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Short communication

Heat capacity and thermodynamic functions of $LuPO_4$ in the range 0–320 K

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Abstract

The heat capacity of $LuPO_4$ was measured in the temperature range 6.51–318.03 K. Smoothed experimental values of the heat capacity were used to calculate the entropy, enthalpy and Gibbs free energy from 0 to 320 K. Under standard conditions these thermodynamic values are: $C_p^0(298.15\,K) = 100.0 \pm 0.1\,J\,K^{-1}\,mol^{-1}$, $S^0(298.15\,K) = 99.74 \pm 0.32\,J\,K^{-1}\,mol^{-1}$, $H^0(298.15\,K) - H^0(0) = 16.43 \pm 0.02\,kJ\,mol^{-1}$, $-[G^0(298.15\,K) - H^0(0)]/T = 44.62 \pm 0.33\,J\,K^{-1}\,mol^{-1}$. The standard Gibbs free energy of formation of $LuPO_4$ from elements $\Delta_f G^0(298.15\,K) = -1835.4 \pm 4.2\,kJ\,mol^{-1}$ was calculated based on obtained and literature data.

Keywords: Lutetium phosphate; Calorimetry; Heat capacity; Thermodynamic functions

1. Introduction

Lutetium phosphate belongs to $M^{III}PO_4$ (M^{III} = Tb–Lu, Y) substances with xenotime structure, YPO_4, isostructural to zircon ($ZrSiO_4$). The substance crystallizes in tetragonal structure (sp. gr. $I\ 4_1/amd$, $Z = 4$) with lattice parameters $a = 6.792$ Å and $c = 5.954$ Å [1]. The structure consists of LuO_8-polyhedral chains, linked one with another polyhedron via edges, and with other chains via vertexes, forming a three-dimensional framework. PO_4 tetrahedra strengthen the framework by binding edges and vertexes of neighboring chains of Lu polyhedra. Phosphates of this group structure possess high thermal stability and no phase transitions till the melting temperature ($T_m = 2150\,°C$). They are almost insoluble in water, non-hygroscopic and have high chemical stability.

Thermodynamic functions of $LuPO_4$ are available in the literature:

$\Delta_f H^0(298.15\,K)$ ($kJ\,mol^{-1}$) = −1945 ± 10 [2], −1936 ± 27 [3], −1886.1 [4], −1955.4 ± 4.2 [5].
$S^0(298.15\,K)$ ($J\,K^{-1}\,mol^{-1}$) = 113 [2], 98.7 ± 7.9 [3], 150.6 [4].

Enthalpy of formation from elements $\Delta_f H^0(298.15\,K)$ in [2] was calculated, while in [3–5] it was determined experimentally by Knudsen mass-spectrometry, precipitation in aqueous solutions and dissolution in melts, respectively. Values of $\Delta_f H^0(298.15\,K)$ obtained in [2,3,5] are close, while the result of Ousoubaliev et al. [4] is significantly less negative. Values of standard entropy of $LuPO_4$, evaluated in [2–4], differ one from another, and this value should be made more precise.

No data on the heat capacity of lutetium phosphate were found in literature.

2. Sample preparation

The lutetium phosphate sample was prepared by the method of precipitation from solution. Lutetium oxide (99.9 mol%) was dissolved in concentrated HNO_3 with heating (323 K). The ammonia solution was added dropwise to the solution of lutetium

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nitrate to obtain a neutral medium (pH 7–8). The Lu(OH)$_3$ was washed from nitrate-ions with distilled water by repeated washing, decantation and centrifugation. Then the calculated quantity of phosphoric acid was added to the solution with intensive mixing. The precipitate of $LuPO_4 \cdot 2H_2O$ was washed repeatedly for 12 h and the solution separated by decantation. Procedure was finished after achieving pH 7. $LuPO_4 \cdot 2H_2O$ was dried initially by heating to 373 K and then fired at 773 and 1173 K. During firing the crystallization of stable tetragonal phase of $LuPO_4$ was observed. X-ray diffraction showed no traces of other phases. Unit cell parameters of the $LuPO_4$ sample ($a = 6.784(2)$ Å and $c = 5.950(3)$ Å) were very close to reference ones (sp. gr. *I* 4(1)/*amd*, $a = 6.7920$ Å, $c = 5.9540$ Å [6]). The white powder sample with grain sizes mainly from 0.01 to 0.1 mm was used for heat capacity measurements.

