

Study on Thermodynamic Properties of Fe³⁺-Substituted Yttrium Iron Garnets

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This paper presents the molar heat capacity at constant volume C_V and characteristic Debye temperature θ , determination for the garnet system, $Y_{3-x}Fe_{5+x}O_{12}$, $x = 0.0, 0.1, 0.3$, and 0.5 at 300 K. The θ values determined from Waldron's approach and those calculated using ultrasonic mean sound velocity, V_{mo} , are in agreement. C_V values calculated from the Einstein theory are consistent with the reported one and theoretically expected values using the Dulong–Petit law, but Waldron's approach based on the Debye theory and the Debye T^3 law fail to estimate consistent C_V values. The result has been discussed in the light of key physical differences between the two theories. The applicability of the Kieffer model for molar heat capacity at constant pressure, C_p , determination has been tested. Finally, an attempt has been made to estimate electronic contribution and the temperature at which the lattice contribution and electronic contribution to the molar heat capacity become comparable.

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1. Introduction

Yttrium iron garnet ($Y_3Fe_5O_{12}$) found large number of applications in single crystalline, coarse grain polycrystalline, nanocrystalline and thin film forms and equal numbers of research articles describing its physical properties are available in literature [1–5]. One can locate only a limited number of articles bearing on studies of the thermodynamic properties of pure and substituted $Y_3Fe_5O_{12}$ garnet ferrites [6–8]. Recently, the thermodynamic stability of Th⁴⁺-doped yttrium iron garnet system, $Y_{3-x}Th_xFe_5O_{12}$ ($x = 0.04–0.07$), as a possible actinide bearing material has been investigated using calorimetric measurements and first principles electron-structure calculations [9]. The thermodynamic results, as a whole, support the possible use of garnet phases as nuclear waste forms. On the other hand, charge-coupled substituted garnets, $(Y_{3-x}Ca_{0.5}M_{0.5x})Fe_5O_{12}$ ($M = Ce, Th$), structure and stability as crystalline nuclear waste forms was investigated by Guo et al. [10]. The thermodynamic analysis demonstrates that the substituted garnets are entropically rather than energetically stabilized. The thermodynamic stability decreases with increasing Ce or Th content but is improved at higher temperature due to the entropic contributions. Thus, this garnet host may be useful for immobilizing lanthanides/actinides under repository conditions.

In solid state physics to study lattice vibrations i.e. phonons (quantized sound waves) the θ is referred as an important physical parameter. It defines a division line between quantum mechanical and classical behavior

of phonons. The physical parameters like mean square displacements, elastic constants, sound velocities, lattice instability etc. are known to depend upon θ of a solid. Various numerical techniques have been worked out for θ calculations [11]. On the other hand, according to the Modi et al. [12] θ determined from different experimental techniques (measurement of elastic constants by ultrasonic pulse transmission technique or the Brillouin scattering, specific heat measurement, infrared and Raman spectroscopy, photoluminescence spectral analysis, etc.) will not be in concordance. Earlier, thermal variation of C_p in the temperature ranges: $1–20$ K, $80–390$ K and $200–673$ K for yttrium iron garnet was studied and that in turn used to calculate the thermodynamic functions [6] while thermodynamic properties of uvarovite garnet ($Ca_3Cr_2Si_3O_{12}$) have been studied by Klemme et al. [13]. Recently, the high-temperature heat capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ has been investigated by Denisov et al. [6]. In a thermodynamic calculation, C_p is necessary to calculate enthalpy and entropy at high temperatures from those at standard state (298.15 K). The vibrational, magnetic and electronic contributions to the molar heat capacity and entropy of $Mg_2SiO_4 + Fe_2SiO_4$ solid solutions have been studied by Dachs and his co-workers [14]. The consequences of oxygen non-stoichiometry and defects on thermodynamic properties in general and Gibbs free energy of formation in particular for three ternary oxide systems, $YFeO_3$, YFe_2O_4 and $Y_3Fe_5O_{12}$, have been investigated by Jacob et al. [15]. We have studied X-ray Debye temperature [12] and thermodynamic properties of mechanically milled $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite composition by means of infrared spectral analysis as well as thermodynamic parameters determination for quenched

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copper-ferri-aluminates from the Raman spectral analysis [16]. This communication reports on molar heat capacity and θ determination for polycrystalline Fe³⁺ substituted Y_{3-x}Fe_{5+x}O₁₂ system with general chemical formula Y_{3-x}Fe_{5+x}O₁₂, $x = 0.0, 0.1, 0.3,$ and 0.5 at room temperature (300 K) using different models in a systematic manner.

