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Some properties of a lead vanado-iodoapatite $Pb_{10}(VO_4)_6I_2$

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Abstract

A lead vanado-iodoapatite $Pb_{10}(VO_4)_6I_2$ was synthesized as a potential waste form to immobilize radioactive iodine and some thermal, mechanical and chemical properties were measured. Thermogravimetry–differential thermal analysis (TG–DTA) showed that the apatite was stable up to about 800 K. The thermal conductivity of the hot-pressed sample, with the theoretical density of 82%, increased gradually with increasing temperature from 0.65 W m^{-1} K^{-1} at room temperature to 0.78 W m^{-1} K^{-1} at 523 K. The micro-Vickers hardness and Young's modulus were lower than those of a typical glass waste form. The leaching rate of iodine for apatite was two orders of magnitude higher than that of an AgI glass waste form. Despite the high leaching rate (compared to AgI embedded in glass), the high chemical stability up to 800 K and acceptable mechanical properties of this apatite suggest that it will be a good waste form when embedded in a suitable matrix material.

1. Introduction

During fuel reprocessing, radioactive iodine is captured by silver zeolite or silver silica and forms silver iodide. It is necessary to control iodine in order not to release it to the environment, but the final disposal method for radioactive iodine has not yet been determined. Therefore, we tried to develop a waste form for immobilizing iodine as an apatite-structured compound, because of the general stability of apatite-type materials. These are compounds of general formula $Me_{10}(XO_4)_6Y_2$ that are relatively insoluble, radiation-damage resistant and that can accept a wide range of ionic substitutions.

A lead vanado-iodoapatite, $Pb_{10}(VO_4)_6I_2$ was previously synthesized by Audubert et al. [1], who also made a waste form by embedding the apatite in a $Pb_3(VO_4)_2$ matrix. They briefly estimated some properties of the waste form but did not report any properties of the apatite itself. In the present study, we have characterized its thermal, mechanical and chemical properties, and discussed the suitability of the apatite as a waste form from the viewpoint of properties and preparation method.

2. Experimental

Because iodine compounds used as starting materials or product were volatile, we synthesized the sample by the following two steps. First, the sample was synthesized in a sealed quartz ampoule in vacuum. Next, a waste form was made by hot-pressing.

The stoichiometric amounts of PbO, PbI_2 and V_2O_5 were mixed and pressed to a pellet at 35 MPa at room temperature. The pellet sample was put in a sealed quartz ampoule in vacuum and heat-treated at 973 K for 5 h. The crystal structure of the product was analyzed by X-ray powder diffraction using a Rigaku Dennki diffractometer with Cu-Kα radiation at room temperature. A quantitative analysis of the sample was performed by energy dispersive X-ray (EDX) microanalysis, using a JEOL JED-2110 instrument.

We estimated the chemical stability and the thermal expansion of the powder apatite sample obtained by the heat treatment in a sealed ampoule. We also measured the thermal and mechanical properties and leaching rate of the waste form prepared by hot-pressing the powder sample.

The thermal stability of the synthesized apatite was examined by thermogravimetry–differentialthermal analysis (TG–DTA) using a Mac Science 2020 unit. The linear thermal expansion coefficient of the sample was evaluated from X-ray diffraction data obtained while heating under argon within the temperature range 298–573 K.

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The uniaxial hot-pressing was conducted at a pressure of about 9 MPa and at 623 or 773 K for 5 h under argon atmosphere. We confirmed that the crystal structure and composition of the hot-pressed samples were identical with those of the powder sample by X-ray powder diffraction and EDX analysis. The density of the sample was calculated from weight and dimension measurements.

The thermal conductivity of the sample was calculated from the reported heat capacity, the experimentally determined density, and the thermal diffusivity measured by a laser flash method using ULVAC TC-7000 in vacuum. The heat capacity C_p of the sample was evaluated from Neumann–Kopp's law

$$C_p = C_{pPbI_2} + 3C_{pV_2O_5} + 9C_{pPbO} \quad (1)$$

using the literature data [2] for PbO, PbI_2 and V_2O_5.

