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High-temperature breakdown of the synthetic iodine analogue of vanadinite, $Pb_5(VO_4)_3I$: an apatite-related compound for iodine radioisotope immobilization?

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ABSTRACT

The thermal stability of the synthetic iodine analogue of vanadinite, $Pb_5(VO_4)_3I$, in air has been investigated by *in situ* high temperature X-ray powder diffraction between 300 and 1070 K. Rietveld refinement of phase fractions shows that breakdown to lead orthovanadate, $Pb_3(VO_4)_2$, begins at temperatures above 540 K, with complete loss of iodine above 680 K. More than 50 K below the onset of breakdown, the unit-cell parameters of $Pb_5(VO_4)_3I$ show anomalous contraction in the crystallographic $x-y$ plane (reduction of a) which we associate with movement of iodine within the [0001] channels of the structure. The implications of these results for immobilization of ^{129}I in potential apatite-related crystalline radioactive waste forms are discussed.

Keywords: iodine analogue of vanadinite, iodine immobilization, radioactive waste management, high temperature X-ray powder diffraction.

Introduction

Apatite-related minerals have the general formula $A_5(BO_4)_3X$, with common examples containing A = Ca or Pb, B = P, As or V and X = OH, Cl or F. The apatite structure is particularly adaptable and is able to accept varied chemical substitutions at the A, B and X sites (White *et al*., 2005). Naturally occurring chlorapatite-related lead chlorophosphate (pyromorphite) and lead chlorovanadate (vanadinite) are typically found in the oxidized zones of lead ore deposits; they also been reported in corroded lead water pipes, and are demonstrably stable in nature. They have large chemical variability, with extensive solid solution. This adaptability, along with the resistance of the apatite structure to radiation damage (Chaumont *et al*., 2002; Lian *et al*., 2010), has led to several different apatite phases being proposed as potentially promising waste forms for the disposal of radioactive fission products, including actinides and iodine (Trocellier, 2000; Trocellier, 2001; Weber *et al*., 1998; Guy *et al*., 2002). Specifically, a lead iodovanadate apatite, the iodine analogue of vanadinite, which is described hereafter as ‘iodovanadinite’, $Pb_5(VO_4)_3I$, has been suggested as a potential host for the immobilization of ^{129}I (Zhang *et al*., 2007; Audubert *et al*., 1997; Audubert and Lartigue, 2000; Uno *et al*., 2001).

Iodine has many radioactive isotopes including ^{123}I, which is used in medical imaging, and ^{129}I and ^{131}I, which are fairly common fission products. The safe disposal of the ^{129}I produced by nuclear power generation presents a particular problem due to its long half-life [15.7 m.y.; Trocellier (2001)], and the difficulty of immobilizing it in a solid phase due to the tendency of iodides to be displaced by other anionic species (Hyatt *et al*., 2004). Currently, during fuel

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reprocessing, ^{129}I is discharged into the sea, where its environmental impact is minimized by dilution (Hyatt *et al*., 2004; Zhang *et al*., 2007). This is unsatisfactory due to the biological risk and it is especially important that a safe method of disposal is found for ^{129}I. Iodine is an essential element in many living organisms, including humans where it is a constituent of thyroid hormones. Any material used for the immobilization of ^{129}I must be stable in the wide range of conditions that it may be subjected to in the period that is required for the ^{129}I radioactivity to fall to an acceptable level.

Various studies have tested the performance of synthetic 'iodovanadinite' under leaching, using spectroscopic techniques (Audubert and Lartigue, 2000; Uno *et al*., 2001; Zhang *et al*., 2007). Uno *et al*. (2001) also studied the mechanical and thermal properties of this compound. They found, using thermogravimetric (TG) and differential thermal analysis (DTA), that their synthetic $Pb_5(VO_4)_3I$ was stable up to approximately 800 K in an argon atmosphere and they measured the volumetric thermal expansion and thermal conductivity up to ~570 K. However, there have been very few studies of the properties of $Pb_5(VO_4)_3I$ when heated to high temperatures in air. In the present study we have analysed the stability of $Pb_5(VO_4)_3I$ when heated in air using high-temperature powder X-ray diffraction.