2. Experimental details

The experimental details regarding the synthesis of Y_{3-x}Fe_{5+x}O₁₂, $x = 0.0, 0.1, 0.3,$ and 0.5 garnet system by high temperature double sintering ceramic technique and ultrasonic pulse transmission technique for elastic wave velocities and elastic constants determination have been described earlier [3]. The longitudinal wave velocity (V_{lo}), mean sound velocity (V_{mo}) determined from ultrasonic measurements [3] (Table I) are further used to calculate C_V and θ at 300 K. The chemical stoichiometry of the powdered samples was checked by energy dispersive analysis of X-rays (EDAX). Powder X-ray diffraction (XRD) patterns for all the four compositions were recorded at 300 K with a Philips (PW 1700) diffractometer using Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$).

TABLE I

Structural parameters and zero porosity corrected sound velocity (V) for Y_{3-x}Fe_{5+x}O₁₂ system at 300 K.

Fe ³⁺ content (x)	V_{lo}	V_{mo}	$M \times 10^{-3}$ [kg]	$a \times 10^{-10}$ [m] ± 0.002	$\rho_x \times 10^3$ [kg/m ³]
	[m/s]	[m/s]			
0.0	8080	5005	737.98	12.379	5.166
0.1	7417	4155	734.60	12.372	5.153
0.3	5397	3189	728.00	12.363	5.119
0.5	5021	3028	721.40	12.359	5.070

3. Results and discussion

The synthesis of pure and substituted garnet materials by the usual double sintering ceramic technique involves very high temperature ($T \geq 1100^\circ\text{C}$), prolong (≥ 12 h) pre and post sintering processes. The garnet systems containing metallic cations which are volatile in nature (e.g. Zn²⁺, Li¹⁺, Ca²⁺, Cd²⁺, etc.), when subjected to such preparative conditions, may results in loss of ingredients [17]. This produces oxygen vacancies and resultant off stoichiometric composition showing an unexpected behaviour, that cannot be explained on the basis of normal stoichiometry of the composition. Thus, before any further characterization, it is essential to check the chemical stoichiometry of each synthesized composition.

The K , L , and M series X-ray increases in energy with increasing atomic number. For the normal energy range, 15–20 kV, typical for most spectrometers, light elements will emit X-rays of the K series only; intermediate elements will emit X-rays of the L series or K and L series only, while heavy elements will emit X-rays of the M series or L and M series [18]. Thus, during a given scan

one can record a wide range of elements simultaneously. In the system under study, Y_{3-x}Fe_{5+x}O₁₂, light elements like oxygen (O) ($Z = 8$), intermediate elements such as iron (Fe) ($Z = 26$), and yttrium (Y) ($Z = 39$) are present, while heavy elements are absent.

