Experimental determination of the high temperature heat capacity of a natural xenotime-(Y) solid solution and synthetic $DyPO_4$ and $ErPO_4$ endmembers

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MANUSCRIPT REVISION 2

To be submitted to Thermochimica Acta

Gysi, A.P., Harlov, D., Costa, D., Williams-Jones, A.E., 2016a. Experimental determination of the high temperature heat capacity of a natural xenotime-(Y) solid solution and synthetic DyPO4 and ErPO4 endmembers. Thermochim Acta 627, 61-67. DOI:10.1016/j.tca.2016.01.016.

ABSTRACT

The heat capacity of natural xenotime-(Y) and synthetic $DyPO_4$ and $ErPO_4$ crystals was determined by differential scanning calorimetry (DSC) at temperatures of 298.15 K to 868.15 K and a pressure of 0.1 MPa. The aim of the study was to develop a method to accurately measure the isobaric heat capacity (C_P) of rare earth element (REE) phosphates, compare the results to data from adiabatic calorimetric experiments, and evaluate the deviation from ideality of the C_P of the natural xenotime-(Y) solid solution. The measured C_P data (in J mol^{-1} K^{-1}) can be described by the relationships: 185.5-751.9T$^{-0.5}$-3.261e+06 T^{-2} for $DyPO_4$; 207.2-1661T$^{-0.5}$-5.289e+05 T^{-2} for $ErPO_4$; and 208-1241T$^{-0.5}$-2.493e+06 T^{-2} for xenotime-(Y); where T is the temperature in K. The heat capacity data for natural xenotime-(Y) were used to determine the excess function for the solid solution, which yields an excess heat capacity ranging between 7.9 and 10.7 %, well within the range of the DSC method used in this study. The experiments indicate that xenotime-(Y) forms a non-ideal solid solution. Future DSC studies will provide important data for developing a solid solution model for the incorporation of REE in xenotime-(Y).

KEYWORDS: REE phosphates; xenotime-(Y); heat capacity; DSC experiments; calorimetry

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1. Introduction

Xenotime-(Y) is the main heavy rare earth element (HREE) mineral in a variety of geological settings and the principal ore mineral in many heavy (H)REE mineral deposits, e.g., those at Browns Range (hydrothermal) in Australia (Cook et al., 2013). It is also useful for dating geological processes and determining temperature (Andrehs and Heinrich, 1998; Gratz and Heinrich, 1997; Heinrich et al., 1997). A knowledge of the thermodynamic properties of xenotime-(Y) will increase our understanding of the relationships between its composition and conditions prevailing in the Earth's crust, and permit quantitative modeling of the processes of HREE concentration.

Xenotime-(Y) has a tetragonal structure and incorporates variable proportions of HREE (i.e., Tb, Dy, Ho, Er, Tm, Yb and Lu) by forming solid solutions with the YPO_4 endmember, the latter being commonly the dominant HREE in natural xenotime. In contrast, the light (L)REE are mainly incorporated in monazite-(Ce), which has a monoclinic structure (Ni et al., 1995). The heat capacity of most HREE phosphate endmembers (i.e., YPO_4, $TbPO_4$, $ErPO_4$, $YbPO_4$ and $LuPO_4$) has been determined in adiabatic calorimetric experiments (Gavrichev et al., 2013a, 2013b, 2012, 2010, 2006). However, the heat capacity for the endmember $DyPO_4$ has not yet been determined. Furthermore, very few experimental data are available on the thermodynamic properties of REE phosphate solid solutions. Despite the similar ionic radii of the REE, calorimetric experiments on binary solid solutions of monazite-(La) with both Nd and Gd have shown that the LREE phosphates may form non-ideal solid solutions (Popa et al., 2007). No experimental data are currently available to establish whether xenotime-(Y) solid solutions are ideal or non-ideal.

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In this study, we used differential scanning calorimetry to determine the heat capacity of synthetic $ErPO_4$, $DyPO_4$ and a natural xenotime-(Y) solid solution for temperatures between 298.15 K and 868.15 K. We also report a new DSC method for calibrating and measuring the heat capacity of REE phosphates, and compare our data with those previously obtained using adiabatic calorimetric methods. The measured heat capacity data for natural xenotime-(Y) were used to determine whether or not YPO_4 forms an ideal solid solution with other HREE.

2. Methods

2.1. Materials

A natural euhedral, homogeneous and inclusion-free xenotime-(Y) crystal from Novo Horizonte, Brazil, was selected for the DSC experiments (Fig. 1). The composition of the crystal was measured on an electron microprobe (Table 1) and its homogeneity verified using X-ray diffraction. The ideal formula of the analyzed crystal fragment is $Y_{0.77}Gd_{0.05}Tb_{0.01}Dy_{0.09}Ho_{0.02}Er_{0.04}Yb_{0.02}PO_4$, with other REE below the limit of detection.

[Table 1 The composition of the natural xenotime-(Y) solid solution from Novo Horizonte, Brazil.][a]

	xenotime-(Y)	σ
P_2O_5 (wt.%)	35.1	0.2
Y_2O_3	42.8	0.3
Eu_2O_3	0.44	0.04
Gd_2O_3	4.77	0.05
Tb_2O_3	1.12	0.02
Dy_2O_3	8.24	0.04
Ho_2O_3	1.84	0.04
Er_2O_3	3.63	0.04
Yb_2O_3	1.80	0.03
Total	99.7	

[a]The standard deviation of the mean is based on the analysis of 16 different spots of a crystal fragment.

