

THERMODYNAMIC BEHAVIOR OF NA-MAJORITE AND KNORRINGITE-MAJORITE GARNET SYSTEMS

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The behavior of thermal parameters pressure (P) and thermoelastic parameters i.e. Isothermal bulk modulus (K_T), its pressure derivative (K'_T) and Thermal expansivity (α) has been analyzed for Na-majorite and knorringite-majorite systems at different compressions down to a maximum value of 0.3 for temperature ranges from 300 K to 1500 K. The pressure dependent compressibility of these garnets have been studied. The comprehensive study of thermodynamic and thermoelastic behavior at different isotherms and isobars respectively has been achieved by employing both Vinet equation of state and Anderson-Isaak equation. The study of thermal expansivity (α) using Anderson-Isaak and Stacy-Davis approach shows a similar trend of MgO system. Based on the validation of Kumar's approach, the lattice parameter of garnet system is computed using Kumar and modified Kumar's approach at high temperature and is found to be very less deviated from the value of lattice parameter at room temperature.

Keywords: Equation of State, garnets, majorite, thermal expansivity, thermoelastic parameters.

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INTRODUCTION

The Earth's structure constitutes of three major parts: upper mantle, lower mantle and core. Garnets are vital geophysical minerals found in the upper mantle [Anderson, 1995]. Garnets have chemical formula of $\{X\}_3\{Y\}_2\{Z\}_3O_{12}$, and are capable of accommodating numerous ionic substitutions signifying diversified chemical constitution of mantle structure [Conrad et al., 1999]. The X-site of dodecahedron and Y-site of octahedron are often taken by divalent ions like Ca^{2+} , Mg^{2+} and trivalent ions like Al^{3+} , Cr^{3+} respectively. Conventional garnets contain Si-atoms inside the tetrahedron structure at low pressures and tends to expand into octahedron replacing Y-sites at higher pressures. Garnets exhibit cubic structure and possesses short-range ordering due to less distinct crystallographic sites. Consequently, the orderings in garnets decreases their symmetry. The most common isochemical garnet $MgSiO_3$ exhibiting high pressure polymorphic structure is called majorite (Maj) structure [Wijbrans et al., 2016]. Structures based on this majorite garnet $MgSiO_3$ like Na-majorite ($Na_2MgSi_2(SiO_4)_3$) and knorringite

($Mg_3Cr_2Si_3O_{12}$) garnets are found to be fascinating because of their origin [Dymshits et al., 2014a; Zou and Irifune, 2012]. Na-majorite (Na-Maj) are discovered as additions in diamonds and in mantle. This Na-majorite are common for eclogitic assemblage. It is interesting to explore multicomponent systems containing elements with different cationic radii. Till date, the physicochemical nature of Si based materials active in magmatic phenomena at high pressures and temperatures is not yet studied extensively.

Another member of garnet family knorringite (Knr) end-member, $Mg_3Cr_2Si_3O_{12}$ (Knr -Maj), is an important component of upper mantle. Peridotite rocks present in mantle have high content of Knr . The enrichment in Cr^{3+} in these garnets is an important aspect from diamond formation perspective and depends on the constitution of lithospheric mantle. There have been some investigations on thermodynamic behavior of knorringites at high-pressure as well as high-temperature experiments [Klemme, 2004; Kuskov et al., 2006; Turkin and Sobolev, 2009]. In addition, ab initio studies have been for determining low-temperature bulk modulus of Knr [Milman et al., 2001]. The thermal expansivity of knorringites are studied only as a part of pyrope solid solutions

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and very recently as single system [Dymshits et al., 2014a].

The equation of state (EOS) of solids is significant in numerous areas of basic and applied science especially physics and geophysics. Various models have investigated the constituents of garnets [Ringwood and Major, 1967; Anderson and Bass, 1984]. Several previous studies have considered the equation of state of garnets. The data obtained from the investigations of some important mantle garnets are not fully valid for understanding naturally occurring mineral assemblies. It is therefore necessary to perform additional calculations under high pressure and temperatures. With this perspective the P - V - T behavior and thermoelastic behavior under high compressions of garnets have been examined using thermodynamic approach. In this work, we report the thermoelastic behavior and P - V - T equation of state of such two garnets i.e. Na-majorite [Na₂MgSi₅O₁₂] and knorringite [Mg₃Cr₃Si₃O₃O₁₂]_{0.80} [Mg₄Si₄O₁₂]_{0.99} solids using thermodynamic approaches [Dymshits et al., 2014b]. These garnets are of significant as they are capable of crystallizing under the condition of deep mantle and transition zone [Dymshits et al., 2014b]. This study of garnets at higher pressure is crucial as these garners comprise as much as half of earth transitions zone [Dymshits et al., 2014a].