Experimental methods

The starting material was synthesized as described by Zhang *et al*. (2007), using a solid-state reaction method derived from that of Audubert *et al*. (1997). The starting materials were lead orthovanadate and lead iodide. Crystalline β-$Pb_3(VO_4)_2$ was ball milled with 75% of the stoichiometric amount of PbI_2 required for full $Pb_5(VO_4)_3I$ formation, to ensure that all iodine was immobilized (i.e. with lead orthovanadate in excess). The mixture was heated to 973 K and maintained at 200 MPa for two hours using hot isostatic pressing in copper cans to ensure phase formation and densification (Zhang *et al*., 2007). The product of this reaction has been studied spectroscopically (Zhang *et al*., 2007) and it was shown to yield $Pb_5(VO_4)_3I$ in the presence of excess lead orthovanadate.

We studied the hot-pressed sample as a function of temperature using *in situ* high-temperature X-ray powder diffraction. Data were recorded using a Bruker D8 X-ray diffractometer in θ-θ geometry, with Cu$K\alpha$ radiation, a Vantec detector and MSI furnace. Diffraction patterns were recorded at 10 K intervals in the temperature range 300−1070 K in an angular range from 5−90° 2θ with a step size of 0.02° 2θ and a counting time of 0.4 s step^{-1}. At each temperature step the sample was thermally equilibrated for five minutes before data collection commenced; heating between steps was carried out at a rate of 30 K per minute. Thus data for each temperature step took approximately 30 minutes to record.

The diffraction pattern of the starting material (Fig. 1) is in agreement with that of Audubert *et al*. (1999). It shows that synthetic iodovanadinite is the dominant phase present. A small excess of lead orthovanadate, β-$Pb_3(VO_4)_2$, from the synthesis was also observed in the room-temperature diffraction pattern.

Rietveld refinement using the *GSAS* software package (Larson and Von Dreele, 1994) on the graphical user interface *EXPGUI* (Toby, 2001) was used to determine the lattice parameters and phase fraction in each diffraction pattern as a function of temperature. The starting model for the iodovanadinite was taken from Audubert *et al*. (1999) with space group $P6_3/m$ and a shifted Chebyshev function was used to fit the background. The β-lead-orthovanadate, space group $P2_1/c$ (Kasatani *et al*., 1992) was fitted to the data below 360 K and γ-lead-orthovanadate, space group $R\bar{3}m$ (Kiat *et al*., 1991) above 360 K as lead orthovanadate undergoes a phase transition to the γ-form at ~357 K (Kuok *et al*., 1989).

Results and discussion

The diffraction patterns show that $Pb_5(VO_4)_3I$ decomposes as the temperature increases to γ-lead-orthovanadate. No iodine-bearing phases were observed in the high-temperature diffraction patterns. This suggests that iodine is lost from the material on decomposition, with the iodine subliming once it is released from the iodovanadinite structure. Uno *et al*. (2001) reported that iodovanadinite was stable in an argon atmosphere at temperatures up to 800 K, a higher temperature than observed in this study. This is probably due to $Pb_5(VO_4)_3I$ reacting with atmospheric oxygen upon heating, although we cannot rule out differences in the sample composition or experimental technique.