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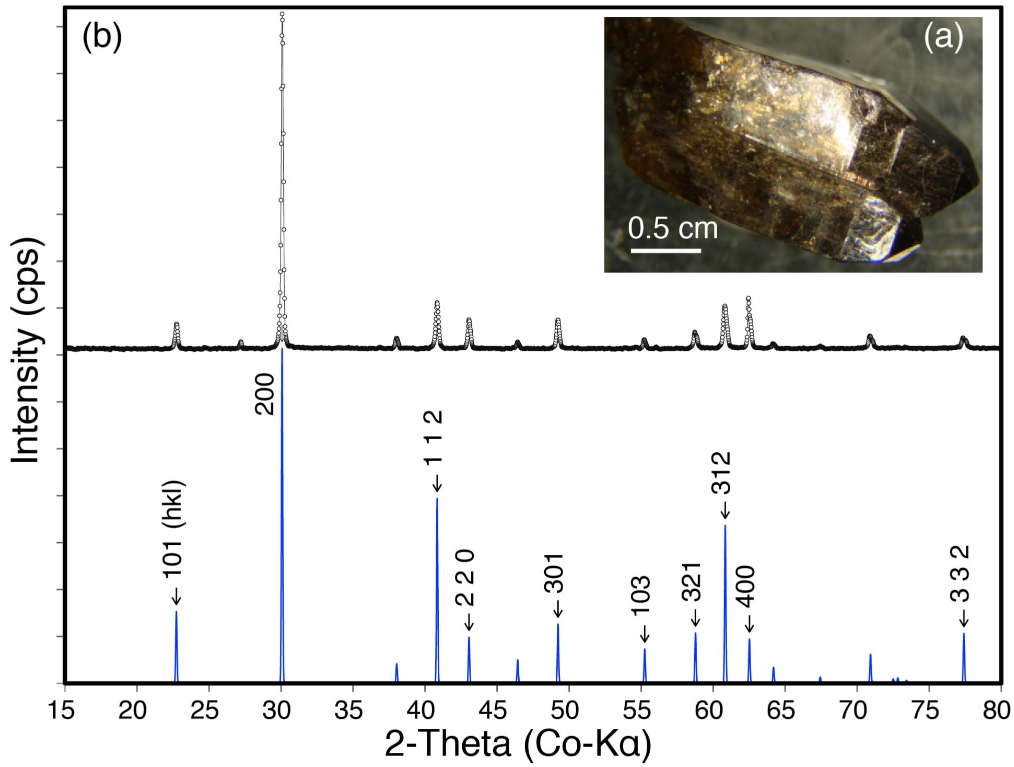

[Fig. 1. a) Photomicrograph of the natural xenotime-(Y) from Novo Horizonte. b) X-ray diffraction spectrum of the natural xenotime-(Y) and for comparison (blue) that for xenotime-(Y) from the study by Ni et al. (1995) in the American Mineralogist database (Downs and Hall-Wallace, 2003).]

Synthetic, inclusion-free crystals of pure $DyPO_4$, $ErPO_4$ and YPO_4 were prepared from melt fluxes using the method described by Cherniak et al. (2004). Each HREE phosphate was precipitated by mixing a Y, Er, or Dy nitrate solution with an ammonium hydrogen phosphate solution, which resulted in very fine YPO_4, $ErPO_4$, and $DyPO_4$ precipitates, respectively. The precipitates were then dry mixed with a $NaHCO_3$-MoO_3 25:75 flux (1 – 2 % $HREEPO_4$ precipitate per 98 % flux) and heated in a Pt crucible to 1375 °C. The molten flux was cooled from 1375 °C to 870 °C at 3 °C per hour over 6-7 days. After quenching in air, a series of gem quality, inclusion-free and chemically pure

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HREE phosphate crystals were separated by boiling the solidified flux and crystals in deionized H_2O until the crystals were freed from the flux. The chemical purity (based on the detection limits of the microprobe analysis) of the synthetic crystals was >99.9 wt. %. The natural xenotime-(Y) and synthetic HREE phosphate crystals were crushed and ground in an agate mortar to produce fine powders (<5 μm) that were placed in the sample pans for subsequent DSC experiments.

2.2. Analytical and Experimental

The DSC experiments were carried out at the Department of Geology and Geological Engineering, Colorado School of Mines, using a SDT Q600 from TA instruments, which measures the temperature difference between a sample and a reference pan heated at the same rate. The temperature difference is related directly to the heat flow (Φ in mW) by measuring the heat capacity of a known calibrant. The instrument was calibrated first for mass and temperature using the procedure recommended by the instrument supplier (www.tainstruments.com). The temperature was calibrated using ceramic (alumina) pans and the melting point of pure metal standards (Sn, In, Pb, Zn and Au). This calibration was also used to determine a cell constant based on the known heat of fusion for Sn. The sample pans employed in the experiments were made of aluminum (Al pans), and therefore, the heat flow calibration was carried out in this pan material using a run with empty pans and a run with a sapphire disc as the calibrant. The heating rate used in the experiments was 20 K/min. Nitrogen gas with a flow rate of 100 ml/min was continuously flushed through the sample chamber. The isobaric heat capacity was derived from the heat flow signal (Φ in mW) using the relationship,

$$C_P = \frac{\Theta 60 M_w}{\beta m_{sample}}$$

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(Eq. 1)

with m_{sample} the sample mass in mg, M_w the molar weight in g mol^{-1}, and β the heat flow in K min^{-1}.

The heat capacity experiments on REE phosphates were performed between 298.15 and 868.15 K at 0.1 MPa using the heat ramping conditions reported above. Samples of powdered solid with masses ranging between 10 and 20 mg were sealed in Al pans with crimped lids to ensure homogeneous dispersion of the powders across the bottom of the pans. Calibration was performed using the method described by Gysi and Williams-Jones (2015). This involved comparing the final corrected heat flow signal for the solid of interest to that for a solid of similar structure and composition for which the heat capacity is known. Each experiment comprised a run with empty pans for background signal subtraction, a run with a powder of synthetic YPO_4 as the calibrant, and a run with the REE phosphate of interest. The heat flow signal was converted to heat capacity and the data compared to the values obtained by low temperature adiabatic and high temperature drop calorimetry (Gavrichev et al., 2010). By comparing the C_P data from this study ($C_{P,analyzed}$) with data from the literature ($C_{P,theoretical}$), a correction factor was determined for each temperature from the relationship:

$$E = \frac{C_{P,analyzed}}{C_{P,theoretical}}$$

(Eq. 2)

Once the correction factor had been determined, an experiment was carried out with $ErPO_4$, for which the heat capacity is known and the results compared with the published adiabatic drop calorimetric data (Gavrichev et al., 2012). The comparison was used to test the accuracy of the DSC method and the correction procedure. This set of experiments was followed by experiments with solids, for which the heat capacity is unknown (i.e.,

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$DyPO_4$ and the natural xenotime-(Y) solid solution). The precision of each analysis was determined by running repeated experiments and by calculating the standard deviation of the mean for all experiments.