3. Heat capacity measurements

For the measurement of C_p^0 of lutetium phosphate in the temperature range of $T = 6.5$–318 K a BKT-3 low-pressure adiabatic calorimeter with an automatic system of maintaining the adiabatic regime of measurements was employed. The calorimeter design and the operational procedure were similar to those in [7]. The iron–rhodium thermometer used was calibrated by IST-90. The reliability of the calorimeter operation was tested by measuring the heat capacities of special-purity copper (OSCh 11-4), standard synthetic corundum [8] and K-1 benzoic acid [9] prepared at metrological institutions of the State Standard Committee of Russian Federation. The apparatus and the measurement procedure gives C_p^0 values of substances in a condensed state with an uncertainty of not more than 2% from $T = 6$ to 10 K, 0.5% between $T = 10$ and 40 K, and within 0.2% in the range $T = 40$–340 K.

The compound (2.4550 g) was placed in a calorimetric ampoule. After evacuating, the ampoule with the substance was filled with special-purity helium as a heat-exchange gas up to a pressure of 6 kPa (at room temperature) and sealed. The measurements of C_p^0 were made between $T = 6.5$ and 318 K. One hundred thirty two experimental C_p^0 values were obtained in nine series reflecting the sequence of the heat capacity measurements (Table S1, Supplementary data). The heat capacity of compound was always about 60% of the total heat capacity of the calorimetric ampoule with substance.

The molecular mass of $LuPO_4$ was calculated with data from [9] (M.W. = 269.939 g mol^{-1}).

The experimental C_p^0 values are summarized in Table S1 (Supplementary data) and illustrated in Fig. 1.

4. Heat capacity data treatment

The experimental data were smoothed by using the ADEK equation

$$C_p^0(T) = a_0 T (C_v)^2 + n \left[\frac{1}{3} \sum_{j=1}^{3} a_j Dj \left(\frac{\theta_j}{T} \right) + a_4 E \left(\frac{\theta_E}{T} \right) + a_5 K \left(\frac{\theta_L}{T}, \frac{\theta_U}{T} \right) \right], \qquad (1)$$

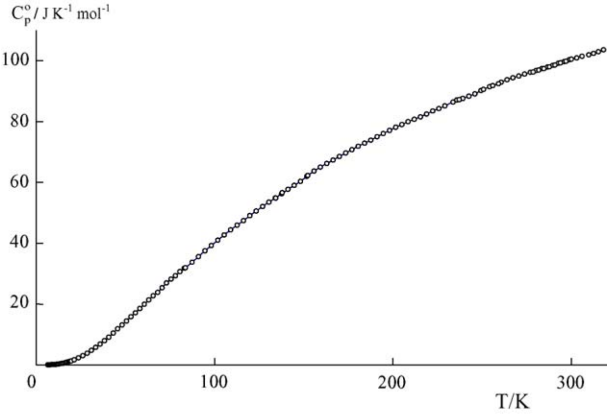

Fig. 1. Experimental C_p(T) curve of $LuPO_4$. Open circles are experimental points.

where *n* is the number of atoms in a molecule (for $LuPO_4$ $n = 6$); *D* and *E* the Debye and Einstein functions; *K* the Kieffer function [10]; θ_1, θ_2, θ_3, θ_E, θ_L, θ_U the characteristic temperatures; a_0, a_1, a_2, a_3, a_4, a_5 are linear coefficients. Equation of $C_v(T)$ is of the following type:

$$C_v = n \left[\frac{1}{3} \sum_{j=1}^{3} a_j D_j \left(\frac{\theta_j}{T} \right) + a_4 E \left(\frac{\theta_E}{T} \right) + a_5 K \left(\frac{\theta_L}{T}, \frac{\theta_U}{T} \right) \right].$$

Abbreviation ADEK implies that Eq. (1) represents the sum of $a_0\ T(C_v)^2$ term [11], three Debye, one Einstein and one K-functions. Detailed description of D-, E-, K-functions summation for Eq. (1) and its application for approximation of $C_p^0(T)$ dependence are given in [11,12]. Values of $a_0, \ldots, a_5, \theta_1, \ldots, \theta_U$ parameters (Table S2, Supplementary data) were determined by nonlinear LSM [13].

