our results are closer to Hofmeister [5] with a deviation of about 5%. As discussed above the Born instability criteria are related to the acoustic phonons at low frequencies only and so would not be affected. This would marginally affect the calculation of various
Fig. 3.3. Phonon frequencies at zone centre compared with available experimental optical data [5,32].

thermodynamic properties (given below) like specific heat at high temperatures only. The group theoretical classification in the three symmetry directions is as given below:

\[ 29 \Sigma_i + 29 \Sigma_2 + 29 \Sigma_3 + 29 \Sigma_4 + 124 \Sigma_5 \]
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[111]: \(40 \Lambda_1 + 40 \Lambda_2 + 160 \Lambda_3\)

[110]: \(59 \Delta_1 + 59 \Delta_2 + 61 \Delta_3 + 61 \Delta_4\)

Table 3.5: Comparison between experimental [41] and calculated Raman active frequencies.

<table>
<thead>
<tr>
<th></th>
<th>(\omega_i) (exp)</th>
<th>(\omega_i) (cal)</th>
<th>((\gamma_i)_{\text{exp}})</th>
<th>((\gamma_i)_{\text{cal}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{2g})</td>
<td>145</td>
<td>137</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>214</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>239</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>254</td>
<td>1.1</td>
<td>1.4</td>
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<td></td>
<td>295</td>
<td>289</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>372</td>
<td>353</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>406</td>
<td>386</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>477</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>438</td>
<td>499</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>594</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>661</td>
<td></td>
<td>0.4</td>
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<tr>
<td></td>
<td>691</td>
<td>705</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>718</td>
<td>738</td>
<td>1.3</td>
<td>0.8</td>
</tr>
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<td></td>
<td>857</td>
<td>886</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>(E_{2g})</td>
<td>163</td>
<td>161</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>261</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>360</td>
<td>1.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>402</td>
<td>386</td>
<td>1.1</td>
<td>1.0</td>
</tr>
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<td></td>
<td>536</td>
<td>545</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>633</td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>712</td>
<td>736</td>
<td>1.1</td>
<td>0.6</td>
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<td></td>
<td>754</td>
<td>803</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>(A_{1g})</td>
<td>370</td>
<td>387</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>559</td>
<td>569</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>783</td>
<td>776</td>
<td>0.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>
The calculated phonon dispersion relations in the high symmetry directions in the low energy range up to 20 meV, at \( P = 0 \) and 100 GPa, are shown in Fig. 3.4. It can be seen that many branches have hardened with pressure. There are no significant changes in any of the branches which might indicate a definite softening in any of the low energy branches. There is also no optic mode softening.

The calculated pressure dependence of phonon spectra, at ambient pressure, is used for the calculation of the Grüneisen parameter \( \Gamma(E) \), averaged for all phonons of energy \( E \). The variation in the values of the Gruneisen values for all the modes is shown in Fig. 3.5.

![Phonon dispersion relation along the three high symmetry directions in the low energy range up to 20 meV at \( P = 0 \) and 100 GPa.](image)

The energy of the modes can be divided into three groups, group I between 0 and 30 meV, group II corresponding to modes between 30 and 60 meV and group III for the modes > 60
the modes below 30 meV exhibit high values of $\Gamma$, with an average around 1.5; the average $\Gamma$ of group II is around 1 and that of group III is 0.5.

*Fig. 3.5.* Variation in the calculated mode Gruneisen parameters at various pressures. meV.

3.3.3 Phonon density of states, partial density of states and thermodynamic properties of YAG

The calculated total and partial phonon density of states are shown in Fig. 3.6. Solid line gives the density of states at ambient conditions. The dynamical contributions from the various species reveal separations in their spectral range. Yttrium atom contributes solely in the low energy region between 0 to 40 meV, with a miniscule contribution around 50 meV. Aluminum atoms with different co-ordinations contribute differently. Aluminum in the octahedral coordination contributes mainly between 30 to 70 meV, while the one in tetrahedral coordination contributes almost in the entire energy range, with a greater contribution on the higher energy end between 80 and 120 meV. Oxygen atoms contribute in the whole region from 0 to 120 meV. While the Al-O tetrahedral bond length is 1.76 Å, the Al-O octahedral bond length is 1.9 Å. These give rise to differences in their bonding
characteristics and vibrational spectra. Modes in the intermediate region are owing to a complex combination of vibrations involving all the polyhedra of Al and Y.

*Fig. 3.6. Total and partial phonon densities of state in YAG at P=0, 50 and 100 GPa*
The computed one-phonon density of states, have been used for the calculation of volume-dependent thermal expansion coefficient, specific heat and other thermodynamic properties. The calculated thermal expansion coefficient and specific heat has been shown in Fig. 3.7(a) and (b) respectively. Calculated specific is in excellent agreement reported with experimental data [34] as given in Fig 3.7(b). The difference \( C_p(T) - C_v(T) = [\alpha_v(T)]^2 BVT \) becomes significant at high temperatures and is about 5% in YAG.