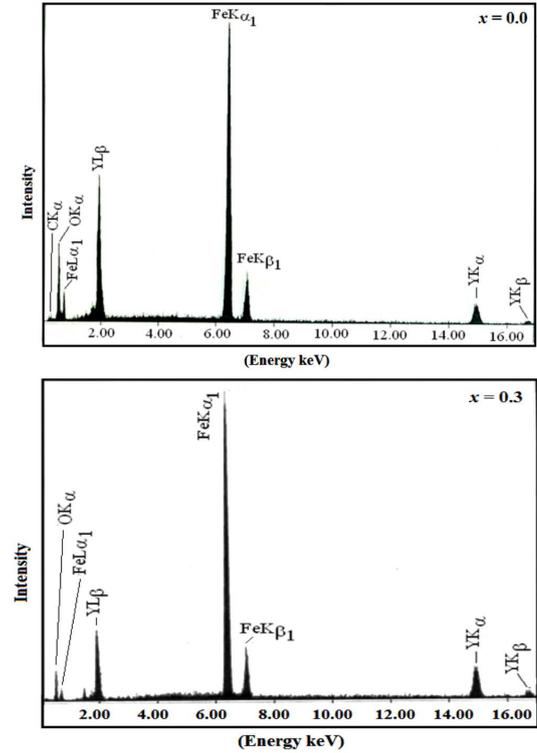


Fig. 1. Room temperature (300 K) EDAX spectra for Y_{3-x}Fe_{5+x}O₁₂ garnet system ($x = 0.0$ and 0.3).

Representative EDAX patterns for Y₃Fe₅O₁₂ ($x = 0.0$) and Y_{2.7}Fe_{5.3}O₁₂ ($x = 0.3$) compositions shown in Fig. 1 clearly show four peaks located between 5.5 keV to 7.5 keV energy. The maximum observed at ≈ 6.4 keV is directly related to iron (Fe) characteristic of line K_α , while that at 7.0 keV is corresponding to Fe $K_{\beta 1}$. The maximum observed in the left part of the spectrum at ≈ 0.5 keV clearly comes from O K_α , while peak that located at ≈ 0.75 keV comes from Fe $L_{\alpha 1}$ characteristic line. The peak at ≈ 2 keV, confirm the presence of yttrium characteristic line Y L_β . The intense peak at ≈ 14.9 keV and peak with small intensity at ≈ 17.0 keV belong to Y K_α and Y K_β line, respectively. It is important to note that if a K_α line is identified in a spectrum then a K_β line should exist having approximately a tenth of counts of the K_α lines (i.e. $K_\alpha : K_\beta = 10 : 1$) [18], we have observed same relationship for Fe $K_{\alpha 1}$ and Fe $K_{\beta 1}$ lines in the spectra.

The atomic percentage and weight percentage of constituent elements, Y, Fe, and O calculated theoretically from the selected chemical composition, Y_{2.3}Fe_{5.7}O₁₂ ($x = 0.3$) and that obtained from EDAX elemental analysis are given in Table II. It can be seen that the

TABLE II

Estimated stoichiometry for $Y_{2.3}Fe_{5.7}O_{12}$ garnet composition from EDAX analysis.

Element	Weight percentage [wt%]		Atomic percentage [at.%]		P/B ratio
	Expected	EDAX analysis ($\pm 3\%$)	Expected	EDAX analysis ($\pm 3\%$)	
Y	32.97	32.98	13.5	13.39	26.83
Fe	40.66	39.91	26.5	26.58	45.45
O	26.37	27.11	60.0	60.03	31.78
total	100.00	100.00	100.00	100.00	–

stoichiometry is very close to the anticipated values. The EDAX results suggested that the precursors had fully undergone the chemical reaction to form garnet material of the expected composition. The peak to background P/B ratio for the different elements is found to be large, so background did not introduce much error. The P/B ratio for constituent elements is also included in Table II.

Figure 2 displays typical Rietveld-fitted XRD patterns for $x = 0.0$ and 0.3 compositions of $Y_{3-x}Fe_{5+x}O_{12}$ garnet ferrite system. Indexing and refinement using general scattering analysis software of XRD patterns revealed that these are monophasic compounds crystallizing in a bcc structure (space group $Ia\bar{3}d$). No reflections from impurity phases could be detected within the limits of X-ray detection ($\approx 5\%$). The Rietveld refinement factor, goodness-of-fit (χ^2), values obtained between 1.3 and 1.6 are quite satisfactory for the refinement. The lattice constant values from the above mentioned refinement and X-ray density values thus calculated are given in Table I. It is found that the lattice constant a (\AA) decreases with increasing Fe^{3+} -content (x), this is due to the replacement of larger Y^{3+} ions with ionic radius of 0.893 \AA by the quite smaller Fe^{3+} ions having ionic radius of 0.64 \AA in the system, $Y_{3-x}Fe_{5+x}O_{12}$. Since X-ray density (ρ_x) is inversely proportional to lattice constant, it is expected to increase with increase in Fe^{3+} concentration. Contrary to the expectation, the X-ray density also decreases with ferric ion concentration (x) (Fig. 3), this is because of the fact that decrease in molecular weight (M) overtakes the decrease in the unit cell volume ($V = a^3 \text{ \AA}^3$).