Eq. (1) was used for the calculation of heat capacity, entropy and enthalpy change in the temperature range 0–320 K (Table S3, Supplementary data). Standard thermodynamic functions at 298.15 K have the following values:

$C_p^0(298.15\ \text{K}) = 100.0 \pm 0.1\ \text{J K}^{-1}\ \text{mol}^{-1}$,
$S^0(298.15\ \text{K}) = 99.74 \pm 0.32\ \text{J K}^{-1}\ \text{mol}^{-1}$,
$H^0(298.15\ \text{K}) - H^0(0\ \text{K}) = 16.43 \pm 0.02\ \text{kJ mol}^{-1}$.

Errors of the heat capacity, entropy and enthalpy change calculation were evaluated by the procedure described in [14]. Deviations of the experimental $C_p^0(T)$ values from the smoothed ones in the range 6.51–318.03 K are presented in Fig. 2.

DSC study of $LuPO_4$ confirms the absence of phase transition up to 1973 K. Using Eq. (1) the extrapolation of $C_p^0(T)$ dependence up to 1000 K was made. Earlier we verified the efficiency of this equation for extrapolating to a high temperature

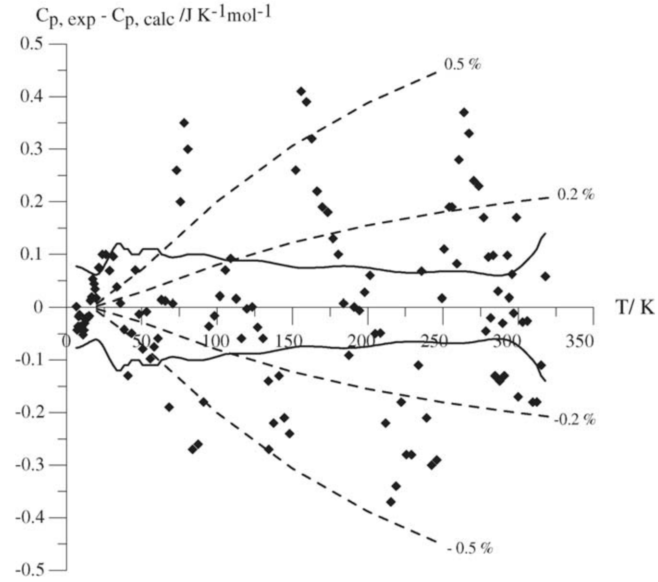

Fig. 2. Uncertainties and deviations of experimental C_p^0 values from fitting curve. Black circles correspond to deviations of experimental points from the fitting curve (1) in range 6.51–318.03 K (base line). Dashed lines correspond to 0.2 and 0.5% of $((C_{p,\text{exp}}-C_{p,\text{calc}})/C_{p,\text{calc}}) \times 100\%$ areas. Solid lines show $\pm 2\sigma$ interval calculated at the 95% confidence level.

region. The extrapolated thermodynamic functions are listed in Table S4 (Supplementary data).

5. Gibbs free energy of LuPO$_4$ formation from elements $\Delta_f G^0$(298.15 K)

The standard Gibbs free energy of LuPO$_4$ formation from elements $\Delta_f G^0(298.15\,\text{K}) = -1835.4 \pm 4.2\,\text{kJ mol}^{-1}$ was estimated with our standard entropy value $S^0(298.15\,\text{K}) = 99.74 \pm 0.32\,\text{J K}^{-1}\,\text{mol}^{-1}$ and the value of formation enthalpy $\Delta_f H^0(\text{LuPO}_4,\ 298.15\,\text{K}) = -1955.4 \pm 4.2\,\text{kJ mol}^{-1}$ [5,15] which is most reliable. Standard entropies of Lu, P, O$_2$ (51.17 ± 0.13, 41.086 ± 0.083 and $205.036 \pm 0.033\,\text{J K}^{-1}$ mol^{-1}, respectively) were taken from [16]. Table S5 (Supplementary data) lists the values of thermodynamic functions recommended for LuPO$_4$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.05.019.

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