COMPUTATIONAL DETAILS

Equation of State

Various types of equation of state had been already developed earlier to study the thermoelastic behavior of minerals [Vinet et al., 1986; Birch, 1952; Shanker et al., 1999]. By knowing the correct EOS, we can find the useful properties like elastic constant, Grüneisen parameter etc. Here in this study, we have considered Vinet [Rydberg, 1932] EOS written as,

$$P = 3K_0x^2(1-x)\exp\left[\frac{3}{2}(K'_0-1)(1-x)\right],$$

$$K_T = K_0x^2\left[1 + \left\{\frac{3}{2}(K'_0-1)x + 1\right\}(1-x)\right]\exp\left[\frac{3}{2}(K'_0-1)(1-x)\right],$$

$$K'_T = \frac{1}{3}\left[\frac{x(1-\eta) + 2\eta x^2}{1 + (\eta x + 1)(1-x)} + \eta x + 2\right],$$

where :

$$x = \left(\frac{V}{V_0}\right)^{1/3}$$

$$\eta = \frac{3}{2}(K'_0 - 1).$$

Thermoelastic behavior

We analyzed the thermoelastic behavior for garnets using different approaches:

Anderson and Isaak approach

The thermoelastic behavior of solids of Anderson-Isaak [Anderson and Isaak, 1993] for obtaining the variation of thermal expansivity (α) with volume can be written as,

$$\left(\frac{d\alpha}{dP}\right)_T = \left(\frac{1}{K_T^2}\right)\left(\frac{dK_T}{dT}\right)_P \tag{1}$$

The quantities Anderson-Grüneisen parameter, isothermal bulk modulus and thermal expansivity can be expressed as:

$$\delta_T(T,P) = -\frac{1}{\alpha K_T}\left(\frac{dK_T}{dT}\right)_P \tag{2}$$

$$K_T(T,P) = -V\left(\frac{dP}{dV}\right)_T \tag{3}$$

and $\alpha(T,P) = \frac{1}{V}\left(\frac{dV}{dT}\right)_T \tag{4}$

(1)–(4) yields [Birch, 1952; Anderson et al., 1968]

$$\left(\frac{V}{\alpha}\right)\left(\frac{d\alpha}{dV}\right)_T = \delta_T \tag{5}$$

If δ_T doesn't depend on pressure, subsequently (5) results in

$$\frac{\alpha(T,P)}{\alpha(T,0)} = \eta^{\delta_T} \tag{6}$$

where η is the compression $V(T,P)/V(T,0)$. Moreover Andersen-Grüneisen parameter $\delta_T(T,P)$ is known to decrease with the compression η [Anderson, 1995]. Subsequently using the previous studies of Chopelas and Boehler [1992] and Anderson-Isaak approach, thermal expansivity can be expressed as

$$\frac{\alpha(T,P)}{\alpha(T,0)} = \exp\left[-\left(\frac{\delta(T,0)}{K}\right)(1-\eta^K)\right] \tag{7}$$

where $K = 1.41$ for MgO at 300 K, 1.25 at 2000 K and 1.20 at 3000 K.

In the *Na-Maj* system data yielded $V_0 = 1475.9 \text{ \AA}$, $K_{0,300} = 184 \text{ GPa}$ and $K'_{0T} = 3.8$, $\left(\frac{\partial K_T}{\partial T}\right) = -0.023 \text{ GPa K}^{-1}$, and parameters for thermal expansion coefficient ($\alpha = a + bT$); $a = 3.18 \times 10^{-5} \text{ K}^{-1}$ and $b = 0.18 \times 10^{-8} \text{ K}^{-2}$. In the *Knrr-Maj* system, $V_0 = 1549.08 \text{ \AA}$; yielded $K_{0,300} = 157 \text{ GPa}$ $K'_{0T} = 4.5$, $\left(\frac{\partial K_T}{\partial T}\right) = -0.019 \text{ GPa K}^{-1}$ and $a = 3.00 \times 10^{-5} \text{ K}^{-1}$, $b = 0.65 \times 10^{-8} \text{ K}^{-2}$. The results obtained using this set of data is reported in Table 1 for *Na-Maj* and *Knrr-Maj* system respectively. The experimental studies have been made by Dymshits et al. [2014b] for *Na-Maj* and *Knrr-Maj* The result has been found for P , K_T and K'_T using these input data (Table 1) and Vinet's EOS at different compression and isotherms are reported in Figure 1 and Figure 2 for *Na-Maj* and *Knrr-Maj* respectively. The study on thermal expansivity of these garnets are discussed in subsequent sections.

