

The high temperature behavior of barium zirconium diorthophosphate

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Abstract

Barium zirconium diorthophosphate $\text{BaZr}(\text{PO}_4)_2$ was synthesised and its high temperature behavior was studied. At room temperature the compound was found to have a monoclinic structure, in agreement with earlier literature reports. A monoclinic-to-hexagonal phase transition at about 733 K was found by differential thermal analysis; this transition was confirmed by X-ray diffraction and drop calorimetry.

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1. Introduction

Phosphates are promising ceramic host materials for the conditioning of separated actinides that are produced in the nuclear fuel cycle. In particular monazite, of which the idealised formula is LnPO_4 , can incorporate significant amounts of Th and U, as is known from mineralogical studies [1,2]. The incorporation of these tetravalent actinides is characterised by the substitution reaction:



This substitution thus yields $\text{CaAn}(\text{PO}_4)_2$, known as the mineral brabantite, as the end-member of the pseudo-binary. Trivalent actinides can substitute on the Ln site of monazite. The resulting solid solutions $\text{Ca}_x\text{An}_x^{\text{IV}}\text{Ln}_{2-2x-y}\text{An}_y^{\text{III}}(\text{PO}_4)_2$ of monazite-like (monoclinic) structure would thus be very suited to host separated Am and Cm, which will contain Np and Pu as decay products.

Since minerals of the monazite-brabantite series show extremely high durability and good resistance to internal

radiation [3,4], we have started a detailed study of various synthetic end-members and their solid solutions [5,6]. An interesting aspect to be studied is an alternative for the above-mentioned substitution reaction, based on zirconium instead of thorium. The monoclinic $\text{M}^{\text{II}}\text{Zr}(\text{PO}_4)_2$ compounds could to be a feasible alternative for $\text{CaTh}(\text{PO}_4)_2$, resulting $\text{M}_x^{\text{II}}\text{Zr}_x\text{Ce}_{2-2x}(\text{PO}_4)_2$ monazite-like compounds.

The compounds $\text{M}^{\text{II}}\text{Zr}(\text{PO}_4)_2$ with $\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}$ and Ba have all been reported in literature [7–11]. $\text{CaZr}(\text{PO}_4)_2$ is tetragonal and monoclinic [10], $\text{SrZr}(\text{PO}_4)_2$ has a monoclinic yavapaiite structure that is somewhat different from monazite and undergoes a transition to a hexagonal structure at 1196 K [11]. Although $\text{BaZr}(\text{PO}_4)_2$ was characterised a long time ago [7,12] only the low temperature phase with yavapaiite structure was reported.

The goal of the present study is to elucidate the high temperature behavior of $\text{BaZr}(\text{PO}_4)_2$ and especially the stability of the yavapaiite structure, for which we used X-ray diffraction, differential thermal analysis and drop calorimetry.

2. Experimental

$\text{BaZr}(\text{PO}_4)_2$ was synthesised by grinding and reacting of BaCO_3 , ZrO_2 (equimolar quantities) and $(\text{NH}_4)_2\text{HPO}_4$ (25% excess) in an alumina crucible. All the chemicals were

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reagent-grade and were purchased from Merck. To obtain the pure compound, different attempts were made in air (with a ramp of 100 K h^{-1}) at temperatures between 1373 [7] and 1473 K, for 5–100 h. We found the optimum synthesis temperature 1473 K with 100 h as reaction time. For smaller temperatures and shorter reaction times ZrO_2 , ZrP_2O_7 and/or $\text{Ba}_3(\text{PO}_4)_2$ were detected as impurities.

The sample purity and its crystal structure were characterised by X-ray powder diffraction data (Cu $\text{K}\alpha_1$ radiation) collected on a Bragg-Brentano Siemens D8 diffractometer, equipped with a PSD detector; the count step was 0.0071° (2θ), the dwell time 1 s step^{-1} and total acquisition time 24 h. The sample environment was controlled using a Anton Paar chamber HTK2000, equipped with the Pt filament. The measurements were made from room temperature to 1073 K in vacuum atmosphere using a staircase heating procedure (with a initial holding time of 3 h). The diffraction patterns were refined by a Rietveld-type method using the Fullprof program [13].