Figure 2 shows that there are three temperatures regions of interest when synthetic $Pb_5(VO_4)_3I$ is heated: from room temperature to

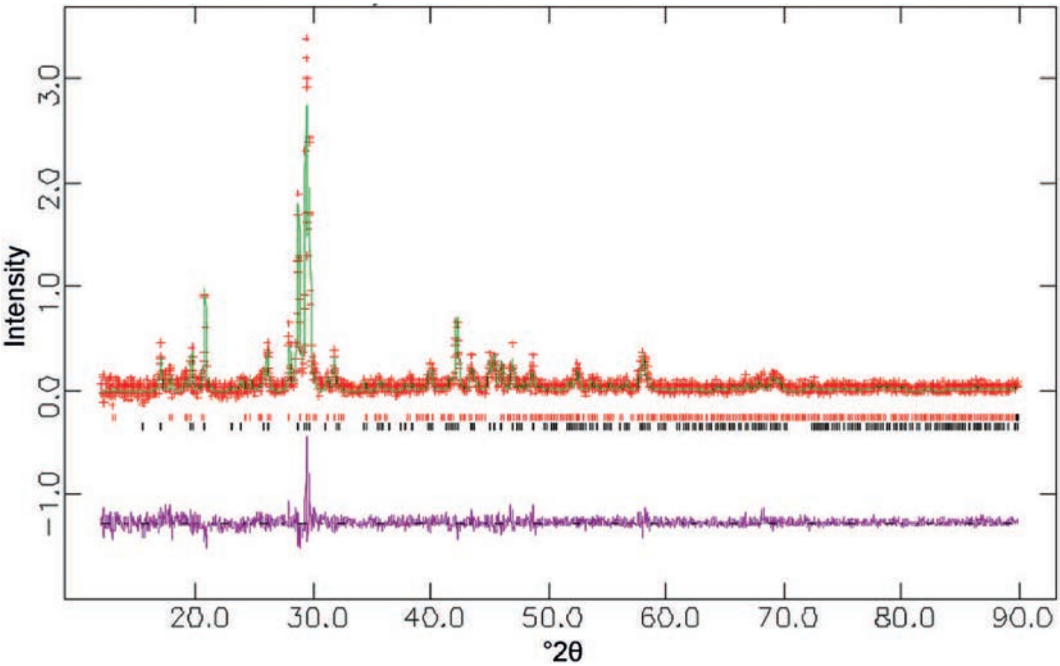

FIG. 1. Diffraction pattern of the sample at ambient temperature before heating. The upper trace shows raw data as markers and the *GSAS* fit as a solid line. The upper tick marks are β-lead-orthovanadate and the lower tick marks iodovanadinite peak positions. The lower trace shows the difference between the data and the *GSAS* fit.

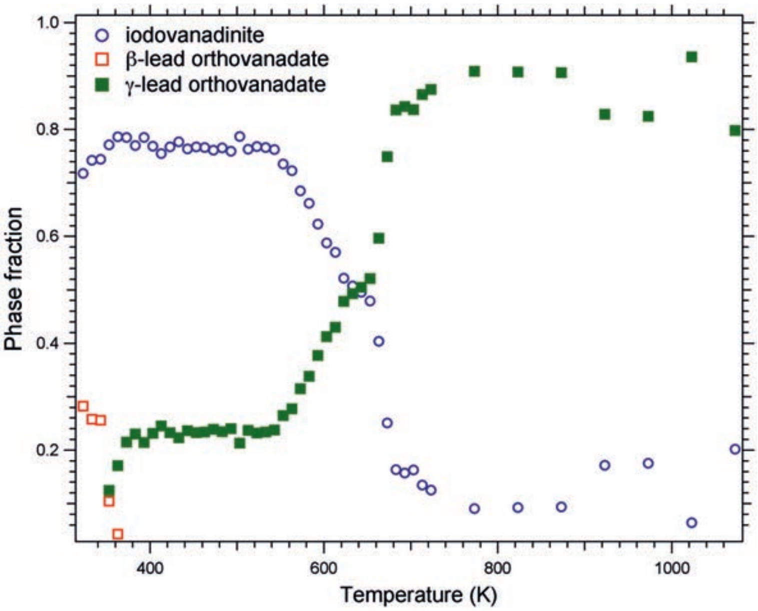

FIG. 2. The fraction of each phase present as a function of temperature determined by Rietveld refinement in *GSAS* of the diffraction data. The lines are visual guides.