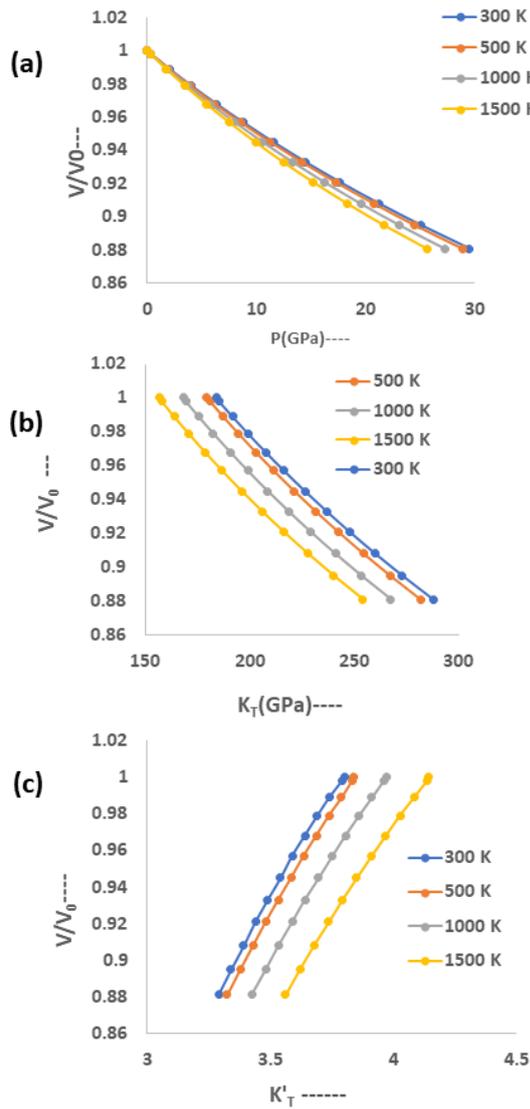


Figure 1: Variation of (a) Pressure, (b) K_T and (c) K'_T with V/V_0 for Na-Maj at different isotherms.

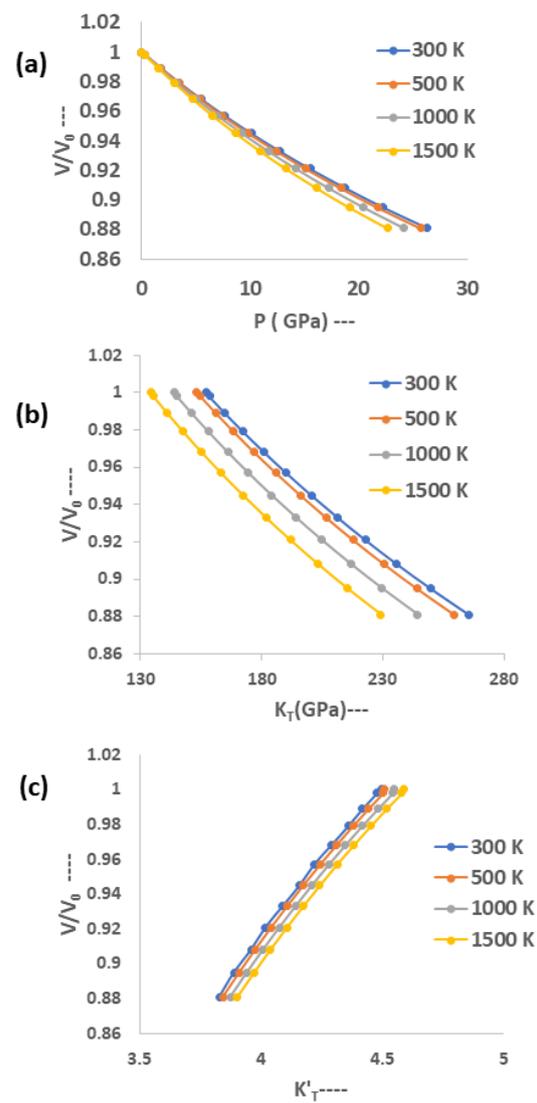


Figure 2: Variation of (a) Pressure, (b) K_T and (c) K'_T with V/V_0 for Knr-Maj at different isotherms.