Electron microprobe (EMP) analysis was carried out at the Department of Earth and Planetary Sciences, McGill University, using a JEOL JXA-8900. The analytical conditions were a 5 µm beam size, a beam current of 30 nA and an acceleration voltage of 20 kV. Natural standards were used for P (Flap) and synthetic glass standards for REE (MAC standards from Mico-analysis consultants Ltd.). Counting times were 50s for Y and 70s for Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu and 20 s for P. Based on the counting statistics of repeated standard analyses, the detection limits were 0.05-0.07 wt.% for the REE and 0.03 wt.% for P. X-ray diffraction analyses were performed using a Bruker D5000 Diffractometer and Co-Kα radiation for a 2θ range between 15° and 80° scanned in 0.02° steps.

3. Results and discussion

The measured C_P values for $ErPO_4$, $DyPO_4$ and natural xenotime-(Y) between 348.15 and 868.15 K are listed in Table 2, the experimental fitting parameters in Table 3 and the fitted data in Table 4. Experimental data for temperatures below 348.15 K were not used in the fits as the DSC technique did not yield reliable signals at low temperature. Experimental values were extrapolated to 298.15 K using the polynomial of Berman and Brown (1985). The C_P values for $ErPO_4$ measured using DSC are in excellent agreement with the adiabatic calorimetric values of Gavrichev et al. (2010) (Fig. 2). The new calibration method for the STD Q600 DSC instrument yields an accuracy between 2 and 4 % based on the comparison of our measured values for $ErPO_4$ (Table 2) to the values of

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Gavrichev et al. (2010). From repeated analysis of $ErPO_4$, $DyPO_4$ and xenotime-(Y), the analytical precision of the DSC instrument for measuring the heat capacity of mineral powders was determined to vary between 1 and 6 % depending on the temperature. The new C_P data for $DyPO_4$ are shown in Figure 2; the C_P values are higher than those for $ErPO_4$. The C_P function for the natural xenotime-(Y) solid solution plots above the C_P data for the pure YPO_4 endmember, and above those for $DyPO_4$ and $ErPO_4$. The fitted C_P functions were used to determine the temperature dependence of their enthalpy according to the relationship,

$$H_T - H_{298.15K} = \int C_P dT \qquad \text{(Eq. 3)}$$

The calculated H_T-$H_{298.15K}$ values are listed in Table 4.

Results of our experiments for $DyPO_4$ and $ErPO_4$ are compared with published calorimetric data for other HREE phosphates (i.e., $TbPO_4$, $YbPO_4$, $LuPO_4$ and YPO_4) in Figure 3. Inspection of the extrapolated values for $DyPO_4$ and $ErPO_4$ to 298.15 K, reveals that the fits for these two species approach but do not intersect each other. This behavior is similar to that of other HREE phosphates, the fits of which approach each other at low temperature but generally do not intersect. The extrapolated C_P values for $DyPO_4$ and $ErPO_4$ are greater than the C_P values for $LuPO_4$, which is expected because all magnetic REE phosphates with the xenotime structure are predicted to have a heat capacity greater than that of $LuPO_4$ (i.e., $DyPO_4$ and $ErPO_4$ exhibit a Schottky anomaly), the latter being diamagnetic (Gavrichev et al. 2012).

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Table 2. Measured C_p values for $ErPO_4$, $DyPO_4$ and xenotime-(Y) at temperatures between 348.15 and 868.15 K and a pressure of 0.1 MPa, with standard uncertainties $u(C_P)$ given in J mol^{-1} K^{-1}.[a]

Mineral T (K)	$ErPO_4$ C_P^0 (J mol^{-1}K^{-1})	$u(C_P)$	$DyPO_4$ C_P^0 (J mol^{-1}K^{-1})	$u(C_P)$	xenotime-(Y) C_P (J mol^{-1}K^{-1})	$u(C_P)$
348.15	113.7	5.0	117.5	7.6	121.2	3.6
353.15	114.5	4.7	119.1	7.3	122.3	3.7
358.15	115.2	4.7	120.4	7.1	123.2	3.9
363.15	115.9	4.8	121.5	7.0	124.1	4.1
368.15	116.4	5.1	122.5	6.9	124.9	4.3
373.15	116.8	5.5	123.3	7.0	125.7	4.6
378.15	117.4	5.8	124.1	7.1	126.5	4.8
383.15	118.1	6.0	124.9	7.2	127.3	5.0
388.15	119.1	5.9	125.7	7.2	128.1	5.1
393.15	119.9	5.8	126.4	7.2	129.0	5.1
398.15	120.7	5.7	127.3	7.2	129.8	5.1
403.15	121.5	5.5	128.1	7.2	130.7	5.0
408.15	122.2	5.5	128.9	7.2	131.5	5.0
413.15	122.9	5.5	129.6	7.2	132.3	5.0
418.15	123.5	5.5	130.4	7.2	133.1	5.0
423.15	124.0	5.6	131.0	7.2	133.8	5.1
428.15	124.5	5.7	131.7	7.3	134.5	5.2
433.15	125.0	5.8	132.3	7.4	135.2	5.2
438.15	125.4	6.0	132.8	7.5	135.8	5.3
443.15	125.9	6.0	133.4	7.6	136.5	5.3
448.15	126.4	6.1	133.9	7.7	137.1	5.3
453.15	126.9	6.1	134.5	7.7	137.7	5.3
458.15	127.4	6.2	135.0	7.8	138.3	5.2
463.15	127.8	6.2	135.5	7.8	138.9	5.1
468.15	128.2	6.3	136.1	7.8	139.4	5.0
473.15	128.7	6.3	136.6	7.8	140.0	4.9
478.15	129.1	6.3	137.0	7.8	140.5	4.8
483.15	129.5	6.3	137.4	7.7	141.1	4.7
488.15	129.9	6.3	137.9	7.7	141.6	4.7
493.15	130.3	6.4	138.3	7.7	142.1	4.6
498.15	130.7	6.4	138.7	7.7	142.6	4.7
503.15	131.1	6.4	139.1	7.7	143.1	4.7
508.15	131.5	6.5	139.5	7.6	143.6	4.6
513.15	132.0	6.4	139.9	7.6	144.0	4.6
518.15	132.4	6.4	140.3	7.6	144.5	4.5
523.15	132.8	6.4	140.7	7.6	145.0	4.5
528.15	133.2	6.2	141.0	7.5	145.4	4.5
533.15	133.6	6.2	141.3	7.6	145.8	4.4
538.15	134.0	6.2	141.6	7.6	146.2	4.3
543.15	134.5	6.1	142.0	7.6	146.5	4.3
548.15	134.8	6.1	142.4	7.6	146.9	4.2
553.15	135.1	6.1	142.7	7.6	147.4	4.1
558.15	135.4	6.0	143.0	7.6	147.8	4.0
563.15	135.8	5.9	143.4	7.7	148.2	3.9
568.15	136.1	5.9	143.7	7.7	148.6	3.8

[a]The standard uncertainty $u(C_P)$ represents the standard deviation of the mean, based on repeated experiments (four runs for $ErPO_4$, three for $DyPO_4$ and three for xenotime-(Y)). The superscript "0" was only used for C_P values of the pure phases. u(T) = 0.5 K.

