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Use of high-temperature differential scanning calorimetry to investigate the β–α transition in calcium pyrophosphate

Susan Jacob · Melodie L. Schmitt · Mark E. Schlesinger

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Abstract High-temperature differential scanning calorimetry was used to investigate the thermodynamic parameters of the γ–β and β–α transitions in calcium pyrophosphate ($Ca_2P_2O_7$). The measured enthalpy of transition compared well with previous results when higher heating rates ($\geq$20 K min^{-1}) were used. Recommendations for optimal use of HTDSC in high-temperature phase transition measurements are presented.

Keywords Thermal analysis · Calcium pyrophosphate · Enthalpy of transformation · HTDSC

Introduction

Introduced in the late 1980s, high-temperature differential scanning calorimetry (HTDSC) is a promising technique for performing thermodynamic and kinetic measurements at temperatures above the 1,000 K limit of traditional DSC [1–3]. The reliability and reproducibility of HTDSC measurements has not been well documented, especially under real world conditions. The research described here was performed to determine the experimental conditions under which HTDSC generates the most reliable results and to determine what impact changing experimental conditions, such as sample mass, heating rate, and the choice of standard and cover gas, have on measured parameters. Previous investigations looked at the use of HTDSC to measure the heat capacity of platinum and the melting point and enthalpy of fusion of silver [4, 5]. The present study of a high-temperature solid-state transformation was the final type of change of state used to assess HTDSC.

The high-temperature polymorphism of calcium pyrophosphate ($Ca_2P_2O_7$) has been well known for over a half-century [6–9]. $Ca_2P_2O_7$ is stable in the tetragonal β structure at lower temperatures but transforms to the orthorhombic α structure at temperatures above ~1,413 K, and is an ideal material to study using HTDSC.

Experimental

The calcium pyrophosphate used for this investigation was reagent-grade, 98% purity $Ca_2P_2O_7$ purchased from Alfa Aesar. X-ray diffraction (XRD) analysis of the as-received material showed that it was present as the γ structure (Fig. 1). Although the γ structure is not thought to be the standard state of $Ca_2P_2O_7$, it is the allotrope commonly formed by the dehydration of monetite ($CaHPO_4$) [10]. Phase identification was completed using the JCPDS database and PDF card numbers 09-0345, 33-0297, and 17-0499 for α-, β- and γ-$Ca_2P_2O_7$, respectively.

The HTDSC used in this investigation was a Netzsch 409 simultaneous thermal analyzer. This plate-type heat-flux DSC [3] measures thermal response based on the difference in temperature of a sample chamber containing the crucible with the material under investigation and that of a reference chamber heated at the same rate. The calibration procedure for the instrument is a three-step process that starts with a baseline trace performed on an empty crucible [11], followed by a trace performed on the same crucible containing a reference standard. The third trace measures the thermal response of the crucible containing the sample material. Sample heat capacities are determined

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S. Jacob · M. L. Schmitt · M. E. Schlesinger (✉)
Department of Materials Science and Engineering, Missouri University of Science and Technology, 1400 N. Bishop Ave., Rolla, MO 65409-0340, USA
e-mail: mes@mst.edu

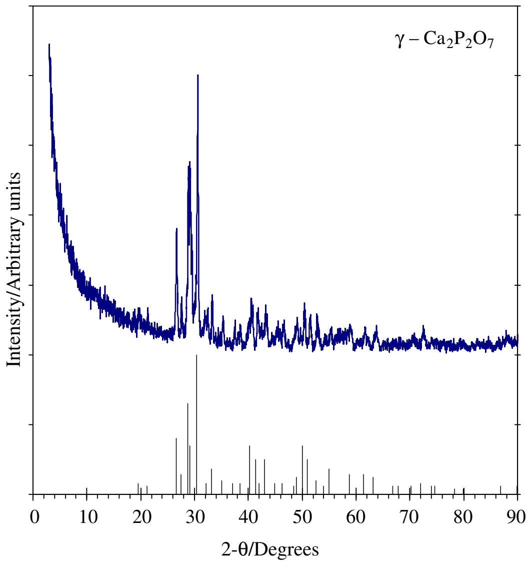

Fig. 1 X-ray diffraction pattern for as-received $Ca_2P_2O_7$, showing a pattern which matches that of the γ-$Ca_2P_2O_7$ phase

