Phonon density of states and thermodynamic properties of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$

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Abstract. Based on the low-temperature heat capacity a set of properties of dimeric lanthanum dipivaloylmethanate were obtained. The phonon density of states was calculated, and characteristic temperatures related to the basic moments of the density of states were obtained. The molar thermodynamic functions at constant volume (heat capacity, entropy, internal energy increment, and Helmholtz energy) in the temperature range of 0–455 K were calculated. The molar zero-point energy and total internal energy were calculated.

1. Introduction

Thin films of lanthanum oxide (La$_2$O$_3$) are promising as a gate dielectric in field-effect transistors [1, 2]. Chemical vapor deposition (CVD) is one of the main methods for producing these films [3]. CVD technology allows obtaining homogeneous coatings on large surfaces on an industrial scale, as well as controlling film thickness and stoichiometry. Lanthanum dipivaloylmethanate is a promising precursor for producing thin films of lanthanum oxide on the surface by the CVD method [4]. For the development and optimization of technological processes involving these complexes, information on their properties is required.

Crystallographic studies have shown [5] that solid lanthanum dipivaloylmethanate exists in the form of a monoclinic dimer (La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$). These complexes crystallize in molecular type lattices [5]. Currently, the thermodynamic properties of lanthanum dipivaloylmethanate are not well understood. There are several studies of vapor pressure [6], the formation enthalpy [7], and low-temperature heat capacity [8] of these substances. High-temperature heat capacity of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ has not been studied at present. Data on heat capacity within a wide temperature range are important. They are used to calculate thermodynamic functions (entropy, enthalpy increment, free Gibbs energy, etc.) [9,10], and serve as a basis for calculation methods [11,12] and generalizations [13,14].

In the present work, based on the results of an experimental study of the lanthanum dipivaloylmethanate heat capacity [8], we calculated the phonon density of states $g(\omega)$. And then the basic characteristic temperatures, zero-point energy, isochoric heat capacity and thermodynamic functions within a wide temperature range were obtained.

2. Phonon density of states

The phonon density of states of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ was calculated from the low-temperature heat capacity data using the numerical method [15,16]. The method allows obtaining the density of states in the three- or four-peak approximation and correctly describing the shape and area of peaks based on low-temperature heat capacity.
2.1. Preparing for $g(\omega)$ calculation

For all solids heat capacity at constant pressure $C_p(T)$ and at constant volume $C_v(T)$ below a certain temperature are practically the same. This is due to the fact that the anharmonic component of the heat capacity of a solid becomes significant only in the temperature range, where the heat capacity approaches its limiting value corresponding to the Dulong and Petit law at high temperatures [17]. The heat capacity of La$_2$(C$_{11}$H$_{10}$O$_2$)$_6$ at 314 K is only 38% of the limiting value. This suggests that the anharmonic contribution to the experimental heat capacity $C_p(T)$ at room temperature and below will be rather small. Also, the experimental curve $C_p(T)$ [8] does not indicate the existence of any anomalies. Therefore, to calculate $g(\omega)$, one can use experimental heat capacity [8] within the range from 6 to 314 K.

The vibrational spectrum of La$_2$(C$_{11}$H$_{10}$O$_2$)$_6$ has no vibrational modes in the frequency range of 2400 to 4100 K, and above 4100 K it contains narrow frequency band of vibrational modes associated with the stretching vibrations of C–H groups [18]. This feature of the vibrational spectrum is typical for molecular crystals, including beta-diketonates. Preliminary accounting of the hydrogen atoms stretching vibrations contribution was done similarly to the works [19–21]. Such accounting will significantly reduce the frequency range in which the phonon density of states will be restored, thereby simplifying the problem being solved. The frequency distribution of the stretching vibrations was studied in [18] by IR and Raman spectroscopy. The corresponding phonon density of states $g_0(\omega)$ is shown in figure 3 within the frequency range of 4096–4544 K, and its characteristic frequency is $\omega_0 = 4244$ K. The heat capacity $C_0(T)$ of the stretching vibrations of hydrogen atoms was subtracted from the experimental heat capacity $C_p(T)$, and thus the heat capacity $C_0(T)$ was obtained. The $C_0(T)$ corresponds to the effective number of atoms equal to $n_0 = 156$, and it was used to calculate the $g(\omega)$.

2.2. The density of states calculation

Calculating the phonon density of states by method [15,16] takes three steps. In the first step, zero approximation $g_0(\omega)$ are chosen, which can take into account some characteristic features of the restored density of states and have a correctly set cutoff frequency. In the second step, the zero approximation is refined by stepwise redistribution of the number of vibrational modes over frequencies. Such redistribution is controlled by a standard deviation of the heat capacity of the target density of states from the initial heat capacity and is performed until the required accuracy is reached. The procedure is repeated several times. In the third step, the obtained solutions are averaged.