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Table 2 (Continued)

Mineral	$ErPO_4$		$DyPO_4$		xenotime-(Y)	
T	C_P^0	$u(C_P)$	C_P^0	$u(C_P)$	C_P	$u(C_P)$
(K)	(J mol^{-1}K^{-1})		(J mol^{-1}K^{-1})		(J mol^{-1}K^{-1})	
573.15	136.3	5.9	143.9	7.7	149.0	3.7
578.15	136.6	5.8	144.3	7.8	149.3	3.5
583.15	136.9	5.8	144.6	7.8	149.7	3.4
588.15	137.2	5.8	144.8	7.9	150.0	3.3
593.15	137.5	5.9	145.1	7.9	150.3	3.1
598.15	137.8	5.9	145.3	7.9	150.5	3.0
603.15	138.0	5.9	145.6	7.9	150.7	2.8
608.15	138.3	6.0	145.9	8.0	151.0	2.6
613.15	138.6	6.0	146.1	8.0	151.1	2.5
618.15	138.8	6.0	146.4	8.1	151.3	2.3
623.15	139.0	6.0	146.7	8.0	151.5	2.1
628.15	139.3	6.0	147.0	8.1	151.7	2.0
633.15	139.6	5.9	147.3	8.2	151.9	1.9
638.15	139.8	5.9	147.5	8.2	152.2	1.8
643.15	140.1	5.8	147.8	8.2	152.5	1.9
648.15	140.3	5.8	148.0	8.2	152.8	2.0
653.15	140.6	5.6	148.2	8.1	153.1	2.0
658.15	140.9	5.5	148.5	8.0	153.5	2.0
663.15	141.2	5.4	148.8	7.9	153.8	1.9
668.15	141.4	5.2	149.1	7.8	154.1	1.9
673.15	141.6	5.1	149.3	7.7	154.5	2.0
678.15	141.8	4.9	149.6	7.5	154.8	2.0
683.15	142.1	4.8	149.9	7.5	155.0	2.1
688.15	142.3	4.6	150.1	7.4	155.4	2.2
693.15	142.6	4.5	150.4	7.3	155.7	2.2
698.15	142.9	4.3	150.7	7.1	156.0	2.3
703.15	143.1	4.1	150.9	7.0	156.3	2.3
708.15	143.5	4.0	151.1	6.9	156.5	2.4
713.15	143.7	3.9	151.4	6.8	156.7	2.4
718.15	143.9	3.8	151.6	6.7	156.9	2.4
723.15	144.2	3.7	151.8	6.6	157.1	2.5
728.15	144.4	3.6	152.0	6.5	157.3	2.5
733.15	144.6	3.6	152.1	6.4	157.6	2.5
738.15	144.8	3.6	152.3	6.2	157.8	2.6
743.15	145.0	3.6	152.5	6.1	158.1	2.8
748.15	145.2	3.6	152.7	6.1	158.2	2.9
753.15	145.5	3.5	152.9	6.0	158.4	3.0
758.15	145.8	3.4	152.9	5.9	158.5	3.1
763.15	146.1	3.3	153.1	5.9	158.6	3.3
768.15	146.3	3.2	153.3	5.8	158.6	3.4
773.15	146.5	3.1	153.4	5.9	158.8	3.6
778.15	146.8	3.0	153.4	5.8	158.9	3.8
783.15	147.0	2.9	153.6	5.7	159.0	3.9
788.15	147.2	2.8	153.5	5.8	159.2	4.1
793.15	147.5	2.6	153.7	5.8	159.5	4.3
798.15	147.8	2.5	153.8	5.7	159.8	4.6
803.15	148.0	2.4	154.0	5.7	160.1	4.8

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Table 2 (Continued)

Mineral T (K)	$ErPO_4$ C_P^0 (J mol^{-1}K^{-1})	$u(C_P)$	$DyPO_4$ C_P^0 (J mol^{-1}K^{-1})	$u(C_P)$	xenotime-(Y) C_P (J mol^{-1}K^{-1})	$u(C_P)$
808.15	148.2	2.3	154.1	5.7	160.5	5.0
813.15	148.5	2.3	154.2	5.7	160.8	5.2
818.15	148.7	2.2	154.3	5.7	161.2	5.5
823.15	148.9	2.2	154.4	5.8	161.4	5.7
828.15	149.1	2.1	154.5	5.8	161.6	5.8
833.15	149.3	2.1	154.5	5.9	161.9	6.1
838.15	149.5	2.1	154.6	6.0	162.2	6.2
843.15	149.7	2.0	154.8	6.0	162.5	6.4
848.15	149.9	1.9	154.9	6.1	162.7	6.5
853.15	150.2	2.0	154.9	6.4	162.7	6.4
858.15	150.3	2.0	155.0	6.5	162.9	6.5
863.15	150.5	2.0	155.1	6.8	163.0	6.7
868.15	150.8	2.1	155.2	7.0	163.0	6.7

Table 3 Fitting parameters for the heat capacity function and standard thermodynamic properties of $ErPO_4$, $DyPO_4$ and xenotime-(Y).[a]

	C_P(T in K)= a+bT$^{-0.5}$+cT^{-2}						
	a	b	c ×10^{-6}	R^2	$\Delta_f H^0_{298.15\,K}$	$S^0_{298.15\,K}$	$\Delta_f G^0_{298.15\,K}$
$ErPO_4$	207.2 ±2.0	-1661 ±64	-0.529 ±0.192	0.9990	-1954.1[b]	116.6[c]	-1832.5[b]
$DyPO_4$	185.5 ±1.7	-751.9 ±53.2	-3.261 ±0.160	0.9993	-1950.6[b]	119.0[d]	-1829.1[b]
xenotime-(Y)	208.0 ±2.0	-1241 ±64	-2.493 ±0.192	0.9992	-	-	-

[a]Uncertainties on the coefficients a-c are within a 95 % confidence limit. [b] Derived from the solubility study of Gysi et al. (2015).[c]Gavrichev et al. (2012).[d]Estimated by linear interpolation.