The thermal behavior was investigated by differential thermal analysis (Netsch STA 449C Jupiter) in alumina crucibles in an air atmosphere up to 1023 K. The temperature was controlled by a Pt–PtRh (10%) thermocouple. The applied heating and cooling rates were 10 and 20 K min^{-1} , respectively.

For the drop calorimetric experiments pellets of $\text{BaZr}(\text{PO}_4)_2$ were made by sintering of the powder for 24 h at 1673 K. The pellets were cut into pieces with masses of 80–90 mg. Platinum metal rods were used as reference material, and the sample and reference were ordered alternatively in the feeding chamber and equilibrated at ambient temperature. The heat contents corresponding to the enthalpy increments from ambient temperature to the respective temperature of a given run were determined using a Setaram Multi-detector High Temperature Calorimeter (MHTC-96) operating in drop mode, using an air atmosphere for the detector chamber. The working procedure and temperature calibration were described previously by Sedmidubský et al. [14].

3. Results and discussion

3.1. X-ray diffraction

In agreement with Masse and Durif [7], the crystal structure at low temperature (Fig. 1a) was refined using the mono-

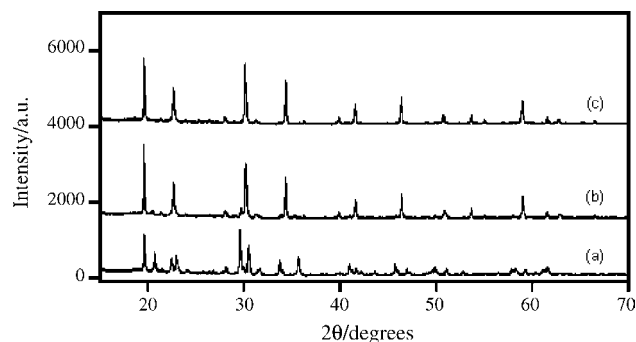


Fig. 1. The X-ray diffraction patterns of the $\text{BaZr}(\text{PO}_4)_2$ phase at 298 K (a), 973 K (b) and 1023 K (c).

clinic structure type of $\text{KFe}(\text{SO}_4)_2$ (space group C_12/m_1) [15] reported in the literature [7,12] with the lattice parameters shown in Table 1. One can notice that only the a lattice parameter is significantly higher than the values reported previously. The refined parameters were the intensities, the sample displacement, the lattice parameters, the shape parameters, the peaks width, the correction of the asymmetry and the atomic positions.

The crystal structure of the low temperature phase of $\text{BaZr}(\text{PO}_4)_2$ corresponds to zirconium in octahedral coordination with oxygen atoms from six separate phosphate groups. The zirconium phosphate octahedra belong to two different sheets. Barium ions, located between the layers, are 10-coordinated to phosphate oxygen atoms.

The in situ X-ray patterns recorded during heating revealed that the monoclinic structure begins to change at about 750 K; nevertheless, the transformation is not achieved instantly. Between 750 and 973 K the two phases coexist; in fact, in the 813–893 K interval we were capable to refine the two corresponding patterns and to estimate the cell parameters in this domain of coexistence; nevertheless, since the overlapping between the two patterns is significant, the calculated values may be less reliable. Even at 998 K there still are traces of the initial structure and only at 1023 K the high temperature structure is entirely adopted.

The X-ray diffraction pattern of the high temperature phase (Fig. 1b) was refined via a profile matching mode (LeBail method) to a hexagonal unit cell, as reported by Fukuda et al. for $\text{SrZr}(\text{PO}_4)_2$ [11]. Several space groups (hexagonal as well as trigonal) could explain the pattern; finally, the choice of $P6/mmm$ gave us the most convenient fit, with a χ^2 of 2.29. The lattice parameters of the high tem-

Table 1
Crystal data of the low temperature phase (at 300 K) of $\text{BaZr}(\text{PO}_4)_2$

a (nm)	b (nm)	c (nm)	β ($^\circ$)	V (nm^3)	D_x (g cm^{-3})	Reference
0.85706(8)	0.53032(9)	0.78868(3)	92.99(1)	0.3579(8)	3.88	Present work
0.8531	0.5295	0.7875	93.08	0.3550	3.91 ^a	Masse and Durif [7]
0.8525	0.5284	0.7874	93.12	0.3542 ^a	3.92 ^a	Paques-Ledent [12]

^a Calculated from the lattice parameters.