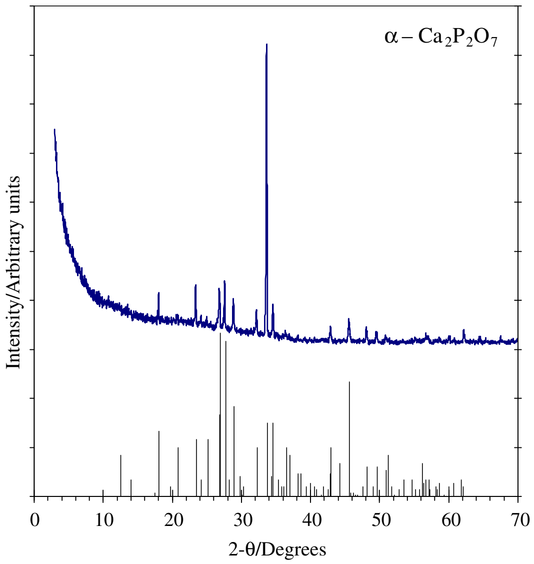

Fig. 2 X-ray diffraction pattern for $Ca_2P_2O_7$ obtained after a DSC run, showing a pattern which matches the main peak positions of the α-$Ca_2P_2O_7$ phase

using the ratio method; the enthalpies of changes of state are calculated from the area under reaction or transformation peaks. A more complete description is provided by Blumm and Kaisersberger [3].

For the experiments described here, $Ca_2P_2O_7$ samples with masses of roughly 50 mg were tested in alumina crucibles using heating rates of 10, 20 and 30 K min^{-1}. Use of heating rates above 30 K min^{-1} is discouraged by the instrument manufacturer. A single baseline and reference trace were made at each heating rate using a 0.5 mm sapphire standard, followed by four traces at the same heating rate using the pyrophosphate. Air was chosen as the cover gas to provide a non-reducing atmosphere and prevent the reduction of phosphate. XRD of the cooled samples showed that they remain in the α structure rather than reverting to β or γ (Fig. 2), and thus it was necessary to replace the $Ca_2P_2O_7$ sample after each trace. These results confirm the sluggish α–β transformation suggested by Monma [9]. It should be noted that the small sample size used in post-heat treatment XRD measurements and possible texturing upon heating resulted in XRD patterns with peak intensity ratios which are not consistent with respect to the reference pattern. Although this result suggests slightly oriented grains, all major peak positions remain consistent between the sample and the reference patterns, corroborating phase identification.

Results and discussion

Figure 3 shows the four HTDSC traces for $Ca_2P_2O_7$ at a heating rate of 30 K min^{-1}. The small exothermic peak observed between 1,100 and 1,200 K represents the conversion of the as-received γ allotrope to β and occurs at a temperature higher than the 773–1,023 K transformation range suggested in the literature [8, 10]. The large endothermic peak observed between 1,400 and 1,500 K represents the β–α transition. Figures 4 and 5 show the results of traces using heating rates of 20 and 10 K min^{-1}, respectively.

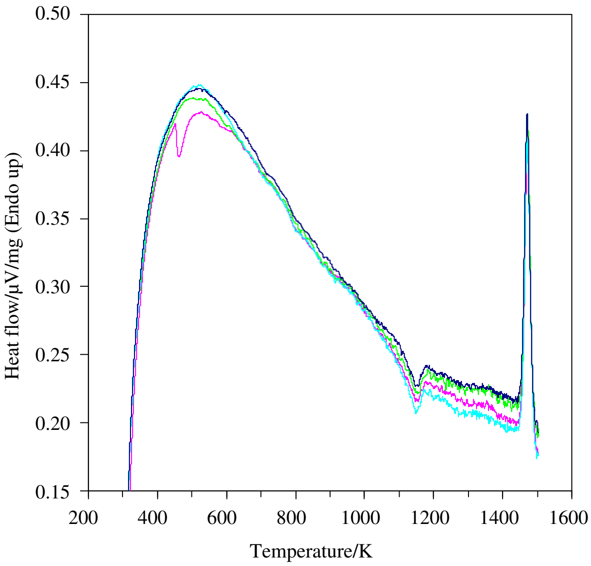

Fig. 3 HTDSC traces for $Ca_2P_2O_7$ at a heating rate of 30 K min^{-1}

Table 1 lists the average transformation temperature and enthalpy of transformation for both peaks at each heating rate. The ability to accurately denote peak limits for