The longitudinal and shear sound velocities were measured by an ultrasonic pulse–echo method at room temperature to evaluate the elastic properties of the sample. Micro-Vickers hardness measurements were performed using a Matsuzawa Seiki MHT-1 Vickers hardness testing machine.

Leaching tests were performed in accordance with the procedure of MCC-5 [3], soxhlet leach method test. The concentration of iodine, lead and vanadium in the leachate were measured by inductively coupled plasma spectrometry (ICP-ES) using a by Shimazu ICP-7500. The leaching period was 7 days.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern for the sample obtained by heat treatment in a sealed quartz ampoule. The X-ray diffraction pattern of the product was in good accordance with the literature pattern shown in Fig. 1(b) [1]. Table 1 shows the EDX element analyses. The content of iodine is 15% less than the stoichiometric composition, probably from the evaporation of PbI_2 during heating in a sealed quartz ampoule. According to these results, it was found that iodine-bearing apatite, $Pb_{10}(VO_4)_6I_2$ could be synthesized, although a little iodine was evaporated.

Fig. 2 shows TG–DTA curves, which indicate that the synthesized apatite was stable up to about 800 K under argon atmosphere. The weight loss above this temperature suggested that the reaction corresponds to the release of iodine from the apatite.

Figs. 3(a), (b) and (c) show the temperature dependence of lattice parameters a, c and c/a, respectively. It was found that the lattice parameters a and c increased smoothly with increasing temperature, whereas c/a was almost constant. Fig. 4 shows the temperature dependence of the volumetric thermal expansion coefficient,

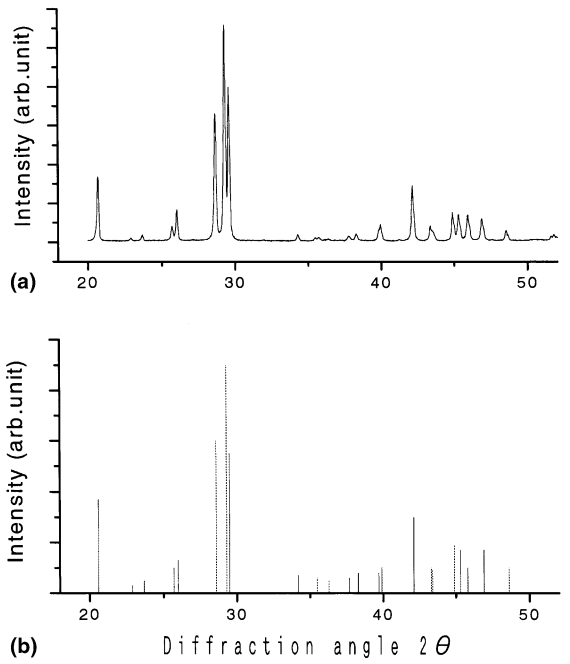

Fig. 1. (a) X-ray powder diffraction pattern for $Pb_{10}(VO_4)_6I_2$. (b) X-ray powder diffraction pattern for reported $Pb_{10}(VO_4)_6I_2$ [1].

Table 1
Chemical analysis of the sample

Element	Composition (at.%)		Composition (wt%)	
	Experimental	Theoretical	Experimental	Theoretical
I	4.42	4.76	7.20	8.42
Pb	27.7	23.8	73.7	68.7
V	11.5	14.3	7.50	10.1
O	56.4	57.1	11.6	12.7

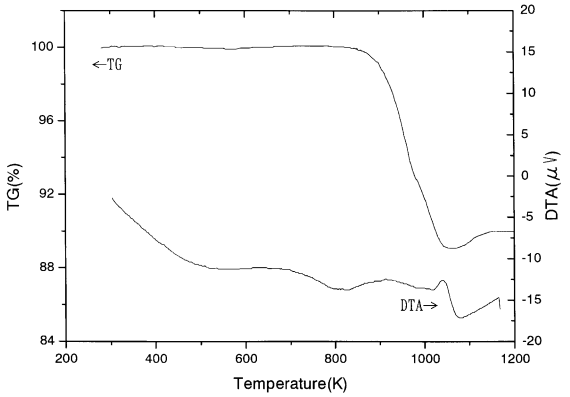

Fig. 2. TG and DTA curve of $Pb_{10}(VO_4)_6I_2$.