3.1. Thermodynamic parameters determination based on Waldron's approach

Thermodynamic properties are divided into two broad types, intensive properties and extensive properties. C_V , C_p and θ belong to an intensive property. Waldron in his classical paper [19] analyzes the infrared spectra of spinel structured ferrite materials for the first time along with detailed discussion on force constants calculations. A classical approach was also suggested for thermodynamic parameters determination for magnetite (Fe_3O_4). We have here extended this approach to other class of ferrite material, $Y_{3-x}Fe_{5+x}O_{12}$ ($x = 0.0, 0.1, 0.3, \text{ and } 0.5$) garnet system.

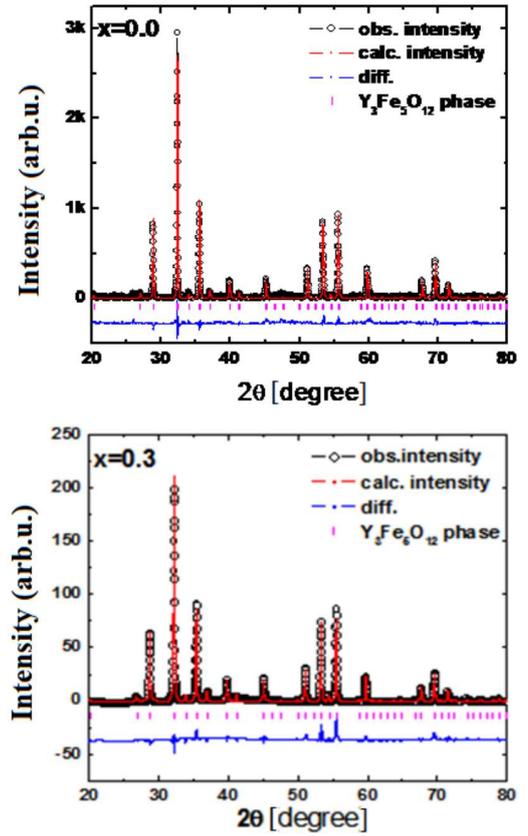


Fig. 2. Rietveld fitted X-ray diffraction patterns for $x = 0.0$ and 0.3 compositions of $Y_{3-x}Fe_{5+x}O_{12}$ garnet ferrite system recorded at 300 K.

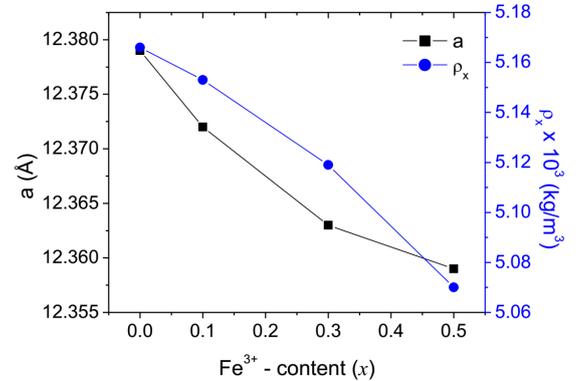


Fig. 3. Variation of lattice constant and X-ray density as a function of Fe^{3+} -content (x).

One can estimate the maximum phonon frequency, f_{\max} , using the equation $f_{\max} = V_{lo}\sigma_{\max}$. To imagine waves with a wavelength shorter than a lattice spacing makes no sense. Since there is a short wavelength limit to λ , λ_{\min} , ($1/\lambda_{\min} = \sigma_{\max}$), there must be a consequent high frequency limit, f_{\max} , and hence a maximum phonon energy, $E_{\max} = hf_{\max}$. Considering the shortest wave corresponds to one half wave per mean inter atomic distance, d , and since d is given by $d = 0.25(3r_0 + r_t) = 1/4(a)$, we obtain $\sigma_{\max} = 2.07/a$ [m].