Thermal expansion of a crystal arises from the anharmonicity of interatomic binding forces. A measure of anharmonicity [31] is given by a parameter called \( \gamma_{\text{thermal}} \) which is given as:

\[
\gamma_{\text{thermal}} = \frac{\beta V B^s}{C_P}
\]  

(2)

where, \( V \) is the atomic volume, \( B^s \) is the adiabatic bulk modulus, \( \beta \) and \( C_P \) are the volume thermal expansion coefficient and specific heat at room temperature. Our calculations yield a value of 1.45 for \( \gamma_{\text{thermal}} \), which is in excellent agreement with reported [31] value of 1.43. The response of the crystal volume to temperature has been compared with experimental data [35] in Fig. 3.8.

The calculations have been done in the quasiharmonic approximation. The agreement is very good up to high temperatures of 1500 K (melting point for YAG is 2213 K). Thus, the percentage relative volume expansion is in excellent agreement with the reported experimental findings.
Fig. 3.7. (a) Calculated volume thermal expansion coefficient ($\alpha_v$) at different pressures. (b) Calculated specific heat at ambient condition in comparison with reported experimental (Konings et al) data [34]. Calculated specific heat at different high pressure has also been plotted for comparison. The inset gives the low temperature specific heat at various pressures. (c) Correction, $C_P-C_V$ due to implicit effects at various pressures.
Fig. 3.8. Thermal expansion of YAG in comparison with reported experimental (Geller et al) data [35]

3.3.4. High pressure studies on YAG

The behavior of the 25 Raman modes (3A$_{1g}$ + 8 E$_g$ + 14 T$_{2g}$) under pressure have been studied and compared with reported data in Fig. 3.9. Majority of the experimental Gruneisen parameters vary between 0.6-1.7 while the calculated values lie between 0.5-1.7. Only the lowest T$_{2g}$ mode at 145 cm$^{-1}$ has an experimental Gruneisen value of 2.4 whose corresponding calculated value is 2.1. The narrow range of these values show that the vibrational anharmonicity is similar for most optical phonons in the system.

Structural response of the garnet to increase in pressure has been derived as in Fig 3.10. YAG is reported to be a stable system [28] and is supposed to retain its cubic phase even beyond 100 GPa [28,12]. The equation of state in YAG has been compared in Fig.3. 9 with reported [28] data from synchrotron XRD experiments on Nd doped YAG. Doping in rare earth garnets is generally of the order of 1%. Elastic constants are observed to have negligible dependence on such small doping levels [28b]. Hence $C_{44}$ of doped YAG [27] would be very close to that of pure YAG. The values of $B_0$ and $B'$
obtained from reported data using Birch-Murughan equation are 383 GPa and 1.77 GPa. These values are very different from the ones obtained by other experimental reported data and our calculations. Experimental [28] equation of state suggests that a compression of ~23% is obtained at 100 GPa, while at the same pressure the compression is 25% as per our calculations.

**Fig. 3.9.** Pressure dependence of Raman modes in comparison with reported data. Open symbols are calculated values, while solid symbols [41] are reported experimental (Aravantidis et al) values.

At ambient conditions, there is no band gap in the phonon density of states of YAG as seen in Fig. 3.6. The density of states of various atoms at P = 50 and 100 GPa have been plotted in Fig. 3.6. With increasing pressure, the low frequency density of states of the Y atom is significantly reduced and the peaks are shifted to higher energies. There is a shift of about 15-20 meV at P = 50 GPa as compared with P=0.
GPa. The YO$_8$ polyhedra experiences maximum compression between 0 and 50 GPa, thereafter it seems that the polyhedra are not as much compressible. Therefore the Y-PDOS does not change much between 50 and 100 GPa. The partial density of states of Al, in both octahedral and tetrahedral sites is also significantly altered at high pressure, and they seem to change continuously between 0 and 100 GPa. The O-PDOS also changes considerably with pressure, the peak around 40 meV reduces and the peak beyond 80 meV gains intensity with increasing pressure. The total density of states show a band gap between 90-100 meV at $P=50$ GPa while the gap widens further up to 110 meV at 100 GPa.

**Fig.3.10.** Equation of state of YAG (calculated results (full line) compared to reported experimental (Hua et al) data [28] (solid circles)).