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Table 4. Calculated C_p values and integrated enthalpy increments (H_T-$H_{298.15\ K}$) for $ErPO_4$, $DyPO_4$ and xenotime-(Y) between 298.15 K and 868.15 K at 0.1 MPa. The fitting parameters are listed in Table 3.

Mineral	$ErPO_4$			$DyPO_4$			xenotime-(Y)		
T (K)	C_P^0 (J mol^{-1}K^{-1})	± [a]	H_T-$H_{298.15K}$ (J mol^{-1})	C_P^0 (J mol^{-1}K^{-1})	± [a]	H_T-$H_{298.15K}$ (J mol^{-1})	C_P (J mol^{-1}K^{-1})	± [a]	H_T-$H_{298.15K}$ (J mol^{-1})
298.15	105.1	0.8	0	105.3	0.7	0	108.1	0.8	0
303.15	106.1	0.8	528	106.9	0.7	530	109.7	0.8	545
308.15	107.0	0.8	1061	108.4	0.7	1068	111.1	0.8	1096
313.15	108.0	0.8	1598	109.8	0.6	1614	112.5	0.8	1656
318.15	108.9	0.7	2140	111.2	0.6	2166	113.9	0.7	2222
323.15	109.8	0.7	2687	112.5	0.6	2725	115.2	0.7	2794
328.15	110.6	0.7	3238	113.7	0.6	3291	116.4	0.7	3373
333.15	111.5	0.7	3793	115.0	0.6	3863	117.6	0.7	3958
338.15	112.3	0.7	4352	116.1	0.6	4440	118.8	0.7	4549
343.15	113.1	0.7	4916	117.2	0.6	5024	119.9	0.7	5146
348.15	113.8	0.7	5483	118.3	0.6	5613	121.0	0.7	5748
353.15	114.6	0.7	6054	119.4	0.6	6207	122.0	0.7	6355
358.15	115.3	0.7	6629	120.4	0.6	6806	123.1	0.7	6968
363.15	116.1	0.7	7208	121.3	0.6	7411	124.0	0.7	7586
368.15	116.8	0.7	7790	122.3	0.6	8020	125.0	0.7	8208
373.15	117.4	0.7	8375	123.2	0.5	8633	125.9	0.7	8836
378.15	118.1	0.7	8964	124.1	0.5	9251	126.8	0.7	9468
383.15	118.8	0.7	9556	124.9	0.5	9874	127.7	0.7	10104
388.15	119.4	0.7	10152	125.7	0.5	10500	128.5	0.7	10744
393.15	120.0	0.6	10750	126.5	0.5	11131	129.3	0.7	11389
398.15	120.6	0.6	11352	127.3	0.5	11766	130.1	0.6	12038
403.15	121.2	0.6	11957	128.0	0.5	12404	130.9	0.6	12690
408.15	121.8	0.6	12564	128.7	0.5	13046	131.7	0.6	13347
413.15	122.4	0.6	13175	129.4	0.5	13691	132.4	0.6	14007
418.15	123.0	0.6	13788	130.1	0.5	14340	133.1	0.6	14671
423.15	123.5	0.6	14405	130.8	0.5	14992	133.8	0.6	15338
428.15	124.1	0.6	15024	131.4	0.5	15647	134.5	0.6	16009
433.15	124.6	0.6	15645	132.0	0.5	16306	135.1	0.6	16683
438.15	125.1	0.6	16270	132.6	0.5	16968	135.8	0.6	17360
443.15	125.6	0.6	16896	133.2	0.5	17632	136.4	0.6	18041
448.15	126.1	0.6	17526	133.8	0.5	18300	137.0	0.6	18724
453.15	126.6	0.6	18158	134.3	0.5	18970	137.6	0.6	19411
458.15	127.1	0.6	18792	134.9	0.5	19643	138.2	0.6	20100
463.15	127.6	0.6	19429	135.4	0.5	20319	138.8	0.6	20793
468.15	128.0	0.6	20068	135.9	0.5	20997	139.3	0.6	21488
473.15	128.5	0.6	20709	136.4	0.5	21677	139.9	0.6	22186
478.15	129.0	0.6	21353	136.9	0.5	22361	140.4	0.6	22887
483.15	129.4	0.6	21999	137.4	0.5	23046	140.9	0.6	23590
488.15	129.8	0.6	22647	137.8	0.5	23734	141.4	0.6	24296
493.15	130.3	0.6	23297	138.3	0.5	24424	141.9	0.6	25004
498.15	130.7	0.6	23949	138.7	0.5	25117	142.4	0.6	25715
503.15	131.1	0.6	24604	139.1	0.5	25811	142.9	0.6	26429
508.15	131.5	0.6	25260	139.5	0.5	26508	143.4	0.6	27144
513.15	131.9	0.6	25919	140.0	0.5	27207	143.8	0.6	27862
518.15	132.3	0.6	26579	140.3	0.5	27907	144.3	0.6	28582

[a]The uncertainties (±) are based on the 95% prediction limits of the corresponding fitted C_P function through the means of the experimental data listed in Table 2.