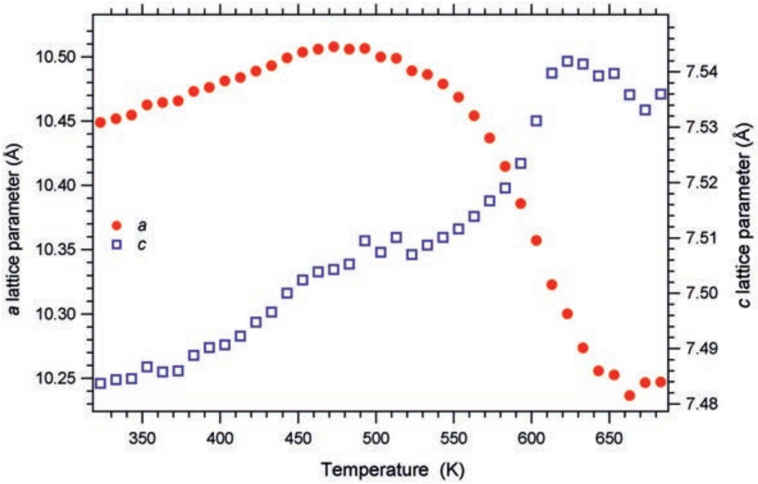

FIG. 3. The *a* and *c* lattice parameters of $Pb_5(VO_4)_3I$ as a function of temperature determined by Rietveld refinement in *GSAS*. The lines are visual guides.

530 K it is thermally stable; from 540 K to 680 K, it gradually decomposes; above 680 K the decomposition to γ-lead-orthovanadate is complete. However, this picture may be incomplete; the apparent temperature range of the decomposition is almost certainly time-dependent and kinetically controlled. We suspect that a slower heating rate would result in a lower apparent limit of thermal stability.

Refinements of the lattice parameters of our synthetic iodovanadinite provide a deeper insight into the high-temperature behaviour. The *a* cell parameter (with a hexagonal setting of the unit cell) decreases on heating at a fairly steady rate between 540 and 670 K (Fig. 3), this suggests that the sample undergoes a structural or compositional change in this temperature range. Below 470 K the lattice parameter increases linearly due to normal thermal expansion, but at approximately 490 K it begins to *decrease* as the temperature is increased. This is a lower temperature than that at which the apparent mass fraction of $Pb_5(VO_4)_3I$ starts to decrease by decomposition, suggesting that the sample changes structurally prior to decomposition. As the lattice parameters are especially sensitive to halogen size and occupation of the [0001] channels (Hyatt *et al*., 2004) (see Fig. 5), this apparent structural change could indicate that a small amount iodine is lost or displaced from low-temperature sites before the $Pb_5(VO_4)_3I$ begins to decompose.

The *c* lattice parameter shows much less variability as a function of temperature than the *a* lattice parameter. It changes by a comparatively small amount and deviates much less from linear thermal expansion (Fig. 3) on heating. It appears that the structural changes that occur during $Pb_5(VO_4)_3I$ decomposition affect the *c* lattice parameter much less than the *a* lattice parameter. Analysis of the linear thermal expansion coefficients, α_a and α_c, confirm this anisotropy, Fig. 4.

The thermal expansion coefficients parallel to the *a* and *c* axes, α_a and α_c, were determined from linear fits to portions of the thermal dependence of the cell parameters over 50 K intervals across the temperature range of the experiments. It was found that α_a is larger than α_c before decomposition; this is consistent with the anisotropy in the compressibility of the isostructural chlorovanadate mineral vanadinite, $Pb_5(VO_4)_3Cl$, in which the *c* axis is stiffer than the *a* axis (Gatta *et al*., 2009) and is seemingly a feature of the apatite structure (Brunet *et al*., 1999; Tonegawa *et al*., 2010). The thermal expansion along *a*, α_a, is negative throughout the temperature range in which decomposition is observed, whereas α_c is positive, reflecting the decrease in the *a* lattice parameter and continued increase in *c* in this temperature range. It is reasonable to conclude that iodine is lost from the structure, especially as Uno *et al.* (2001) report a mass loss in this temperature range by thermogravimetry. Iodine is hosted by the [0001] channels in iodovanadinite (Fig. 5) and if