The high frequency cut-offs of the elastic waves (f_{\max}) thus computed for different garnet ferrite compositions are given in Table III. The characteristic Debye temperature is defined by $\theta_1 = hf_{\max}/k_B = E_{\max}/k_B$. The value of θ_1 is further used to compute C_V by the equation $C_V = 60Rf(T/\theta_1)$ (relation corrected considering 20 atoms per formula unit of garnet structure instead of 7 atoms per formula unit of spinel ferrite [19]), where f is the Debye function. The Debye theory predicts that at temperatures less than $\approx 0.1\theta$, C_V should vary as T^3 according to $C_V = (12/5)(3.14)^4 R(T/\theta_1)^3$, where R is the gas constant (8.31 J/(mol K)) and T is temperature. The calculated values of C_p assuming $C_p - C_V = 0.0011T$ [K] [19] for different compositions of $Y_{3-x}Fe_{5+x}O_{12}$ garnet system are summarized in Table III. According to the law of Dulong and Petit [20],

theoretically expected value of C_V can be deduced using the relation $C_V = 3pR$, where p is the number of atom per chemical formula, and R is the gas constant. In the case of garnet materials of the type $R_3^{3+}Fe_5^{3+}O_{12}^{2-}$ (R is yttrium or rare earth ion), the number of atoms per chemical formula is 20. Thus, $C_V = 498.6$ J/(mol K), which is the limiting value of heat capacity at $T \sim \theta$. It is found that Waldron's approach and Debye T^3 law fail to estimate consistent C_V values when compared with reported and limiting value theoretically expected from the Dulong and Petit law. We see that at room temperature, C_V value will be close to $C_V = 3pR$ if θ is of the order of room temperature or less. However if θ is much greater than room temperature as in the present case (Table III), then the C_V at room temperature will appear to anomalously low as observed.

TABLE III

Thermodynamic parameters for $Y_{3-x}Fe_{5+x}O_{12}$ garnet system at 300 K.

Fe ³⁺ content (x)	$\sigma_{\max} \times 10^9$ ± 0.002 [m ⁻¹]	$f_{\max} \times 10^{13}$ ± 0.002 [s ⁻¹]	$\nu_{\max} \times 10^2$ ± 1 [m ⁻¹]	θ_1 ± 1 K	C_V	C_p	θ_0 ± 1 K
					± 1 [J/mol K]		
0.0	1.672	1.351	450.33	648.9	93.13 (191.60)*	93.46 (191.93)	632.5
0.1	1.673	1.241	413.67	596.1	110.66 (247.10)	110.99 (247.43)	541.7
0.3	1.674	0.903	301.00	433.7	188.66 (641.20)	188.99 (641.53)	416.8
0.5	1.675	0.841	280.33	403.9	211.46 (794.50)	211.79 (794.83)	395.8

*Values in parenthesis are determined from the Debye T^3 law.

3.2. Debye temperature and molar heat capacity determination from mean sound velocity

Within the isotropic continuum approximation θ in terms of mean sound velocity corrected to zero porosity (V_{mo}) is defined as:

$$\theta_0 = \frac{h}{k_B} \left[\frac{3N_A}{4\pi(M/\rho_x/q)} \right]^{1/3} V_{\text{mo}}, \quad (1)$$

where h is Planck's constant (6.63×10^{-34} J s), k_B is Boltzmann's constant (1.38×10^{-23} J/K), N_A is Avogadro's number (6.023×10^{23} molecules/mol), M is the molecular weight (Table I), ρ_x is X-ray density and q is the number of atoms in the formula unit (in the present case $q = 20$). The acoustic Debye temperature (θ_0) at which nearly all modes of vibrations in a solid are excited is found to decrease with Fe³⁺ content (x) suggests that lattice vibrations are enhanced due to Fe³⁺ substitution.