Table 2
The lattice parameters as function of temperature (with an averaged standard deviation less of 1×10^{-4})

Temperature (K)	Monoclinic phase					Hexagonal phase		
	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	β (°)	<i>V</i> (nm ³)	<i>a</i> (nm)	<i>c</i> (nm)	<i>V</i> (nm ³)
300	0.8570	0.5303	0.7886	92.9911	0.3579			
373	0.8577	0.5301	0.7888	92.9354	0.3582			
473	0.8592	0.5299	0.7892	92.8346	0.3589			
573	0.8617	0.5297	0.7895	92.6843	0.3600			
673	0.8633	0.5294	0.7897	92.5644	0.3606			
693	0.8646	0.5293	0.7898	92.4918	0.3611			
713	0.8657	0.5294	0.7899	92.4516	0.3619			
733	0.8671	0.5296	0.7903	92.4254	0.3627			
753	0.8677	0.5299	0.7905	92.3713	0.3632			
773	0.8683	0.5300	0.7908	92.3087	0.3637			
793	0.8683	0.5300	0.7907	92.2601	0.3636			
813	0.8683	0.5300	0.7898	92.3864	0.3635	0.5206	0.7837	0.3680
833	0.8676	0.5299	0.7879	92.4181	0.3618	0.5201	0.7813	0.3661
873	0.8667	0.5299	0.7869	92.3508	0.3611	0.5202	0.7811	0.3661
893	0.8658	0.5297	0.7872	92.2958	0.3608	0.5203	0.7811	0.3662
913						0.5203	0.7812	0.3664
933						0.5203	0.7814	0.3667
953						0.5204	0.7816	0.3667
998						0.5205	0.7817	0.3668
1023						0.5206	0.7821	0.3671
1073						0.5206	0.7825	0.3673

perature phase are $a = 0.52059(8)$ nm and $c = 0.78255(0)$ nm at 1073 K and the cell volume is $V = 0.3673(3)$ nm³ (Table 2).

The variation of the lattice parameters with temperature is shown in Figs. 2 and 3 for monoclinic and hexagonal phases, respectively. For the monoclinic phase, the *a* parameter regularly increases, *b*, *c* remain constant and β decreases from the room temperature until 700 K. The cell volume follows

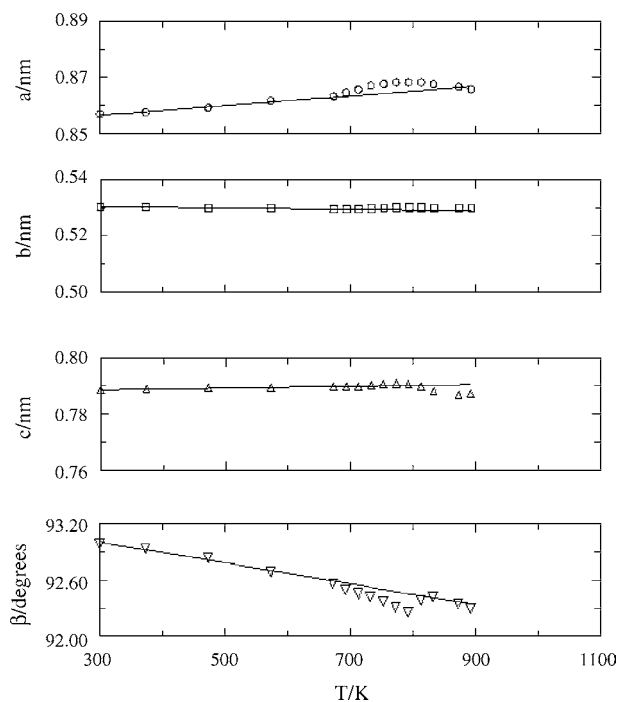


Fig. 2. Variation of cell parameters of the monoclinic phase of BaZr(PO₄)₂ with temperature; the line shows the linear fit of the results below 700 K.

the trend of the *a* parameter, that strongly increases during the heating up (~1%). From 730 to 900 K, the range where the monoclinic and hexagonal phase coexists, distortions can be observed for all the parameters of the monoclinic phase. The cell parameters of the hexagonal phase are not so much affected by the temperature: *a* remains almost constant till 1073 K and *c* slowly increases between 833 and 1073 K.