Stacey and Davis Approach

Stacey and Davis [2004] observed the variations of K with pressure to be nonlinear and the slope of the curve ($K' = dK/dP$) was observed to decrease with increasing pressure. Considering extreme limiting compression, $V \rightarrow 0$, $P \rightarrow \infty$, K also tends to reach to ∞ but the ratio P/K remains finite with $t = 1.13$. Under this condition, we use the following relationship for estimating thermal expansivity.

$$\alpha = \alpha_0 \left[1 - K' \left(\frac{P}{K} \right)^t \right] \tag{8}$$

(8) gives $\alpha = \alpha_0$ at $P = 0$, and $\alpha \rightarrow 0$ at infinite pressure in view of (8). Taking log on both sides of the equation, we get,

$$\ln \frac{\alpha}{\alpha_0} = t \ln \left[1 - K' \left(\frac{P}{K} \right) \right] \tag{9}$$

Kumar’s Approach

Kumar [Singh and Chauhan, 2004] has developed a formula using the linear relationship between thermal expansivity and temperature,

$$\alpha = \alpha_0 + \alpha' T, \tag{10}$$

where α_0 is the value of α at $T = T_0$ i.e. at room temperature and $\alpha' = d\alpha/dt$, but found inconsistent with the initial boundary condition viz. $\alpha = \alpha_0$ at $T = T_0$. In order to satisfy the correlation, Singh and Chauhan [2004] have modified (10) as follows:

$$\alpha = \alpha_0 + \alpha'(T - T_0) \tag{11}$$

Coefficient of thermal expansivity

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \tag{12}$$

Table 1: Values of Initial Parameters

Parameters	300 K	500 K	1000 K	1500 K
<i>Na-Maj</i>				
$\alpha \times 10^{-5}$	3.23	3.27	3.36	3.45
K_T (GPa)	184.0	179.4	167.9	156.4
K'_T	3.800	3.842	3.970	4.146
δ_T	3.870	3.921	4.077	4.263
<i>Knrr-Maj</i>				
$\alpha \times 10^{-5}$	3.195	3.325	3.650	3.975
K_T (GPa)	157.0	153.2	143.7	134.2
K'_T	4.500	4.518	4.558	4.595
δ_T	3.788	3.730	3.622	3.562

on putting the value of α from (11) in (12) and after integrating the resulting equation on both sides we get

$$\alpha_0(T - T_0) + \frac{1}{2}\alpha'(T - T_0)^2 = \ln\left(\frac{V}{V_0}\right) \quad (13)$$

To find the value unknown parameter α' Kumar [Singh and Chauhan, 2004] used the relation obtained by [Dhoble and Verma, 1986] based on thermodynamic approximation, given as:

$$(\alpha') = \alpha_0^2 M, \quad (14)$$

where $M = [2\delta_T - (dK_T/dP)]$ and δ_T is the Andersen-Grüneisen parameter defined as,

$$\delta_T = -(1/\alpha K_T) \left(\frac{dK_T}{dT} \right)_P \quad (15)$$

Since, the product of α and K_T remains constant for solids at high temperatures i.e. temperature range from $T_0 = 300$ K up to melting temperatures. Under this condition the relationship will be written as,

$$\delta_T = dK_T/dP \quad (16)$$

Using (16), (14) can be written as,

$$(\alpha') = \alpha_0^2 \delta_T \quad (17)$$

Lattice parameter (r)

Here in this study, we have used the relationship for lattice parameter or interionic separation 'r' based on the thermal expansivity (α) obtained by Kumar [Singh and Chauhan, 2004] to find the interionic separation of garnet materials. The variation of interionic separation based on Kumar's approach is given as

$$r = r_0 \left[\frac{1}{3} \left\{ \alpha_0(T - T_0) + \frac{1}{2}\alpha'(T^2 - T_0^2) \right\} \right] \quad (18)$$

Also we have used the modified expression obtained by Singh and Chauhan [2004] which is given as,

$$r = r_0 \left[\frac{1}{3} \left\{ \alpha_0(T - T_0) + \frac{1}{2}\alpha'(T - T_0)^2 \right\} \right] \quad (19)$$

to find the interionic separation for garnet materials.

The other approach is to evaluate the variation of lattice parameter $r = a(p)$ under high pressure by using Murnaghan equation of state [Murnaghan, 1944]

$$a(p) = a(0) \left[1 + \frac{K'_0}{K_0} P \right]^{-\frac{1}{3K_0}} \quad (20)$$

where $a(0) = r_0$ is the lattice parameter at 300 K.

Result and discussion

The values of P , K_T and K'_T for *Na-Maj* and *Knrr-Maj* systems obtained at different compressions and temperature using Vinet EOS' are shown in Figure 1 and Figure 2 respectively. It can be observed that variation of P , K_T and K'_T matches with experimental data of earlier works of *Na-Maj* [Dymshits et al., 2014a] and *Knrr-Maj* [Dymshits et al., 2014b]. This suggests the reliability of the Vinet [Rydbberg, 1932] EOS employed. It can be observed from the P - V - T results of *Na-Maj* and *Knrr-Maj* that for producing the same amount of pressure (V/V_0), the required pressure magnitude becomes smaller and smaller as the temperature rises from 300 K to higher temperatures up to 1500 K. The values of most modulus K increases with increasing pressure and decreasing temperature. As the modulus is generally resistant to pressure, it becomes difficult to pressurize hard at high pressures due to the increasing volume modulus. On the contrary, solids at higher temperatures are softer and can be pressed at the same rate with less pressure. K achieves a perfect value equal to K_∞ at very high pressures at the extremes of extreme pressure. K' values decrease steadily with increasing pressure because of the rate of modulus switching in quantities. Si-based garnets contain majorite constituent which increases significantly with increasing pressure [Akaogi et al., 1987]. In addition, the impact of varying temperature at constant pressure was also observed negligible [Akaogi et al., 1987]. The impact of temperatures from 1000 K to 1500 K for the *Na-Maj* and *Knrr-Maj* are shown in Figure 1a and Figure 2a. The present results are in concordance with earlier reported results [Akaogi et al., 1987]. The majorite component in garnets is influenced strongly by pressure and this principle has been employed for estimating the depth of majorite garnets.