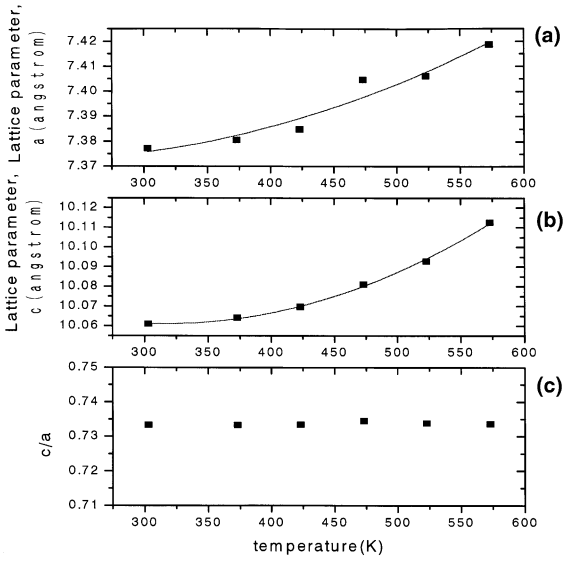

Fig. 3. (a) Temperature dependence of lattice parameter a of $Pb_{10}(VO_4)_6I_2$. (b) Temperature dependence of lattice parameter c. (c) Temperature dependence of c/a.

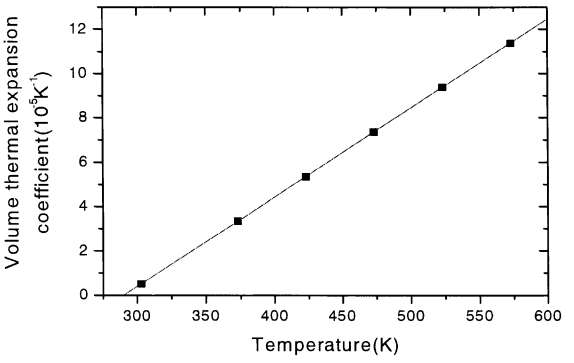

Fig. 4. Temperature dependence of volume thermal expansion coefficient of $Pb_{10}(VO_4)_6I_2$.

which was of the order of 10^{-5} (K^{-1}), and increased linearly with temperature.

The thermal diffusivity was measured for the two hot-pressed samples, sintered at 623 or 773 K for 5 h, whose densities were 66.8% and 82.3%, respectively. The thermal conductivity κ was calculated from the measured thermal diffusivity λ, specific heat capacity C_p and density d using the following relationship,

$$\kappa = \lambda C_p d. \tag{2}$$

These calculated data were corrected to 100%T.D. by using Schulz's equation [4]

$$1 - C_D = (\lambda_M/\lambda_D)^{1/3}(\lambda_D - \lambda_C)/(\lambda_D - \lambda_M), \tag{3}$$

where C_D is the concentration of the dispersed phase, λ_M the thermal conductivity of matrix, λ_D the thermal conductivity of disperse phase, λ_C the total thermal conductivity.

The thermal conductivity of $Pb_{10}(VO_4)_6I_2$ increased gradually with increasing temperature from 0.65 W m^{-1} K^{-1} at 318 K to 0.78 W m^{-1} K^{-1} at 523 K as shown in Fig. 5.

The longitudinal and shear sound velocities of $Pb_{10}(VO_4)_6I_2$ were measured at room temperature. The shear modulus G and Young's modulus E can be written in terms of the longitudinal sound velocity V_L and shear sound velocities V_S [5] by

$$G = \rho V_S^2, \tag{4}$$

$$E = \frac{G(3V_L^2 - 4V_S^2)}{(V_L^2 - V_S^2)}, \tag{5}$$

$$K = \rho\left(V_L^2 - \frac{4}{3}V_S^2\right), \tag{6}$$

where ρ is the sample density. Poisson's ratio v can be expressed in terms of V_L and V_S as

$$v = \frac{1}{2}\frac{V_L^2 - 2V_S^2}{V_L^2 - V_S^2}. \tag{7}$$

The shear sound velocity V_S of the sample could not be measured because the internal friction was too large to