The pressure dependence of mode Gruneisen parameters under different pressure has been plotted along with those at 0 GPa in Fig. 3.5. At 50 GPa, the average value between 0-30 meV is 0.5, between 30-60 meV it is 1 and beyond 60 most of the modes have a
value around 0.5. At 100 GPa, the average value for modes between 0-30 meV is -0.25, between 30-60 meV, the average value is around 0, while for modes > 60 meV the average value is around 0.75.

We can deduce that the maximum change seems to have occurred in the lowest values energy modes below 30 meV, with some perceptible changes occurring in the highest energy modes. These modes mainly correspond to the YO\(_8\) modes, and to the AlO\(_4\) polyhedra. Thus this figure helps us to understand the microscopic scenario at these pressures. These changes in the vibrational spectra have an important bearing on its high pressure and high temperature properties. Our studies indicate significant atomic rearrangements in the AlO\(_6\) and AlO\(_4\) polyhedra, as well as the YO\(_8\) dodecahedra. The opening of the phonon band gap between 90-110 meV at 100 GPa is due to the Al(2)-O stretching vibrations shifting to higher energies.

Table 3.2 gives the structural parameters and the bond lengths at various pressures. The average bond lengths of the Y-O, Al(1)-O and Al(2)-O bonds have changed with increasing pressure. There are subtle readjustments and reorientations of the various polyhedral units.

The volume dependent thermal expansion coefficient, specific heat and the correction, \(C_\text{P}-C_\text{V}\) of YAG at high pressures have also been computed and compared with ambient phase values in Fig. 3.7. The ambient phase has the maximum thermal expansion coefficient. The correction, \(C_\text{P}-C_\text{V}\) (due to volume dependent anharmonic effects) is maximum for the ambient phase, and it decreases with increasing pressures. Thus, the specific heat decreases with increasing pressure. At lower temperatures below 100 K, the ambient phase has a higher specific heat, almost 1.5 times compared to that at 100 GPa.
These results are consistent with the variations observed in the values of the mode Gruneisen constants.

In this work, we have provided an atomic level understanding of the macroscopic vibrational and thermodynamic properties of high pressure YAG, which have not been studied in detail earlier. Our studies indicate that YAG structure is mechanically unstable at high pressures, due to violations of the Born stability criteria. Aluminosilicate garnets which are principal components of earth’s mantle, are known to transform into an oxide phase along with chemical decomposition typically around 25-30 GPa [16]. Due to large kinetic hindrances, such a transformation has not been observed in YAG. Various previous works indicate that YAG may persist metastably up to high pressures of 180 GPa [12], while some of its diffraction peak [12] vanish between 100 -150 GPa [12]. The exact transition has not been observed experimentally so far, although high pressure diffraction experiments [12] indicate a disordered phase above P=100 GPa.

Our theoretical calculations indicate that various polyhedral units contribute differently in different pressure regimes in YAG. There are significant changes in the phonon density of states with increasing pressure. Significant atomic rearrangements take place in the different polyhedral units as can be seen from their bond lengths and bond angles. While at ambient pressure, the YO$_8$ dodecahedra strongly influences the elastic and thermodynamic properties, at higher pressures, the YO$_8$, AlO$_6$ and AlO$_4$ polyhedra continuously deform with pressure giving rise to important manifestations in their elastic, vibrational and thermodynamic properties. We do not observe optical phonon softening upto fairly high pressures like 100 GPa. YAG however becomes mechanically unstable around 108 GPa (section 3.3.1) due to violation of the Born stability criteria. The $c_{44}$ elastic constant involving a transverse acoustic phonon becomes soft under hydrostatic
loading of 108 GPa and the structure becomes elastically unstable. This pressure is an upper bound for YAG retaining even a metastable garnet phase and a certain structural phase transition is indicated above this pressure although free energy crossover to a thermodynamically favorable phase at a lower pressure is not ruled out.

Under high pressures and temperatures, it is expected that cubic YAG would decompose into $3\text{YAlO}_3 + \text{Al}_2\text{O}_3$. Due to the large volume collapse of the perovskite structure, which is typically around 20% lower than the garnet volume, the PdV term would lower the free energy of the perovskite phase. The perovskite phase could thus remain the favored high pressure phase due to its dense atomic packing. However, due to the intrinsic complexity in dealing with chemical decomposition involved in this transition, theoretical studies of the exact pressure for such a garnet to perovskite crossover have not been undertaken for YAG.

High pressure YAG is significantly harder than the ambient phase (the bulk modulus at 100 GPa is thrice its value at $P=0$ GPa), garnet to perovskite transition would involve further substantial increase of the bulk modulus. The garnet GGG under dynamic compression has yielded a novel incompressible oxide phase with hardness greater than diamond [17]; perhaps similar phases with unusual hardness may be realized in YAG.