The variation of cell volume of both phases with temperature is shown in Fig. 4. The volume of the cell linearly increases for the both phases, except in the region where the phases coexist. The volumetric expansion coefficient is ~ 0.1 K⁻¹ both for the low and the high temperature phases.

3.2. Differential thermal analysis

A single endothermic event was observed by DTA (Fig. 5) during heating at 733 K (onset temperature). This was

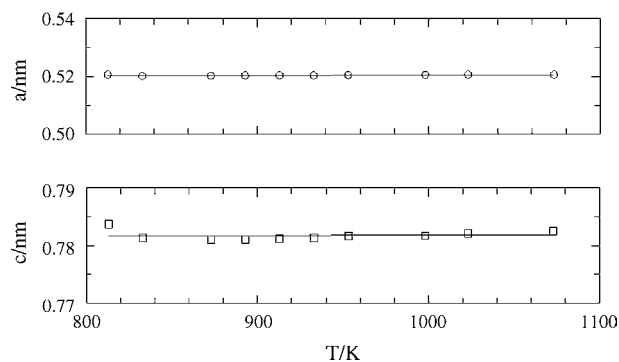


Fig. 3. Variation of cell parameters of the hexagonal phase of BaZr(PO₄)₂ with temperature; the line shows the linear fit of the results over 840 K.

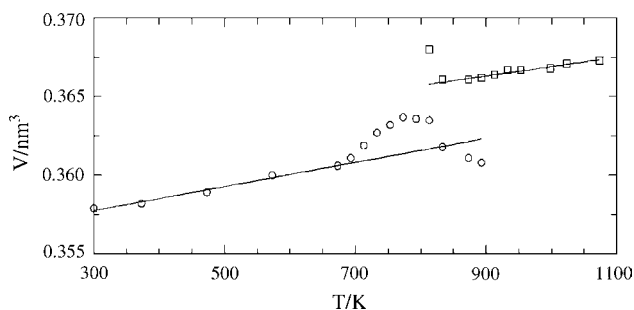


Fig. 4. Variation of cell volume of the monoclinic (○) and hexagonal (□) phases with temperature; the line shows the linear fit of the results below 700 K and over 840 K, respectively.

assigned to the phase transition from the monoclinic to the hexagonal structure. During the cooling down, the reverse phase transition took place at 704.5 K and only the monoclinic phase was observed at the room temperature, as checked by XRD. The difference between the two temperatures originates in the different applied heating/cooling rates.

3.3. High temperature drop calorimetry

The high temperature enthalpy increment was measured from 487 to 1579 K and plotted in Fig. 6; the insert shows the reduced enthalpy increment $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}/(T - 298.15)$ in $\text{J K}^{-1} \text{ mol}^{-1}$. This figure shows that a discontinuity occurs at between 692 and 743 K, attributed to the transition between the two modifications of $\text{BaZr}(\text{PO}_4)_2$, which is consistent with the XRD and DTA results. Since the measurements were performed in a random order and the results show a good

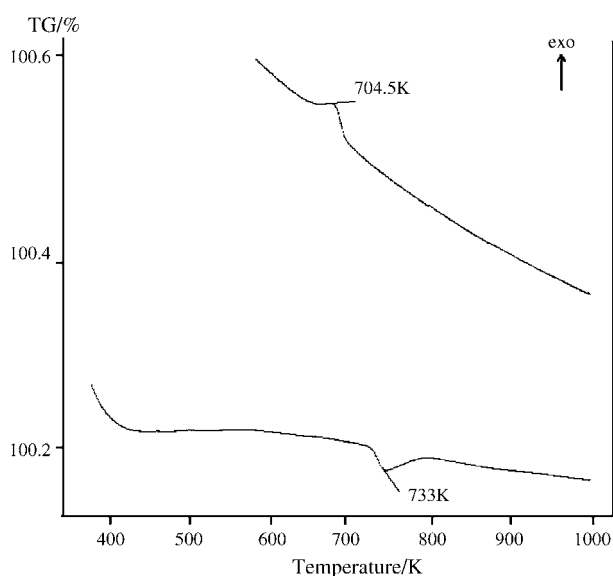


Fig. 5. DTA/TG curve for $\text{BaZr}(\text{PO}_4)_2$ from room temperature to 1023 K; the DTA curve is in arbitrary units.