By using the Einstein theory of the heat capacity of solids [20], the C_V values at $T = 0$ K to 800 K (well above θ) for all the compositions of $Y_{3-x}Fe_{5+x}O_{12}$ garnet system were calculated using the equation given below and shown graphically in Fig. 4.

$$C_V = 3pR \left(\frac{\theta_0}{T} \right)^2 \frac{\exp(\theta_0/T)}{[\exp(\theta_0/T) - 1]^2}. \quad (2)$$

We have found that at 300 K, $C_V = 348.6, 382.6, 426.2, 432.3$ J/(mol K) for $x = 0.0, 0.1, 0.3$ and 0.5 compositions of $Y_{3-x}Fe_{5+x}O_{12}$ system, respectively. C_V at 300 K for the different compositions is consistent with limiting value as derived from the Dulong and Petit law. The heat capacity at 298 K for $Y_3Fe_5O_{12}$ is reported to be 426.77 ± 8.36 J/(mol K) [6]. The factors such as the deviation of the garnet composition from stoichiometry, formation of vacancies, antisites and other defects including magnetic "dilution" etc. were found to cause a difference between thermodynamic properties measured by different methods, as well as between the properties of samples with different prehistory [6]. On the other hand, θ_1 and θ_0 comparing reasonably well with previous results for $Y_3Fe_5O_{12}$ [21] validate the applicability of present approaches.

The failure of Waldron's approach and Debye T^3 law and success of the Einstein theory for the determination of consistent C_V value is subject of interest. This can be

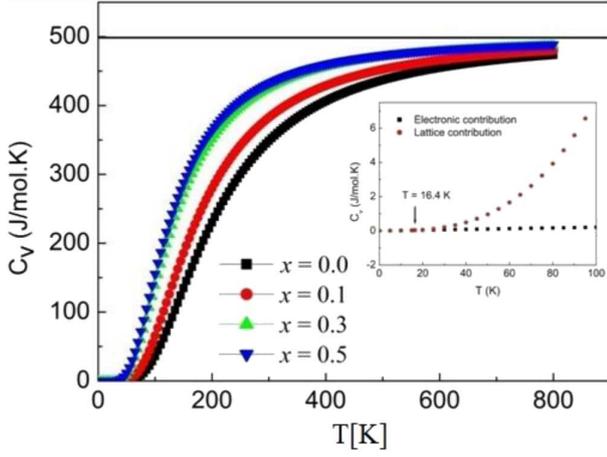


Fig. 4. Molar heat capacity at constant volume (C_V) as a function of temperature for the different compositions of $Y_{3-x}Fe_{5+x}O_{12}$ system generated based on the Einstein theory [20]. The solid horizontal line (—) corresponds to the classical limit of the Dulong–Petit law [20]. Inset of the figure shows the thermal variation of lattice ($76.62 \times 10^{-7}T^3$) and electronic ($20.71 \times 10^{-4}T$) contributions to molar heat capacity for pristine composition, $Y_3Fe_5O_{12}$ ($x = 0.0$).

explained considering following facts: (i) The Einstein theory considers the thermal component of the internal energy of a solid to be held by atoms vibrating independently in identical simple harmonic potentials. In contrast, the Debye theory considers the thermal component of the internal energy to be held by displacement (sound) waves. (ii) In the Debye theory, the quantum states of the solid are considered to be wave-like states that are occupied by phonons while in the Einstein theory, the quantum states of the solid are the quantum states of each individual simple harmonic potential. However, for phonons there are two key differences in the Debye analysis. First, there is only one quantum state for each value of \mathbf{k} . Second, for phonons the energy is directly proportional to $|\mathbf{k}|$ since the energy of a phonon is $E = \hbar\omega = \hbar V|\mathbf{k}|$. This expression has assumed that the speed of sound (V) that relates the frequency to the wavelength is independent of wavelength. This is not quite correct for wavelengths of the order of lattice spacing or so, but this is neglected in the Debye theory [20]. Further, this also suggests that the Einstein theory is suitable to estimate the molar heat capacity of materials with high values of θ ($\theta \gg 300$ K).