Our studies further indicate that the mechanical instability of YAG at high pressure is accompanied by large vibrational anharmonicity and changes in the mode Gruneisen parameters. The ambient phase mode Gruneisen values are all positive, while with increasing pressure many of the low energy modes ($<30$ meV) show negative values and some of the high energy modes ($>60$ meV) show sharp increase. The middle range remains more or less unchanged. The calculated partial density of states (Fig. 3.6) shows that Y and Al(2) atoms mainly contribution below 30 meV and above 60 meV respectively. The negative $\Gamma$ values of low energy modes results in a lower value of
overall positive thermal expansion coefficient, which in turn gives rise to a lower specific heat with increasing pressure.

### 3.3.5 Phonons and Born instability in Rare-earth Garnets

**Fig. 3.11.** Zone-centre phonon frequencies, open circles are this calculation and solid circles are experimental [36] data.
Rare-earth Yb$_3$Al$_5$O$_{12}$ and Lu$_3$Al$_5$O$_{12}$ behave similarly to YAG. They have the same crystal structure and have 80 atoms in the unit cell. Fig. 3.11 gives the phonon frequencies at the zone center in comparison with available data.

**Fig. 3.12.** Born instability in Yb$_3$Al$_5$O$_{12}$ and Lu$_3$Al$_5$O$_{12}$. Here, $c_{11} = C_{11} - P$, $c_{12} = C_{12} + P$ and $c_{44} = C_{44} - P$, where $C_{11}$, $C_{12}$ and $C_{44}$ are the elastic constant values derived from slopes of the acoustic phonon branches.
The calculated phonon frequencies are in very good agreement with available experimental data. Similar to YAG, these compounds also exhibit Born instability as can be seen from Fig. 3.12. Both the compounds violate the stability criteria above 100 GPa.

3.4 CONCLUSIONS

The author has reported detailed lattice dynamical calculations for the garnet YAG using a shell model. The calculated structure, elastic constants, phonon frequencies, specific heat, thermal expansion and equation of state of the ambient phase are in good agreement with available experimental data. At 100 GPa, YAG develops a large phonon band gap (90-110 meV) and its microscopic and macroscopic physical properties are found to be profoundly different from that at ambient pressure phase. The detailed high pressure studies conclude that YAG is mechanically unstable beyond 108 GPa, due to the violation of the Born stability criteria. Yb aluminium garnet and Lu aluminum garnet exhibit similar behavior. High pressure x-ray diffraction measurements report occurrence of a disordered phase between 100-150 GPa, and our studies suggest that these may perhaps be due to elastic instabilities.

Pressure induced amorphization has been observed in GGG and YIG. However, the cubic garnet structure is found to be stable in YAG upto significantly higher pressures and these studies reveal that upto 100 GPa there are no dynamical instabilities in YAG. Our results are in agreement with experimental studies which have suggested that YAG undergoes a phase change to a disordered metastable phase between 100-150 GPa. The observed high pressure phase beyond 100 GPa has not been clearly understood. The disordered phase perhaps occurs due to the large kinetic barriers for decomposition into the expected perovskite structure at high pressure.
Yttrium aluminum garnet, YAG and rare earth Yb$_3$Al$_5$O$_{12}$, Lu$_3$Al$_5$O$_{12}$ under ambient conditions, shows differences with the previous calculations on aluminosilicates garnets, namely there is no gap in the vibrational spectrum as seen in them. The Al atoms in tetrahedral and octahedral coordinations are dynamically distinct with aluminum in the tetrahedral coordination contributing between 90 and 120 meV. Yttrium atoms contribute mainly in the low energy range, while intermediate energy states are due to a combination of movements of all the atoms. YAG is found to be thermally stable in the temperature range (up to 1500 K) studied. Gruneisen constants of the low energy modes (< 30 meV) show great variation with increasing pressure, going from positive at 0 GPa to negative at 100 GPa. These modes become softer with pressure increase. The modes beyond 30 meV do not change much with changing pressure, excepting some modes which change drastically with ascending values of pressure. Thus, our results may have important implications for the proposed technological applications of YAG based materials as pressure sensors over a wide range of pressure.

Although author has employed an atomistic approach, the model is in good agreement with experiments and reported ab initio works. Furthermore the present work helps to understand the dynamical characteristics associated with the high pressure disordering and pressure induced amorphization. These aspects have not been clearly understood earlier. These results have important implications for use of YAG as pressure sensors in the high pressure regime. The shell model successfully gives a fair and comprehensive description of the dynamics and various thermodynamic properties at high temperatures and pressures which are otherwise difficult to access experimentally. Our studies are able to interpret complex high pressure data of YAG. This model has been successfully used to study rare-earth garnets and their elastic stability. It can be further used to study other similar garnets.
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