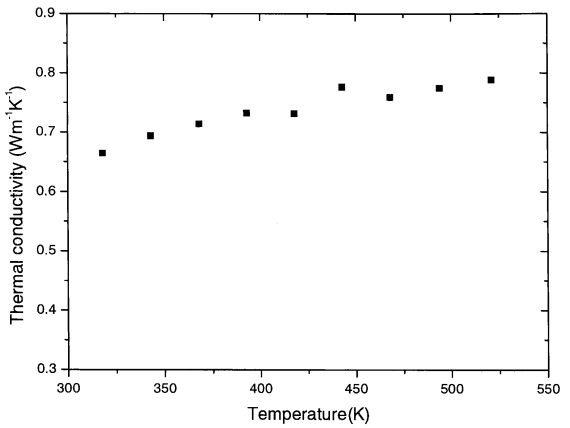

Fig. 5. Temperature dependence of thermal conductivity for $Pb_{10}(VO_4)_6I_2$.

Table 2
Mechanical properties of $Pb_{10}(VO_4)_6I_2$ and a typical glass waste [6]

	Young's modulus (GPa)	Vickers hardness (GPa)
Apatite	26	4.3
Glass waste	81	6.1

Table 3
Leaching rate of $Pb_{10}(VO_4)_6I_2$ AgI glass [7]

	Apatite			AgI glass waste
	Iodine	Lead	Vanadium	Iodine
Leaching rate (g cm^{-2} d^{-1})	3.98×10^{-5}	1.55×10^{-5}	1.61×10^{-4}	4.0×10^{-7}

record the reflected ultrasonic sound. Therefore, Young's and shear moduli of the samples were evaluated by the equation

$$V_S = \frac{1}{\sqrt{3}} V_L \tag{8}$$

assuming that the sample has no anisotropy. The values of Young's modulus E and micro-Vickers hardness determined for the apatite with the theoretical density of 82.3% are reported in Table 2. These figures are smaller than those of a typical glass waste, also listed in Table 2 [6].

The leaching rate of iodine, lead and vanadium from $Pb_{10}(VO_4)_6I_2$ are compared with the iodine value for an AgI glass waste form (Table 3) [7]. The iodine value for apatite was two orders of magnitude higher than that of the AgI glass waste form.

Generally iodine captured by silver zeolite or silver silica during reprocessing is separated from the adsorbent for the further solidification process and converted to silver iodide or other iodine compounds as a starting material for the waste form. However, it is necessary to use HIP or other special furnaces whatever iodine compounds, such as AgI, PbI_2, etc., are chosen since they have low melting points (e.g., AgI: 828 K; PbI_2: 675 K) and they are volatile. In the present study, loss of iodine at 973 K due to the melting of PbI_2 and thermal decomposition of the formed apatite might be suppressed to some extent. Thus, heat treatment in a sealed quartz vial is considered to be an easy and reasonable synthesis method.

The most important factor in determining the suitability in geological disposal is the leaching rate. Because the leaching rate of the apatite was higher than that of the AgI glass waste or a typical glass waste, it is considered that the apatite must be embedded in a matrix for utilization as a waste form, as reported by Audubert et al. [1]. Further study is needed for the development of the material and method to embed the apatite in a matrix, but the stability of the apatite up to 800 K may be advantageous to the treatment.

4. Summary

We succeeded in synthesizing an apatite-structure lead vanado-iodoapatite, $Pb_{10}(VO_4)_6I_2$ by a relatively easy method: heat treating the starting powders in a sealed quartz ampoule. The apatite was stable up to 800 K. The density of the waste form prepared by hot-pressing the powder sample at 773 K was about 82% of theoretical density. The volume thermal expansion coefficient was in the order of 10^{-5} (K^{-1}), and increased linearly with temperature. The thermal conductivity was about 0.7 W m^{-1} K^{-1}. The Vickers hardness and Young's modulus were less than those of a glass waste. The leaching rate of iodine from apatite was two orders of magnitude higher than that of an AgI glass waste form. Despite the high leaching rate (compared to AgI embedded in glass), the high chemical stability up to 800 K and acceptable mechanical properties of this apatite suggest that it will be a good waste form when embedded in a suitable matrix material.

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