The variation of compressibility of garnets are shown in Figure 3. From the figure, the garnets compressibility can be found in the order of *Knrr-Maj* < *Na-Maj* < *Maj*. Zou and Irifune [2012] confirmed that Knr doesn't contain majorite component instead contain two combinations of minerals namely knorringite-eskolaite and of stishorite-

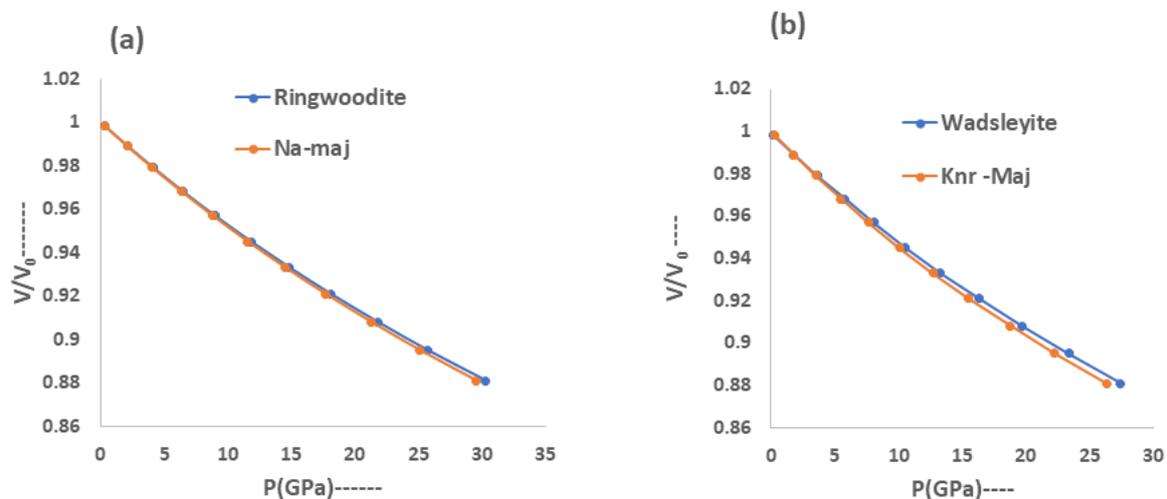


Figure 3: Compressibility variation for (a) *Knr-Maj* and wadsleyite and (b) *Na-Maj* and ringwoodite at 300 K.

wadsleyite. It can be observed from Figure 3a that variation of compressibility with pressure in *Knr-Maj* is matching with the variation for wadsleyite at completely different pressures. Similarly, Figure 3b shows an equivalent behavior of Na-majorite with ringwoodite.

The thermoelastic properties of the *Na-Maj* and *Knr-Maj* are estimated using the P, K_T and K'_T tabulated in Table 1. The variation of thermal expansivity ' α ' with pressure at different temperatures for both garnet systems have been obtained using (a) Stacey approach (8) and (b) Anderson-Isaak approach (7) and are shown in Figure 4 and Figure 5. The values of thermal expansivity obtained are in agreement with earlier reported work of *Na-Maj* [Dymshits et al., 2014a] and *Knr-Maj* [Dymshits et al., 2014b]. The dispersion of thermal expansivity is lower in case of Na-Maj as compared to *Knr-Maj* over the studied temperature range which could be due to different compositions of these garnet systems.

The thermal dependence of thermal expansivity ' α ' is also calculated from Stacy-Davis approach (8) and has been compared with Anderson-Isaak approach (7) at a fixed pressure of ~10 GPa. The compared values have been plotted in Figure 6a and Figure 6b for *Na-Maj* and *Knr-Maj* respectively. It can be observed that from Figure 6a that for *Na-Maj* both the approaches display similar increasing behavior. However, Anderson-Isaak approach is observed to give more accurate values and is in agreement with existing work [Dymshits et al., 2014a]. Similarly, in Figure 6b, the Anderson-Isaak and Stacy-Davis approach for *Knr-Maj* show similar trend. Furthermore, Anderson-Isaak approach is again observed to give promising results matching with existing literature [Dymshits et al., 2014b].