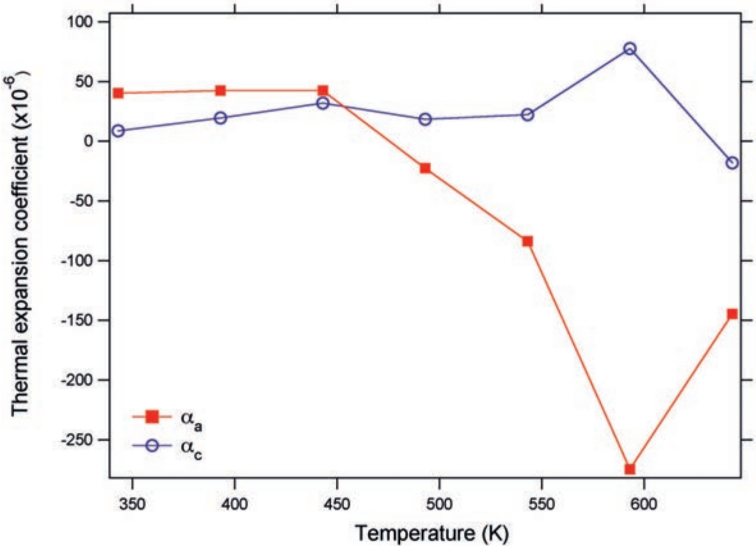

FIG. 4. The temperature dependence of the linear coefficients of thermal expansion of $Pb_5(VO_4)_3I$.

vacancies appeared in these channels a reduction in the *a* (and *b*) cell parameter would result. As the channels lie parallel to the *z* axis, and the remainder of the structure remains largely unaffected, there is a much less noticeable effect on the *c* lattice parameter.

The temperature dependence of the volumetric thermal expansion coefficient of iodovanadinite, α_V, shown in Fig. 6, is of the order of 10^{-4} K^{-1} and it increases linearly with temperature before the sample decomposes. The linear trend is broadly in agreement with Uno *et al*. (2001), but the thermal expansion observed in the present study is greater than that reported by Uno *et al*. (2001), and their sample decomposed at >800 K. These differences are most probably due to the differing experimental conditions in the two studies. Uno *et al*. (2001) carried out their

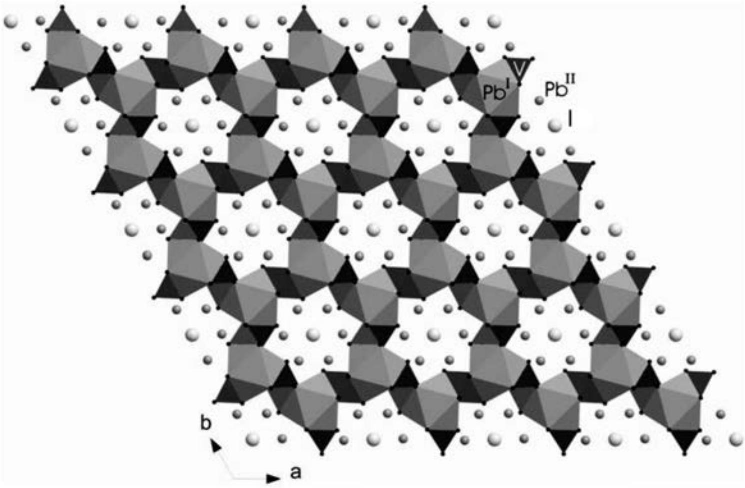

FIG. 5. The crystal structure of iodovanadinite, $Pb_4^IPb_6^{II}(VO_4)_6I_2$, viewed down the *c* axis, showing the [0001] channels. The Pb^{II} and I atoms may be slightly displaced from the positions shown (adapted from Gatta *et al*., 2009).