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Table 4. (Continued)

Mineral	$ErPO_4$			$DyPO_4$			xenotime-(Y)		
T (K)	C_P^0 (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})	C_P^0 (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})	C_P (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})
523.15	132.7	0.6	27241	140.7	0.5	28610	144.7	0.6	29305
528.15	133.1	0.6	27906	141.1	0.5	29315	145.1	0.6	30029
533.15	133.4	0.6	28572	141.5	0.5	30021	145.5	0.6	30756
538.15	133.8	0.6	29240	141.9	0.5	30730	146.0	0.6	31484
543.15	134.2	0.6	29910	142.2	0.5	31440	146.4	0.6	32215
548.15	134.5	0.6	30582	142.6	0.5	32152	146.8	0.6	32948
553.15	134.9	0.6	31255	142.9	0.5	32865	147.1	0.6	33683
558.15	135.2	0.6	31930	143.2	0.5	33581	147.5	0.6	34419
563.15	135.6	0.6	32607	143.6	0.5	34298	147.9	0.6	35158
568.15	135.9	0.6	33286	143.9	0.5	35016	148.3	0.6	35898
573.15	136.2	0.6	33966	144.2	0.5	35737	148.6	0.6	36641
578.15	136.6	0.6	34648	144.5	0.5	36458	149.0	0.6	37385
583.15	136.9	0.6	35332	144.8	0.5	37182	149.3	0.6	38131
588.15	137.2	0.6	36017	145.1	0.5	37906	149.7	0.6	38878
593.15	137.5	0.6	36704	145.4	0.5	38632	150.0	0.6	39627
598.15	137.8	0.6	37392	145.7	0.5	39360	150.3	0.6	40378
603.15	138.1	0.6	38082	145.9	0.5	40089	150.7	0.6	41131
608.15	138.4	0.6	38774	146.2	0.5	40820	151.0	0.6	41885
613.15	138.7	0.6	39467	146.5	0.5	41551	151.3	0.6	42641
618.15	139.0	0.6	40161	146.8	0.5	42284	151.6	0.6	43398
623.15	139.3	0.6	40857	147.0	0.5	43019	151.9	0.6	44157
628.15	139.6	0.6	41554	147.3	0.5	43755	152.2	0.6	44917
633.15	139.9	0.6	42253	147.5	0.5	44491	152.5	0.6	45679
638.15	140.2	0.6	42953	147.8	0.5	45230	152.8	0.6	46442
643.15	140.4	0.6	43655	148.0	0.5	45969	153.1	0.6	47207
648.15	140.7	0.6	44358	148.2	0.5	46710	153.4	0.6	47973
653.15	141.0	0.6	45062	148.5	0.5	47451	153.7	0.6	48741
658.15	141.3	0.6	45768	148.7	0.5	48194	153.9	0.6	49510
663.15	141.5	0.6	46474	148.9	0.5	48938	154.2	0.6	50280
668.15	141.8	0.6	47183	149.1	0.5	49683	154.5	0.6	51052
673.15	142.0	0.6	47892	149.3	0.5	50429	154.7	0.6	51825
678.15	142.3	0.6	48603	149.6	0.5	51177	155.0	0.6	52599
683.15	142.5	0.6	49315	149.8	0.5	51925	155.2	0.6	53375
688.15	142.8	0.6	50028	150.0	0.5	52674	155.5	0.6	54151
693.15	143.0	0.6	50743	150.2	0.5	53425	155.7	0.6	54929
698.15	143.3	0.6	51459	150.4	0.5	54176	156.0	0.6	55709
703.15	143.5	0.6	52176	150.6	0.5	54929	156.2	0.6	56489
708.15	143.8	0.6	52894	150.8	0.5	55682	156.4	0.6	57271
713.15	144.0	0.6	53613	151.0	0.5	56436	156.7	0.6	58054
718.15	144.2	0.6	54334	151.1	0.5	57192	156.9	0.6	58838
723.15	144.4	0.6	55055	151.3	0.5	57948	157.1	0.6	59623
728.15	144.7	0.6	55778	151.5	0.5	58705	157.4	0.6	60409
733.15	144.9	0.6	56502	151.7	0.5	59463	157.6	0.6	61196
738.15	145.1	0.6	57227	151.9	0.5	60222	157.8	0.6	61985
743.15	145.3	0.6	57953	152.0	0.5	60982	158.0	0.6	62774

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Table 4. (Continued)

Mineral	$ErPO_4$			$DyPO_4$			xenotime-(Y)		
T (K)	C_P^0 (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})	C_P^0 (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})	C_P (J mol^{-1}K^{-1})	±	H_T-$H_{298.15K}$ (J mol^{-1})
748.15	145.6	0.6	58680	152.2	0.5	61742	158.2	0.6	63565
753.15	145.8	0.6	59409	152.4	0.5	62504	158.4	0.6	64357
758.15	146.0	0.6	60138	152.5	0.5	63266	158.6	0.6	65149
763.15	146.2	0.6	60869	152.7	0.5	64029	158.9	0.6	65943
768.15	146.4	0.6	61600	152.9	0.5	64793	159.1	0.6	66738
773.15	146.6	0.6	62333	153.0	0.5	65558	159.3	0.6	67534
778.15	146.8	0.6	63066	153.2	0.5	66323	159.5	0.6	68331
783.15	147.0	0.6	63801	153.3	0.5	67090	159.6	0.6	69128
788.15	147.2	0.6	64536	153.5	0.5	67857	159.8	0.6	69927
793.15	147.4	0.6	65273	153.6	0.5	68625	160.0	0.6	70727
798.15	147.6	0.6	66010	153.8	0.5	69393	160.2	0.6	71527
803.15	147.8	0.6	66749	153.9	0.5	70163	160.4	0.6	72329
808.15	148.0	0.6	67488	154.1	0.5	70933	160.6	0.6	73131
813.15	148.2	0.6	68228	154.2	0.5	71703	160.8	0.6	73935
818.15	148.4	0.6	68970	154.4	0.5	72475	160.9	0.6	74739
823.15	148.5	0.6	69712	154.5	0.5	73247	161.1	0.6	75544
828.15	148.7	0.6	70455	154.6	0.5	74020	161.3	0.6	76350
833.15	148.9	0.6	71199	154.8	0.5	74794	161.5	0.7	77157
838.15	149.1	0.6	71944	154.9	0.5	75568	161.6	0.7	77965
843.15	149.3	0.6	72690	155.0	0.5	76343	161.8	0.7	78773
848.15	149.5	0.7	73437	155.2	0.5	77118	162.0	0.7	79583
853.15	149.6	0.7	74185	155.3	0.5	77894	162.1	0.7	80393
858.15	149.8	0.7	74933	155.4	0.5	78671	162.3	0.7	81204
863.15	150.0	0.7	75683	155.6	0.5	79449	162.5	0.7	82016
868.15	150.1	0.7	76433.2	155.7	0.5	80226.8	162.6	0.7	82829