The validation of Kumar's approach in garnets assists in determining the lattice parameter separation for both the systems as a function of temperature. The lattice parameter at different isotherms is obtained by Kumar's (a) and modified Kumar's (b) approaches using (17) and (18) for *Na-Maj* and *Knr-Maj* systems. The variation of lattice parameter with pressure for *Na-Maj* and *Knr-Maj* obtained using (20) are shown in Figure 7a and Figure 7b respectively. Both of the approaches show similar trend for *Na-Maj* and *Knr-Maj* and are compatible with each other. The estimated values of lattice parameter versus pressure for *Na-Maj* in Figure 7a closely agrees with experimental results [Hazen et al., 1994]. Figure 8a and Figure 8b shows the thermal variation of lattice parameter for *Na-Maj* and *Knr-Maj*. It can be observed that as the temperature increases from 300 K to 2000 K, the lattice parameter increases for both garnet systems. The estimated values of lattice parameter versus temperature for *Knr-Maj* in Figure 8b closely agrees with experimental results [Dymshits et al., 2014a]. The maximum increase in lattice parameter for *Na-Maj* is of 12.25% and for *Knr-Maj* is 5.2%. These results are corroborating the hardness, stiffness and rigidity of these garnets.

Conclusion

A comprehensive thermodynamic study on Na-majorite (*Na-Maj*) and knorringite-majorite (*Knr-Maj*) garnet systems have been obtained. The values of P, K_T and K'_T for *Na-Maj* and *Knr-Maj* systems at different compressions and isotherms are obtained using Vinet EOS'. The compressibility of the garnets is compared to the conventional majorite and compressibility is found in the order of *Knr-Maj* < *Na-Maj* < *Maj*. The variation of

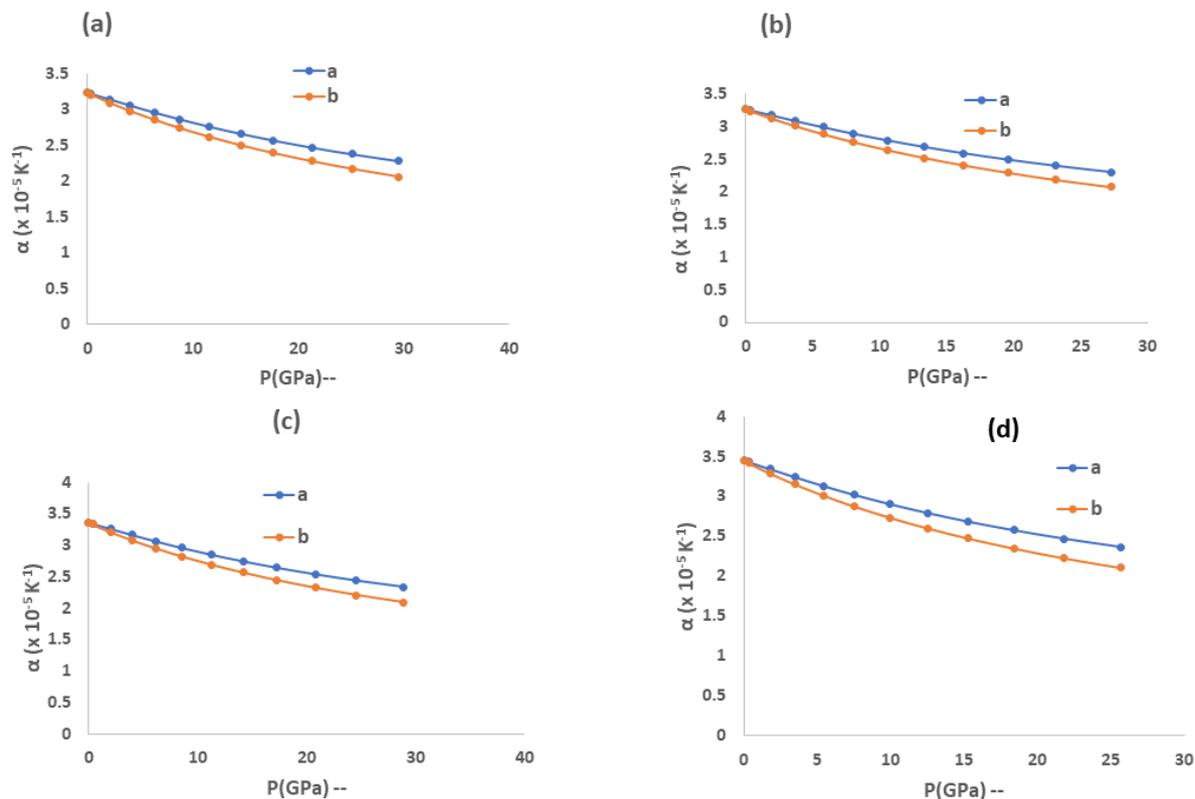


Figure 4: α vs. P for Na-Maj at (a) 300 K, (b) 500 K, (c) 1000 K and (d) 1500 K.

