



Review

Thermodynamics of PrPO₄ whiskers

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ABSTRACT

The heat capacity of PrPO₄ whiskers, up to 1000–1500 nm in length and 45 ± 15 nm in diameter, was measured in the temperature range 1.93–1173.2 K. The heat capacity was measured by three methods: in the low temperature region by relaxation and adiabatic methods, and in the high temperature region by the DSC method. Based on the data obtained, values of thermodynamic functions were calculated. The heat capacity of a PrPO₄ sample with isometric particles was measured in the range 325.2–1173.2 K. A comparative analysis of the thermodynamic data and IR spectra for samples with different particle habits was carried out. The influence of morphology on the enthalpy and entropy contributions to the total energy of the system was estimated. According to these data, the predominance of the entropy contribution raises the thermodynamic stability of the PrPO₄ structure with whisker particles as the temperature rises.

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1. Introduction

Interest in rare earth orthophosphates is explained by a combination of functional properties with high chemical stability [1], poor solubility in water ($pK_{AP} = 26.06 \pm 0.18$) [2] and high melting points [3]. These properties of rare earth phosphates have been the objective of experimental thermodynamic investigations of pure materials [4,5] as well as REPO₄ solid solutions [6–8]. Praseodymium belongs to the group of light lanthanides whose

orthophosphates are characterized by a monazite monoclinic structure (sp. gr. P2₁/c) [9].

The variety of synthesis methods makes it possible to obtain orthophosphates of lanthanides with different structure, size and shape of particles [10]. At the same time, particle morphology is one of the key parameters affecting the physical and mechanical properties of compounds, and therefore their practical application [11]. An unusual form of whiskers is interesting not only from the point of view of studying the mechanism of its formation, but also because of its specific characteristics. Thus, whiskers are ten times stronger than ordinary crystals, and they exhibit amazing flexibility, corrosion resistance and crystallographic anisotropy of

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properties, which makes any new research in this field very relevant. In this paper, an attempt is made to evaluate the influence of morphology on the thermodynamic characteristics of praseodymium orthophosphate, over a wide range of temperatures.

The low-temperature heat capacity of praseodymium orthophosphate with isometric particles has been experimentally studied on a single crystal [6] and a polycrystalline sample [12]. The temperature dependencies of the PrPO_4 heat capacity are a good agreement in these studies. Meanwhile, for the high-temperature range, there have been only estimated calculated data on $C_p(T)$ dependence [4], presented in equation form:

$$C_p(T)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 124.4998 + 30.3743 \cdot 10^{-3} \cdot (T/\text{K}) - 2.4495 \cdot 10^6 \cdot (T/\text{K})^{-2}, \quad (1)$$

Information on the experimental study of the heat capacity or enthalpy of this compound in the region above 350 K has not been found in the literature.

Earlier, we published an article [10] with the results of work on the synthesis of well-formed lanthanide orthophosphate whiskers with a monazite structure not containing hydrated and surface adsorbed water.

This work focuses on obtaining temperature dependence of the heat capacity, calculating the thermodynamic functions of PrPO_4 whiskers in the temperature range 3–1173 K and performing a comparative analysis of thermodynamic and spectral characteristics of samples with the same structure and chemical composition but with different particle morphology. In order to evaluate the influence of particle shape on the thermodynamic characteristics of praseodymium orthophosphate it is necessary to have reliable data on the heat capacity of isometric PrPO_4 . Therefore, praseodymium orthophosphate with isometric particles (henceforth – *s-PrPO*₄) was also synthesized, and its heat capacity was measured in the high-temperature region.

2. Experimental details

2.1. Synthesis and characterization of samples

As initial reagents for preparation of the praseodymium orthophosphate, we used Pr_6O_{11} oxide, ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, 34.68% hydrochloric acid (HCl) and distilled water. All the initial reagents had the qualification “highly purified materials” and did not require further purification (Table 1). A crystalline sample of the praseodymium orthophosphate with isometric particles (*s-PrPO*₄) was obtained by precipitation from a solution, according to the procedure described in [13]. This method was used earlier for the synthesis the bulk PrPO_4 [12]. In turn, a crystal sample with whisker particles (*w-PrPO*₄) was obtained using the hydrothermal synthesis method at 473 K and 55 h described in [10].

The phase purity was determined using a Bruker Advance D8 diffractometer ($\text{CuK}\alpha = 1.5418 \text{ \AA}$, reflection geometry, $2\Theta = 10\text{--}60^\circ$, pitch 0.02). X-ray patterns indicated single-phase samples, and they had sufficiently clear resolution of all reflections, indicating a high degree of crystallinity of both samples with a monazite structure (Supporting information, Fig. S1). Parameters of a unit

cell were determined using the TOPAS 4.2 program. The calculated unit cell parameters of both samples are in good agreement with the literature data for the polycrystalline sample [12] and were somewhat larger than for single crystal [9].