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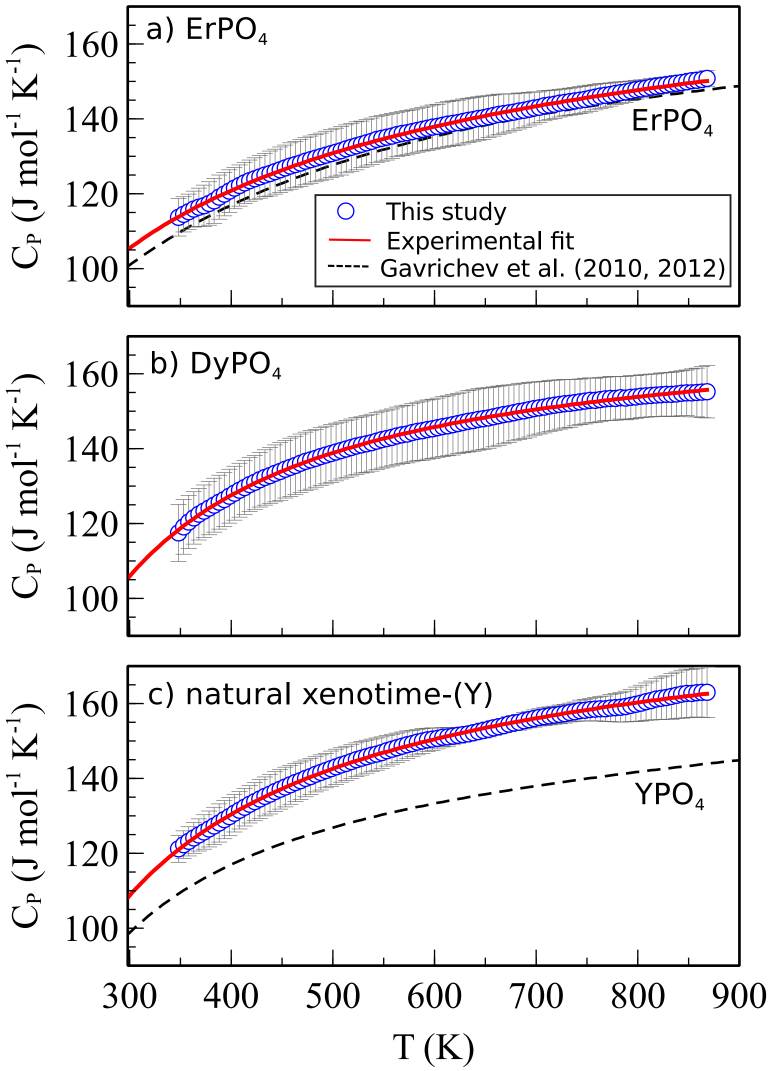

[Fig. 2. The measured C_P data and experimental fits for $ErPO_4$, $DyPO_4$ and natural xenotime-(Y) as a function of temperature (in K). The grey bars indicate the standard deviation of the mean from multiple measurements. Experimental values are listed in Table 2 and fitting parameters in Table 3.]

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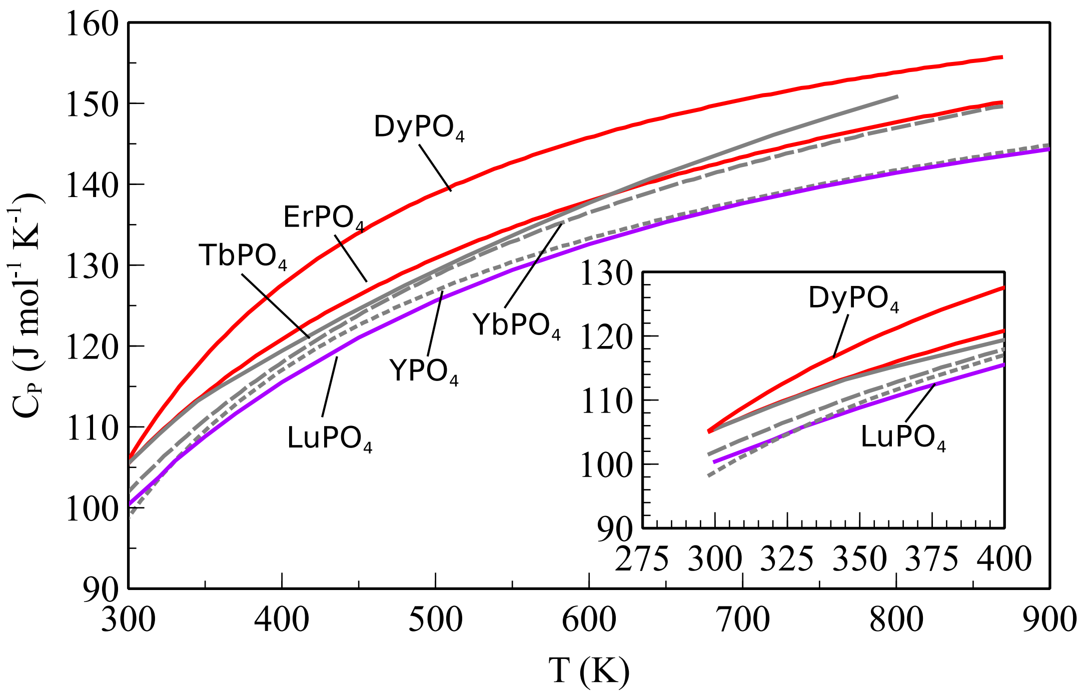

[Fig. 3. Comparison of our fitted C_P data for $ErPO_4$ and $DyPO_4$ with adiabatic calorimetric data for other HREE phosphates. $YbPO_4$ from Gavrichev et al. (2013a); $TbPO_4$ from Gavrichev et al. (2013b); YPO_4 from Gavrichev et al. (2010); $LuPO_4$ from Gavrichev et al. (2006).]