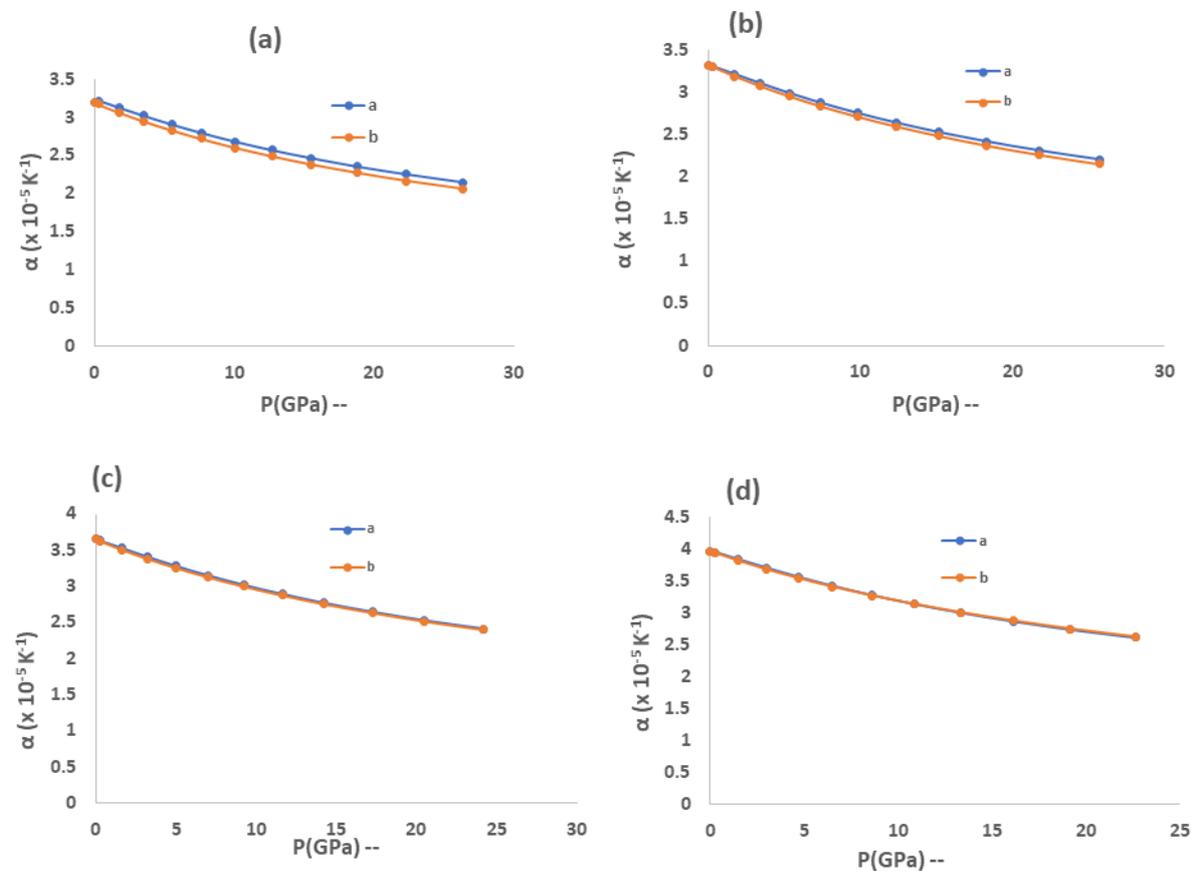


Figure 5: α vs. P for Knr-Maj at (a) 300 K, (b) 500 K, (c) 1000 K and (d) 1500 K.