Observed decrease in θ or increase in molar heat capacity with Fe^{3+} substitution in the system $Y_{3-x}Fe_{5+x}O_{12}$ (Table III) may be explained in the light of observed reduction in lattice energy, that suggests a weakening of the strength of inter atomic bonding [3]. This weakening in bonding enhances the lattice vibrations, thus the temperature at which maximum phonon vibrations take place (i.e. θ) decreases and that leads to increase in molar heat capacity with Fe^{3+} substitution (Table III). In other words, due to weakening in bonding strength some sort of

disorder is produced in the system and disordered system requires more amount of energy to raise the temperature by $1^\circ C$ (i.e. molar heat capacity) (Table III).

A good approximation of molar heat capacities and vibrational entropy can be given by the Kieffer model in spite of rather simplified density of state for phonon dispersion. Thus, this model is successfully applied to many oxides and silicates [22]. In the Kieffer model C_V is calculated by modeling a simplified phonon density of state of a crystal [16]. C_p is calculated using the relation

$$C_p = C_V + \alpha^2 B_0 V_m T, \quad (3)$$

where α , B_0 , and V_m refer to thermal expansivity, isothermal bulk modulus, and molar volume, respectively. The value of α ($= 1.04 \times 10^{-5} \text{ }^\circ C^{-1} = 1.04 \times 10^{-5} \text{ K}^{-1}$) is taken from the literature [23], the value of bulk modulus, B_0 ($= 155.7 \times 10^9 \text{ N/m}^2$) from our recent elastic properties study on the system $Y_{3-x}Fe_{5+x}O_{12}$ [3] and V_m ($= 142.85 \times 10^{-6} \text{ m}^3$) and C_V ($= 348.6 \text{ J/(mol K)}$) from the present study at $T = 300$ K, are used to calculate C_p :

$$C_p = (348.6) + (1.04 \times 10^{-5})^2 (155.7 \times 10^9)$$

$$\times (142.85 \times 10^{-6})(300) = 349.32 \text{ [J/(mol K)]}.$$

3.3. The electronic contribution to the molar heat capacity of polycrystalline yttrium iron garnet ($Y_3Fe_5O_{12}$) ($x = 0.0$) at 300 K

One can estimate the electronic contribution to total molar heat capacity C_{elV} by using equation [20]:

$$C_{elV} = \frac{\pi^2 k_B^2 g(E_F) T}{3}, \quad (4)$$

where k_B is Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$), $T = 300$ K, and $g(E_F)$ is the density of states function given by

$$g(E_F) = \frac{V_m (2m_e^3 E_F)^{1/2}}{\pi^2 \hbar^3}, \quad (5)$$

where V_m is the molar volume, m_e is the mass of electron ($9.1 \times 10^{-31} \text{ kg}$), E_F is the Fermi energy.

The Fermi energy, E_F (eV), is given by the equation

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}, \quad (6)$$

where the Fermi wave vector, k_F , is given by $k_F = (3n\pi^2)^{1/3}$; here $n = N/V$ is the electron density.

There are several ways to estimate n , but perhaps the simplest is to divide the X-ray density by the mass of the garnet ferrite composition to get the number density. It is found that the X-ray density, ρ_x , of pristine yttrium iron garnet is $5.166 \times 10^3 \text{ kg/m}^3$, while the mass is given by $(737.98)(1.66 \times 10^{-27} \text{ kg})$ (Table I). Considering average valence for the composition, then our estimate for n is

$$n = (2.4)(5.166 \times 10^3) / (737.98)(1.66 \times 10^{-27}) = 1.012 \times 10^{28} \text{ [electrons/m}^3\text{]}. \quad (7)$$

Therefore,

$$k_F = [3(3.14)^2 (1.012 \times 10^{28})]^{1/3} = 0.669 \times 10^{10} \text{ [m}^{-1}\text{]}. \quad (8)$$

By substituting the value of k_F in the Fermi energy, E_F , equation we find

$$E_F = [(1.054 \times 10^{-34})^2(0.669 \times 10^{10})^2]/((2) \times (9.1 \times 10^{-31})) = 2.73 \times 10^{-19} \text{ [J]} = 1.703 \text{ [eV]}. \quad (9)$$