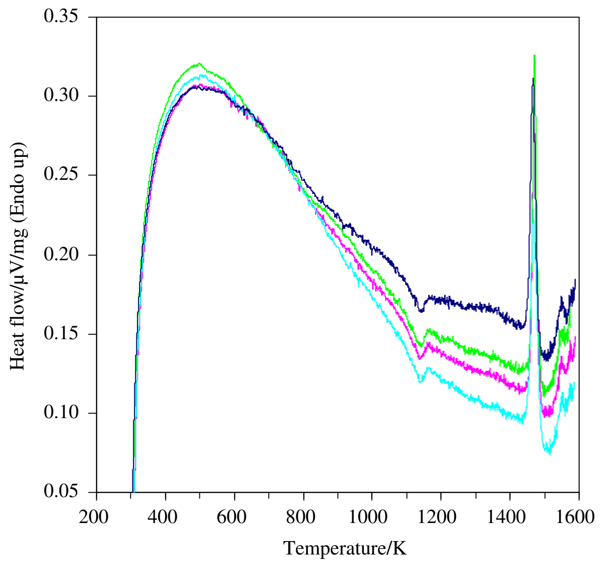

Fig. 4 HTDSC traces for $Ca_2P_2O_7$ at a heating rate of 20 K min^{-1}

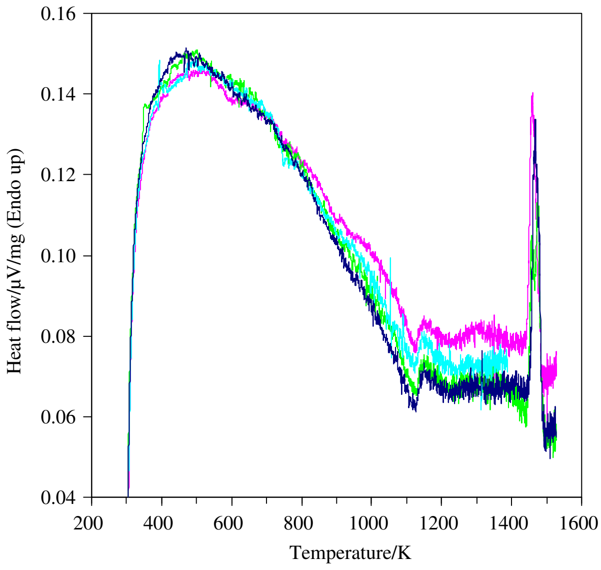

Fig. 5 HTDSC traces for $Ca_2P_2O_7$ at a heating rate of 10 K min^{-1}

measuring enthalpies of transition and to mark peak onset temperatures was complicated by the increased noise at lower heating rates. This increased difficulty can be seen in the corresponding increase in uncertainty of enthalpy values. The reduced level of uncertainty at higher heating rates agrees with results of previous measurements of the heat capacity of platinum using HTDSC [5]. The average measured enthalpies of transformation are substantially greater at 10 K min^{-1} than at higher heating rates. The only previously reported value for the enthalpy of transformation was determined using drop calorimetry by Egan and Wakefield (6,786 J mol^{-1}) [7], which agrees within the experimental uncertainty with that determined in this study at a heating rate of 20 K min^{-1}.

The values reported here for the β–α transition onset temperature (1,430–1,440 K) are slightly higher than those previously reported, which range between 1,408 and 1,438 K [6–9]. The measured onset temperature appears to be a function of heating rate, despite calibrating the instrument at each heating rate before analysis of the $Ca_2P_2O_7$, and is likely a result of thermal lag. This finding is even more apparent for the γ–β transition. Monma reported peak temperatures for the β–α transition of 1,464 and 1,474 K at DTA heating rates of 10 and 20 K min^{-1}, respectively [9]; average peak temperatures for the same heating rates using HTDSC were 1,462 and 1,469 K.

Summary

The use of HTDSC is relatively new and little literature exists to date on the experimental conditions under which this type of instrument is most likely to yield accurate and reproducible results. Based on the measurements reported here, some recommendations can be made:

- The choice of standard used for calibrating the instrument depends on the type of measurement to be made. If the goal is to measure the heat capacity of a substance, the heat capacity of sapphire or platinum standard should be used. If the intent is to measure temperatures and enthalpies of phase transitions, the temperature and enthalpy of a phase transition (such as the melting of silver) is a better choice. Calibrations should always be made at the same heating rate as that to be used for the sample itself.
- The choice of heating rate for a HTDSC experiment is a balancing act. Heat-flux DSC traces are impacted by thermal lag, which increases as the heating rate increases. As a result, minimizing the heating rate

Table 1 Transition temperatures and enthalpies for $Ca_2P_2O_7$

Heating rate/ K min^{-1}	γ–β		β–α		
	T_{onset}/K	ΔH/J mol^{-1}	T_{onset}/K	T_{peak}/K	ΔH/J mol^{-1}
10	1,068 ± 12	−1218.6 ± 438.1	1,430 ± 1	1,462 ± 6	8867.6 ± 503.7
20	1,074 ± 6	−882.6 ± 160.6	1,435 ± 3	1,469 ± 3	6551.4 ± 686.6
30	1,088 ± 5	−904.2 ± 39.2	1,440 ± 3	1,472 ± 2	6319.6 ± 67.1

should increase the accuracy of measurements, particularly transition temperatures. However, the increased noise at lower heating rates (compare Figs. 3 and 5) makes accurate measurement of peak temperatures and peak areas difficult to accomplish. Furthermore, the reproducibility of measurements is better at higher heating rates. Thus, the measurement of thermodynamic properties at heating rates >20 K min^{-1} is recommended.

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