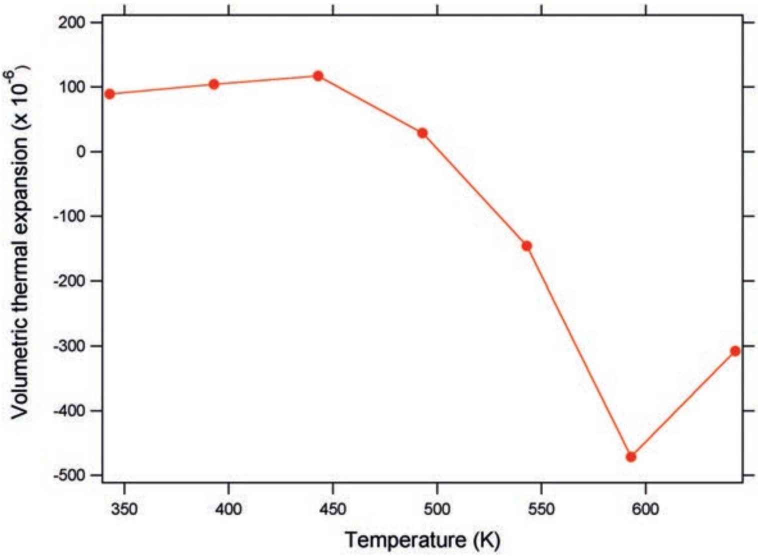

FIG. 6. The temperature dependence of the volumetric thermal expansion coefficient of $Pb_5(VO_4)_3I$. The lines are visual guides.

heating in an argon atmosphere, whereas the present study was carried out in air. This suggests that the breakdown of $Pb_5(VO_4)_3I$ is caused or accelerated by a chemical reaction with air. It is probable that $Pb_5(VO_4)_3I$ is oxidized, or that the iodide ions within the structure are displaced by oxygen on heating, as is noted in hydroxylapatite above 1073 K (Trombe, 1973), causing the material to decompose. During decomposition α_V decreases, becoming negative as iodine is lost from the structure, and the unit cell also decreases in volume.

Conclusion

The relatively low decomposition temperature of iodovanadinite when it is heated in air at atmospheric pressure indicates that it is probably unsuitable as a candidate for the immobilization of ^{129}I in waste repositories that are likely to be subjected to oxidizing conditions. Nonetheless, it may be considered an improvement on dispersal at sea. We have demonstrated that the onset of the release of iodine from the structure is accompanied by anisotropic lattice strains, and it is interesting to speculate on the role of pressure on the possible stabilization of iodine in the $Pb_5(VO_4)_3I$ lattice. The sample under study was synthesized in a closed system at 973 K and 200 MPa, conditions in which iodine clearly enters the vanadinite lattice. These pressure and temperature conditions are much more extreme than those anticipated in even a deep geological waste repository (where the lithostatic pressure may be of the order of 10 MPa). In any case, the fate of iodine in $Pb_5(VO_4)_3I$ in such a situation is likely to be dependent on its exchange with the other phases in the waste assemblage. If iodovanadinite is to be considered as an ^{129}I-bearing waste form, its efficacy might be improved by adopting a method to control its stability at high temperatures. One possibility would be to confine it in a suitable host matrix, as has already been suggested as a means of improving other material properties (Uno *et al*., 2001). If the matrix was chosen carefully, iodine would not be lost from the $Pb_5(VO_4)_3I$ structure to the environment as easily, and the structure would be anticipated to be more stable at higher temperatures. It should also be noted that the experiments described here were conducted on powders; dense bulk ceramics would be expected to have a slower rate of decomposition. However, this alone would probably not be an effective method for containing ^{129}I on the timescales required in a repository environment.

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