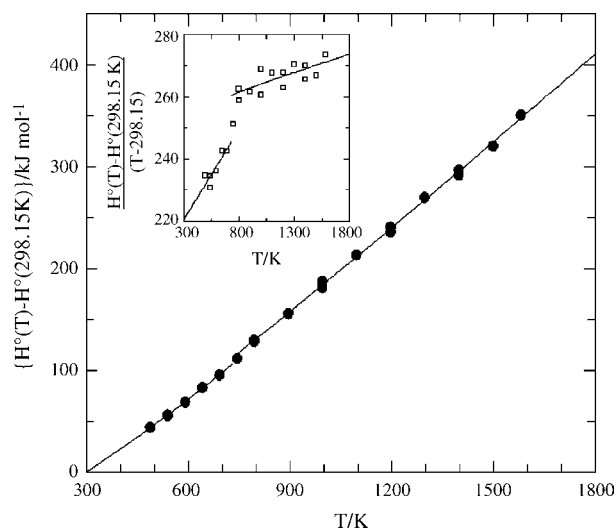


Fig. 6. The high temperature enthalpy increment of $\text{BaZr}(\text{PO}_4)_2$ as a function of temperature; the insert shows the reduced enthalpy increment $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}/(T - 298.15)$ in $\text{J K}^{-1} \text{ mol}^{-1}$.

consistency, we conclude that the transition was reversible (Table 3).

The enthalpy increments for the monoclinic phase have been fitted to the equation:

$$\begin{aligned} & \{H^\circ(T) - H^\circ(298.15 \text{ K})\}/\text{J mol}^{-1} \\ & = 88.3136(T/\text{K}) + 0.13961(T/\text{K})^2 - 3.11794 \times 10^4 \end{aligned} \quad (2)$$

Table 3

The measured and the calculated values for the $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ function

T (K)	$\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ (J mol^{-1})	
	Measured	Calculated
482.2	44327	43681.9
536.5	56371	56314.7
536.8	55523	56389.2
588.1	69022	69332.7
639.1	83322	82506.9
689.2	95479	95773.4
740.3	111852	^a
790.1	130014	129401.1
790.3	128272	129454.8
890.7	155996	156633.9
990.4	181525	183875.3
990.6	187314	183929.9
1090.4	213348	211395.5
1190.4	240445	239167.8
1190.5	236013	239185.5
1290.6	269904	267193.0
1391.0	292016	295500.0
1391.0	296842	295500.0
1491.6	320289	324118.5
1572.4	350628	347240.1

^a Close to the temperature of the phase transition.

and the enthalpy increments for the hexagonal phase to:

$$\begin{aligned} & \{H^\circ(T) - H^\circ(298.15\text{K})\}/\text{J mol}^{-1} \\ & = 252.0530(T/\text{K}) + 1.1179 \times 10^{-2}(T/\text{K})^2 - 7.6727 \times 10^4 \end{aligned} \quad (3)$$

From these equations we obtain for the enthalpy of transition ($T_{\text{trs}} = 733\text{ K}$) $\Delta_{\text{trs}}H^\circ = 5.46\text{ kJ mol}^{-1}$, assuming that complete conversion to the high temperature phase took place.

4. Conclusions

$\text{BaZr}(\text{PO}_4)_2$ could act as an end-member for the $\text{Ba}_x\text{Zr}_x\text{Ce}_{2-2x}(\text{PO}_4)_2$ phase which could be a ceramic waste form for actinides. We have already shown that the solubility of $\text{BaZr}(\text{PO}_4)_2$ in CePO_4 is limited [6]. To understand this limited solubility, the high temperature behavior of $\text{BaZr}(\text{PO}_4)_2$ was studied by X-ray diffraction, differential thermal analysis and drop calorimetry. Our results all are consistent with a monoclinic to hexagonal transition in $\text{BaZr}(\text{PO}_4)_2$ around 733 K. The transition seems to be thermally activated: the thermal analysis and calorimetry suggest that this transition is sharp and reversible, whereas the high temperature XRD indicates a gradual transformation taking place over about 250 K. In spite of this phase transition, the cell volume does not dramatically change between the two phases.

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