The size and habit of particles obtained were determined by scanning electron microscopy (SEM), with a Cross Beam Zeiss NVision 40 device ($U = 1 \text{ kV}$) (Fig. 1).

The characteristics obtained are summarized in Table 2.

The absence of adsorbed water was confirmed by thermogravimetric analysis (TGA), using thermoscales (sensitivity $0.025 \mu\text{g}$) of the synchronous thermal analyzer STA 449F1 Jupiter (Netzsch) when heating in the temperature range 300–1273 K (Supporting information, Fig. S2).

IR spectra of praseodymium phosphates were recorded in the range $4000\text{--}550 \text{ cm}^{-1}$, using the Nexus-Nicolet FTIR spectrophotometer on a diamond crystal from PIKE. In Fig. 2, there are no peaks in the region $3600\text{--}3000 \text{ cm}^{-1}$ corresponding to stretching vibrations of adsorbed and crystallized water, and a characteristic band of $\sim 1670 \text{ cm}^{-1}$ of deformation vibrations H–O–H, and bands of vibrations of CO_3 groups at ~ 1450 and 1420 cm^{-1} , and an intense line at $\sim 745 \text{ cm}^{-1}$, related to symmetric P–O–P oscillations in diphosphates. This confirms the data of thermogravimetric and XRD analyzes on single-phase compounds, and also confirms the absence of impurities of carbonate, crystallohydrated and adsorbed water in the samples.

In the monoclinic monazite structure (sp. gr. $\text{P2}_1/\text{c}$, $Z = 4$), the symmetry of tetrahedrons PO_4 decreased to C_1 [14], corresponding to complete removal of degeneracy of internal vibrations of PO_4 groups and activity of all modes in IR spectra. Wave numbers (in cm^{-1}) of absorption bands recorded in IR spectra, and their attribution to the vibrations of the phosphate anion, are presented below, and shown in Fig. 2:

*s-PrPO*₄: 1090 (F_2, ν_3), 1007 (F_2, ν_3), 990 (F_2, ν_3), 954 (A_1, ν_1) – stretching vibrations PO_4 ; 613 (F_2, ν_4), 577 (F_2, ν_4), 560 (F_2, ν_4) – deformation vibrations PO_4 .

*w-PrPO*₄: 1090 (F_2, ν_3), 1058, 1021 (F_2, ν_3), 993 (F_2, ν_3), 956 (A_1, ν_1) – stretching vibrations PO_4 ; 612 (F_2, ν_4), 582 (F_2, ν_4), 567 (F_2, ν_4) – deformation vibrations PO_4 .

Deformation vibrations E_2 of the PO_4 group which occur at $\nu_2 \sim 400 \text{ cm}^{-1}$ are not recorded, as they exceed measurement limits.

2.2. Heat capacity measurements

Heat capacity of *w-PrPO*₄ in the low-temperature region was measured by relaxation and adiabatic methods. Measurements of the heat capacity at the lowest temperature (1.93–29.86 K) were performed with a PPMS-9 Quantum Design device [15]. For the purpose of measurement, the powder was compressed with a hydraulic press. The mass of the studied sample was 0.03139 g. The accuracy of the PPMS heat capacity measurements is within $\pm 5\%$.

In the temperature range 25.79–339.79 K, the heat capacity of *w-PrPO*₄ was measured with a low-temperature adiabatic calorimeter BKT-3 designed and manufactured at AOZT Termis [16]. The sample was placed in a thin-walled titanium cylindrical container with an internal volume of 1 cm^3 . The container was

Table 1
Characterization of chemical samples used in this study.

Chemical name	Chemical formula	Source	State	Mass fraction purity	Purity analysis method
Praseodymium oxide	Pr_6O_{11}	Chimmed, Russia	Powder	>0.99	as stated by the supplier
Ammonium dihydrogenphosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	Chimmed, Russia	Powder	>0.99	as stated by the supplier
Hydrochloric acid	HCl	Chimmed, Russia	Liquid	>0.98	as stated by the supplier
Praseodymium orthophosphate	<i>s-PrPO</i> ₄	Synthesized	Powder	>0.99	XRD, TGA, ATR-IR
Praseodymium orthophosphate	<i>w-PrPO</i> ₄	Synthesized	Powder	>0.98	XRD, TGA, ATR-IR

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