The heat capacity for a hypothetical ideal solid solution was calculated from a linear combination of the C^0_P data for using the mole fraction of the REE phosphate endmembers and the composition of the natural xenotime-(Y) solid solution (Table 1),

$$C_{P,ideal\ ss} = \sum X_i C^0_{P,i} \qquad \text{(Eq. 4)}$$

with $C^0_{P,i}$ the heat capacity data for the ith endmember, X_i its mole fraction in the mineral formula and $C_{P,ideal\ ss}$ the heat capacity of the ideal solid solution. Using this calculated heat capacity function and our measured C_P values for xenotime-(Y), we determined the excess heat capacity ($C_{P,excess}$) due to non-ideal mixing from the relationship

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$$C_{P,excess} = C_{P,xenotime-(Y)} - C_{P,ss\ ideal} \qquad \text{(Eq. 5)}$$

As there are currently no high temperature C_P data available for $HoPO_4$, and it is only a minor component in the mineral formula (apfu ≤0.02), we used a simplified composition for determining the heat capacity of the ideal solution ($Y_{0.79}Gd_{0.05}Dy_{0.09}Tb_{0.01}Er_{0.04}Yb_{0.02}PO_4$). The C_P data for these calculations were taken from the present study for the $DyPO_4$ and $ErPO_4$ endmembers, and from Gavrichev et al., (2013a, 2013b, 2010), Gurevich et al. (2012), and Popa et al. (2006) for the $GdPO_4$, YPO_4, $TbPO_4$ and $YbPO_4$ endmembers. It has to be noted here that Equation 4 applies to isostructural endmembers, but as data for $GdPO_4$ are currently only available for the monoclinic (monazite structure) endmember, these data were used in the calculations. This is justified by results of a study of a $Gd(VO_4)_{0.5}(PO_4)_{0.5}$ solid solution predicting that the heat capacity of the tetragonal (xenotime structure) $GdPO_4$ endmember is only slightly lower than that of the monoclinic endmember (Kritskaya et al., 2015). Our experimental fit of C_P for xenotime-(Y) is compared to that for the calculated ideal solid solution in Figure 4. The calculated excess C_P values for xenotime-(Y) are between 7.9 and 10.7 % of the fitted experimental values, and therefore well above the limit of precision for the DSC method. Although, the ionic radii of the different REE are similar (e.g., 1.019Å for Y and 1.027Å for Dy), the calculated excess function indicates that xenotime-(Y) forms a non-ideal solid solution when incorporating different proportions of other REE in its crystal lattice. The same conclusion was reached for monazite by Popa et al. (2007), who found that binary solid solutions of LREE have significant excess values for enthalpy. However, the excess values for xenotime-(Y) observed in our study increase with temperature, whereas those for monazite-(Ce) decrease with temperature.

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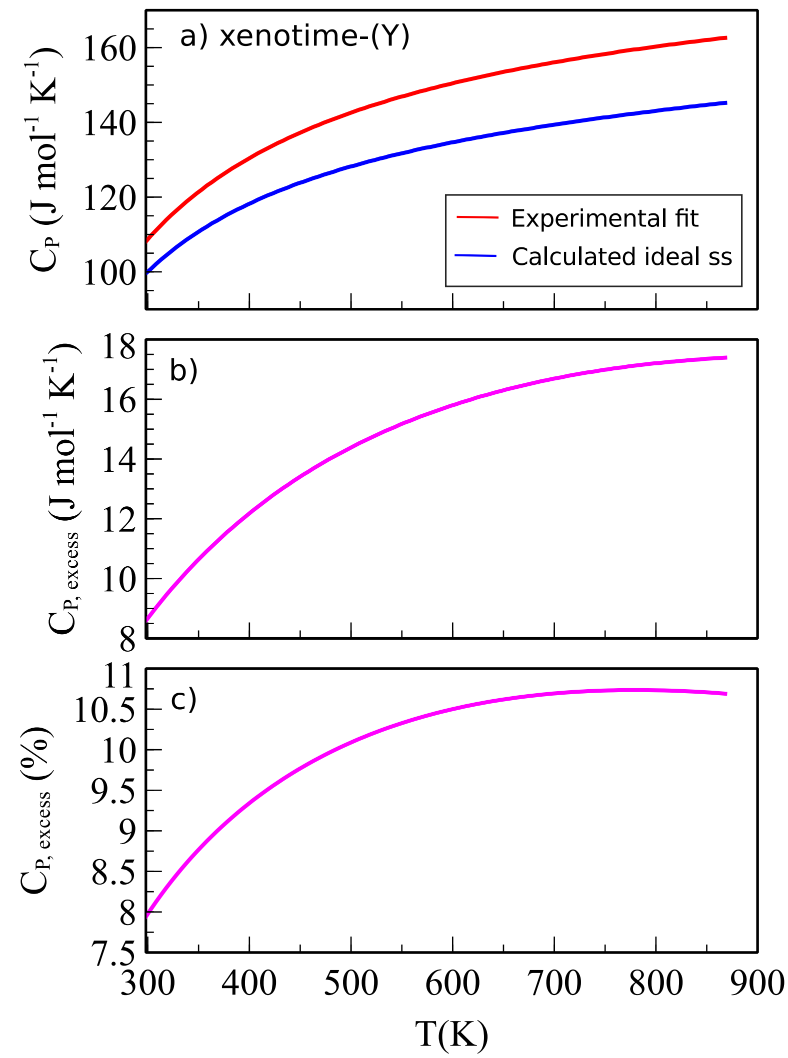

[Fig. 4. a) Comparison of the C_P functions for xenotime-(Y) from our experimental fit and the calculated ideal solid solution (Eq. 4). b-c) Calculated excess heat capacity for xenotime-(Y) (Eq. 5).]

4. Conclusions

We have measured the C_P functions for the $DyPO_4$ and $ErPO_4$ endmembers, and a natural xenotime-(Y) solid solution using a DSC. The new data allow us to model the stability of tetragonal REE phosphate minerals using our measured C_P data for $DyPO_4$. The resulting

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data provide evidence for non-ideal mixing in xenotime-(Y) solid solutions. The calculated excess C_P function is above the precision limit for the DSC method, and indicates that the DSC method yields a fast and reliable method of data acquisition for the study of REE phosphate solid solutions. Future DSC studies of the heat capacity of binary and ternary solid solutions, combined with measurements of the enthalpy of mixing made using other calorimetric methods, will aid in the construction of a solid solution model of REE incorporation in natural xenotime-(Y) solid solutions.

Acknowledgement

This study was supported by the Colorado School of Mines with a professional development grant to A. P. Gysi and by a Brazil Scientific Mobility Program Scholarship from the U. of Brasilia to D.C. Filho. This manuscript benefited significantly from the constructive comments of two anonymous reviewers.

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