The function $g_0(\omega)$, which has a constant value below the cutoff frequency of 2400 K, was chosen as a zero approximation. The frequency step for calculating the density of states was selected as 32 K. At calculations, each $i$-th unit frequency interval in $g(\omega)$ was represented by the Einstein function with the characteristic frequency $\theta_k = (32i - 16)$ K.

The density of states $g^{(k)}(\omega)$ was independently calculated from the zero approximation $g_0(\omega)$ 12 times ($k = 1..12$). The $g^{(k)}(\omega)$ are located in a band determining the uncertainty of solutions to be obtained. Further, the phonon density of states $g_\lambda(\omega)$ corresponding to the heat capacity $C_\lambda(T)$ was obtained by averaging the solutions $g^{(k)}(\omega)$. It does not include modes related to the C–H stretching vibrations and has the cutoff frequency of 2400 ± 48 K. It should be noted that as a result of averaging, the uncertainty of $g_\lambda(\omega)$ associated with random local features that are present in each $g^{(k)}(\omega)$ solution is significantly reduced.

The absolute deviations $\Delta g^{(k)}(\omega)$ of the solutions $g^{(k)}(\omega)$ from the averaged $g_\lambda(\omega)$ are shown in figure 1. It can be seen that the calculated uncertainty of the density of states is random and, on average, it increases along with the frequency. The standard deviation was 0.027 at the frequencies of 0–32 K; 0.17 at 32–64 K; 0.5 at 64–288 K; 0.8 at 288–960 K; and 1.3 at 960–2400 K.

The relative standard deviation of the experimental values [8] without component associated with the stretching vibrations of C–H groups $C_\lambda(T)$ from the heat capacity of the averaged $g_\lambda(\omega)$ is 0.8% (8–16 K) and 0.11% (16–314 K).
For all solutions $g^{(k)}(\omega)$, corresponding heat capacities $C_v^{(k)}(T)$ were calculated, and heat capacity $C_v^{(A)}(T)$ corresponding to averaged $g_A(\omega)$ was calculated. Then we estimated the uncertainty of the heat capacity $C_v(T)$ calculation. The root mean square deviation was 1.1% (1–8 K); 0.12% (8–17 K); 0.03% (17–55 K); 0.011% (55–135 K); 0.005% (135–314 K); and 0.04% (314–455 K). The increasing uncertainty, as the temperature decreases below 55 K is due to both an increase in experimental uncertainty and an interval of discretization ($\Delta \omega (\hbar/k_B) = 32$ K) of the density of states $g(\omega)$. The relative deviations $\Delta_C^{(k)}(T)$ of calculated heat capacities $C_v^{(k)}(T)$ from the heat capacity $C_v(T)$ within the range of 20–455 K are shown in figure 2.

As a result, the phonon density of states $g(\omega)$ of $\text{La}_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_6$ was obtained as a sum of the calculated density of states $g_A(\omega)$ and the density of states $g_H(\omega)$ of the stretching vibrations of C–H groups. The result is shown in figure 3 (the scales of vertical axes in figures 1 and 3 are the same). As can be seen, the density of states $g(\omega)$ has two main parts. The low-frequency part has two peaks, connected with both intramolecular and intermolecular vibrations. The high-frequency part is represented in the two-peak approximation; it is connected with only intramolecular vibrations.

**Figure 1.** The absolute deviations $\Delta g^{(k)}(\omega)$ of the $g^{(k)}(\omega)$ calculations from the averaged $g_A(\omega)$. Different symbols correspond to different calculation runs $k$.

**Figure 2.** The relative deviations $\Delta_C^{(k)}(T)$ of the heat capacities $C_v^{(k)}(T)$ from the heat capacity $C_v^{(A)}(T)$ in the temperature range of 20–455 K.

**Figure 3.** The phonon density of states of $\text{La}_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_6$. The vertical lines represent the uncertainties of the corresponding values of $g(\omega)$. 

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2.3. Characteristic temperatures

The basic characteristic temperatures $\Theta_i$ of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ associated with moments of the phonon density of states for $i = 1; 2; 4; 6; -1; -2$:

$$\Theta_i = \frac{h}{k_B} \sqrt{\frac{\int \omega g(\omega) d\omega}{\int g(\omega) d\omega}}$$ (1)

The Debye characteristic temperature $\Theta_D(\infty)$ at $T \rightarrow \infty$ is related to the characteristic temperature $\Theta_2$ by the following equation [22]:

$$\Theta_D(\infty) = \sqrt[3]{5} \Theta_2$$ (2)

The obtained values of characteristic temperatures of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ are given in table 1.

| Quantity$^a$ | Value       | Quantity$^a$ | Value       |
|--------------|-------------|--------------|-------------|
| $\Theta_1$   | 1725.8 ± 2.3 K | $\Theta_1$   | 443.2 ± 0.6 K |
| $\Theta_2$   | 2226 ± 3 K   | $\Theta_2$   | 180.2 ± 0.9 K |
| $\Theta_4$   | 2878 ± 6 K   | $\Theta(0)$  | 190.0 ± 2.4 K |
| $\Theta_6$   | 3246 ± 8 K   | $\Theta(\infty)$ | 2873 ± 5 K   |
| $\Theta$     | 2400 ± 48 K  | $\Theta$     | 4244 K       |