On the other hand, molar volume, V_m , is given by $V_m = \text{molar mass}/\text{X-ray density}$

$$V_m = 737.98 \times 10^{-3}/5.166 \times 10^3 = 142.85 \times 10^{-6} \text{ [m}^3\text{]}. \quad (10)$$

Substituting these values of V_m and E_F into the $g(E_F)$ yields

$$g(E_F) = [142.85 \times 10^{-6}][2(9.1 \times 10^{-31})^3 \times (0.273 \times 10^{-18})]^{1/2}/(3.14)^2(1.05 \times 10^{-34})^3 = 7.93 \times 10^{42} \text{ [states J}^{-1} \text{ mol}^{-1}\text{]}, \quad (11)$$

which predicts an electronic heat capacity of

$$C_{elV} = \frac{\pi^2 k_B^2 g(E_F) T}{3} = [(3.14)^2(1.38 \times 10^{-23})^2 \times (7.93 \times 10^{42})300]/3 = (1.489) \text{ [J/(mol K)]}. \quad (12)$$

This is to be compared with the contribution due to the lattice of around 348.6 J/(mol K). In other words, the electronic contribution to the heat capacity is only around 0.43% of the total heat capacity. This can be understood from the following facts. The electrons contributing to the conduction are very close to the Fermi energy. However, to contribute to bulk specific heat all the valence electrons would have to receive energy from the nominal thermal energy, $k_B T$. But, the Fermi energy is much greater than $k_B T$ and the large majority of the electrons cannot receive such energy. Since there are no available energy levels within $k_B T$ of their energy, the small fraction of electrons which are within the $k_B T$ of the Fermi level does contribute a small specific heat and hence the electron specific heat is significant only at very low temperature.

Thus, the total molar heat capacity at 300 K is given by

$$C_V(\text{total}) = C_V(\text{lattice}) + C_V(\text{electronic}) = (348.6 + 1.489) \text{ [J/(mol K)]} = (350.09) \text{ [J/(mol K)]}. \quad (13)$$

Alternatively, it is possible to calculate C_{elV} for non-substituted garnet at 300 K using the Debye expression

$$C_{elV} = (3.14)^2(Rk_B T)/(2E_F) = 1.696 \times 10^{-19}/E_F \text{ [J]} = 0.62 \text{ [J/(mol K)]}. \quad (14)$$

Finally, an attempt has been made to estimate temperature where electronic and lattice molar heat capacities are comparable by equating respective Debye equation [24]:

$$C_{elV} = [(3.14)^2 R k_B T]/2E_F = [12(3.14)^4 R(T/\theta)^3]/5 = C_{LaV}, \quad (15)$$

therefore,

$$(T^3/\theta) = [(3.14)^2 R k_B (\theta)^3 5]/[24E_F R(3.14)^4] \quad (16)$$

and

$$T^2 = 5k_B(\theta)^3/24(3.14)^2 E_F, \quad (17)$$

that results in [24]:

$$T = [5k_B(\theta)^3/24(3.14)^2 E_F \text{ [J]}]^{1/2}. \quad (18)$$

The temperature at which the two molar heat capacities are equal is found to be 16.4 K (Fig. 4 (inset)). Further work is in progress.

4. Conclusion

The thermodynamic parameters C_V , C_p and θ for $Y_{3-x}Fe_{5+x}O_{12}$ garnet system with $x = 0.0, 0.1, 0.3,$ and 0.5 have been studied at 300 K. The Einstein theory is successfully employed to determine molar heat capacity but Waldron's approach and Debye T^3 law fail to estimate consistent C_V values. The Debye temperatures determined from Waldron's approach based on the Debye theory and mean sound velocity are in agreement. The determination of C_p using the Kieffer model is found to be quite satisfactory. It is found that the electronic contribution to C_V is smaller than 0.5% compared to the lattice molar heat capacity and at 16.4 K electronic and vibrational molar heat capacities are comparable for pristine yttrium iron garnet.

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