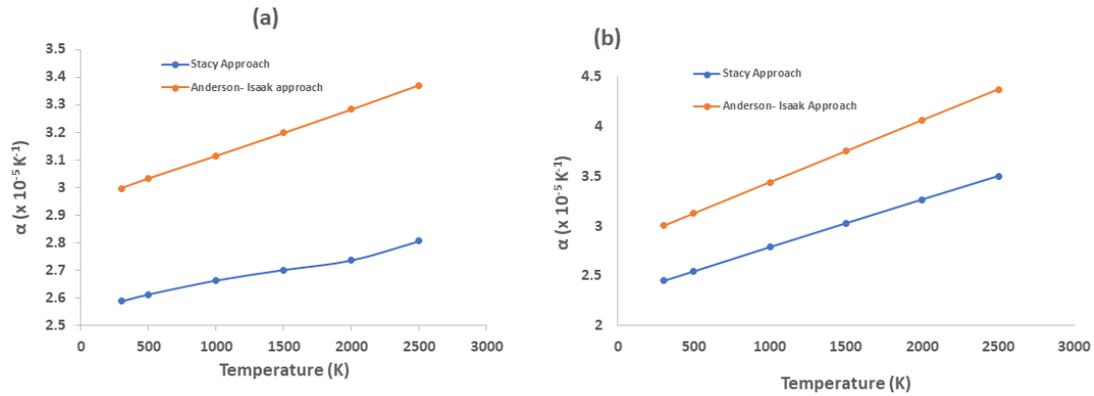


Figure 6: α vs. T for Na-Maj (a) and Knr-Maj (b) at ~10 GPa.

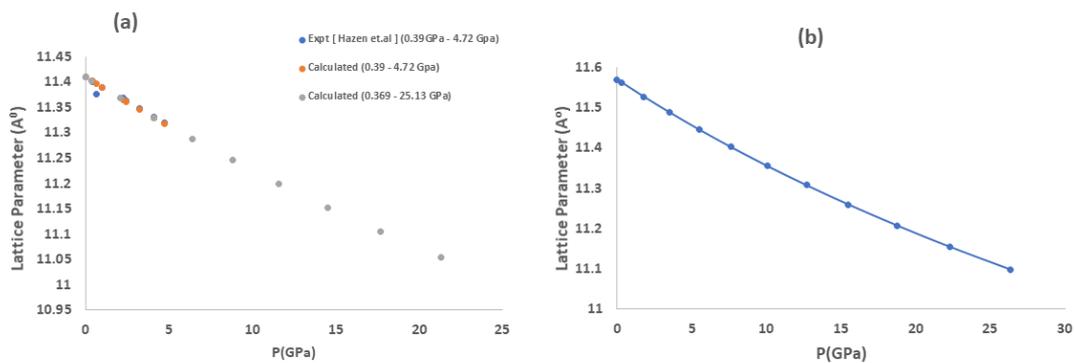


Figure 7: (a) Variation of Lattice Parameter vs. P for Na-Maj at 300 K
(b) Variation of Lattice Parameter vs. P for Knr-Maj at 300 K.

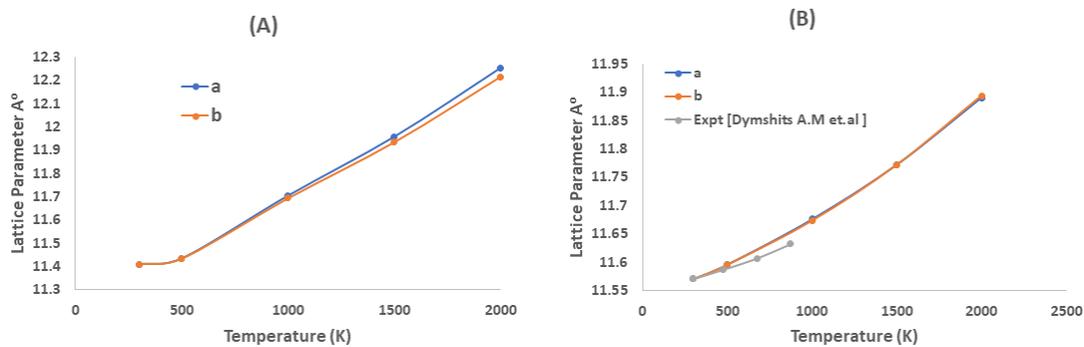


Figure 8: (A) Variation of Lattice Parameter vs. T for Na-Maj
(B) Variation of Lattice Parameter vs. T for Knr-Maj.

thermal expansivity ' α ' with pressure at different isotherms for both garnet systems have been studied using Stacey as well as Anderson-Isaak approach and the low dispersion in thermal expansivity for Na-Maj as compared to Knr-Maj is attributed to difference in compositions of these garnet systems. The thermal variation of thermal expansivity ' α ' for Na-Maj and Knr-Maj for a particular isobar shows a linear variation shown by most of the materials and has the same trend shown by experimental data for NaCl and KCl, which ex-

pands the validation of Kumar's linear relationship from alkali halides to garnets also. The validation of Kumar's approach in garnets has been used to estimate the lattice parameter for both garnets as a function of temperature. Based on the results, it can be deduced that the value of lattice parameter extended upto a maximum of 12.25% in case of Na-Maj system and 5.20% for Knr-Maj system at very high temperature and such variations are related to the hardness, stiffness and rigidity of these garnets.

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