$^a$ $\Theta_i$ are the characteristic temperatures related to the $i$-th moments of the $g(\omega)$; $\Theta_c$ is the cutoff frequency of $g(\omega)$ without taking into account the stretching vibrations of hydrogen atoms; $\Theta_H$ is the characteristic temperature of stretching vibrations of hydrogen atoms; $\Theta_D(0)$ and $\Theta_D(\infty)$ are the Debye characteristic temperatures at $T \rightarrow 0$ and $T \rightarrow \infty$ respectively.

The Debye characteristic temperature at 0 K $\Theta_D(0)$ was obtained based on the experimental heat capacity below 8 K [8] using the low-temperature expansion of the Debye temperature [23]. The obtained value $\Theta_D(0)$ is presented in table 1.

3. Thermodynamic properties

3.1. Heat capacity and thermodynamic functions at constant volume

The thermal stability and phase transition testing of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ were studied using a thermomicrobalance Netzsch TG 209 F1 Libra (10 K min$^{-1}$ heating rate, under helium gas flow at 75 ml min$^{-1}$). The c-DTA analysis presented an endothermic peak at 455–456 K, which is associated with the structural phase transition. In this way, we determined a temperature region of the dimeric solid phase existence.

The obtained density of states $g(\omega)$ of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ should describe the isochoric heat capacity $C_V(T)$ in the entire region of the dimeric solid phase existence (figure 4). And the heat capacity $C_V(T)$ in the range up to 455 K given by the $g(\omega)$ was used to calculate molar thermodynamic functions at constant volume: entropy $S_v(T)$, internal energy increment $\Delta U(T)$ and Helmholtz free energy $\Delta F(T)$ (figures 4 and 5).
Figure 4. The isochoric heat capacity $C_V(T)$ and entropy $S_V(T)$ of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ within the range of 0–455 K.

Figure 5. The internal energy increment $\Delta U(T)$ and Helmholtz free energy $\Delta F(T)$ of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ in the range of 0–455 K.

3.2. Zero-point energy

The zero point energy $E(0)$ associated with the “quantum” fluctuations of atoms in their lowest energy state can be calculated by the following formula [16]:

$$E(0) = \frac{3Rn}{2} \Theta_1$$  \hspace{1cm} (3)

The molar zero-point energy of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ was calculated as $E(0) = 4176 \pm 6$ kJ mol$^{-1}$ or $E'(0) = E(0)/n = 21.52 \pm 0.03$ kJ mol$^{-1}$ if you consider the molecule as a whole.

The total energy of a solid includes both internal energy associated with the “thermal” fluctuations of atoms, and zero point energy associated with the “quantum” fluctuations of atoms: $U(T) = E(0) + \Delta U(T)$.

Conclusions

A set of important characteristics of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ molecular crystal based on the experimental heat capacity data was presented. The thermal stability of dimeric lanthanum tris-dipivaloylmethanate at high temperatures was determined by DTG and DTA techniques.

The phonon density of states of La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ was obtained for the first time. The $g(\omega)$ has three areas – the low-frequency, high-frequency, and a narrow high-frequency band near 4244 K separated from the high-frequency area by a wide range of zero function value. The low-frequency region of the spectrum shows two peaks, of which the first one is split into two peaks; and the high-frequency region has a two-peak shape. The low-frequency area of $g(\omega)$ can be associated with both intramolecular and intermolecular vibrations; the high-frequency area is associated with intramolecular vibrations. The narrow frequency band near 4244 K is related to the stretching vibrations of C–H groups. This shape is characteristic of all the obtained solutions, which confirms the reliability of the revealed features of the $g(\omega)$. The obtained phonon density of states is in agreement with the data on IR and Raman spectroscopy [18].

The basic characteristic temperatures related to the moments of the phonon density of states were calculated. The high accuracy of the obtaining characteristic temperatures is the result of correct distribution of the number of vibrational modes at different frequency intervals in $g(\omega)$.

The heat capacity, entropy, internal energy increment, and Helmholtz free energy at constant volume for La$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ were calculated within the entire region of the dimeric solid phase existence. The obtained thermodynamic functions can be considered as isobaric since, in our estimation, the $C_p(T) - C_V(T)$ difference at room temperature is at the level of tenths of a percent and near the temperature of 455 K is no more than one-two percent.
The zero-point energy and Debye characteristic temperature at \( T \to \infty \) were determined using first and second moments of \( g(\omega) \). The knowledge of the zero point energy made it possible to obtain full internal energy of \( \text{La}_2(\text{C}_{11}\text{H}_{19}\text{O}_2)_6 \).

The analysis of the uncertainty of characteristics considered in the work was done.

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