



Effect of the preparation conditions of zirconium phosphate on the characteristics of Sr immobilization

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ABSTRACT

The proton-type crystalline zirconium phosphate, $\text{HZr}_2(\text{PO}_4)_3$, was obtained by a thermal decomposition of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at different temperatures from 400 to 800 °C, where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ was obtained in advance by a hydrothermal synthesis using a mixed solution of ZrOCl_2 , H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ with different processing times from 5 to 72 h. Sr ion was immobilized to $\text{HZr}_2(\text{PO}_4)_3$ by treating the mixture of $\text{HZr}_2(\text{PO}_4)_3$ and $\text{Sr}(\text{NO}_3)_2$ aqueous solution in an autoclave at 250 °C. Immobilizing and leaching performance of Sr in $\text{HZr}_2(\text{PO}_4)_3$ were discussed.

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1. Introduction

Zirconium phosphate materials are being developed as ion exchangers, and crystalline proton-type zirconium phosphate, $\text{HZr}_2(\text{PO}_4)_3$, is especially resistant to heat, chemicals, radiation, oxidation/reduction, corrosion and mechanical shock [1–3]. However, $\text{HZr}_2(\text{PO}_4)_3$ does not readily exchange its proton ion H_3O^+ for various metal ion M^{n+} in the aqueous mixture at room temperature and atmospheric pressure except for Li^+ and Na^+ of which ionic radii are relatively small, although $\text{Zr}(\text{HPO}_4)_2$ with a two-dimensional layer structure has no such limitation. Therefore, we proposed the immobilization method of M^{n+} to $\text{HZr}_2(\text{PO}_4)_3$ by mixing $\text{HZr}_2(\text{PO}_4)_3$ and $\text{M}(\text{NO}_3)_n$ in a dry state and subsequently thermally treating at 700 °C. The ion exchange would undergo by the melting heat of $\text{M}(\text{NO}_3)_n$. Supposing the storage of radioactive atoms as Cs137 and Sr90 [4,5], the immobilization of Cs^+ and Sr^{2+} to $\text{HZr}_2(\text{PO}_4)_3$ have been done. The obtained crystalline complex was thermally and chemically stable, and exhibited the excellent ion leaching resistance for acid or alkali [6–8]. This method was also applied to alkali metal ions (Li^+ , Na^+ and K^+), alkaline earth metal ions (Mg^{2+} , Ca^{2+} and Ba^{2+}) [9], and other metal ions; Mn^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} as harmful ones for water and soil pollution [10]. However, the following problems for this method are pointed out; metal ions should form nitrate like $\text{M}(\text{NO}_3)_n$ and the nitrate should not be oxidized and decomposed prior to melting during heating. In addition, this immobilization method is a little complicated and troublesome. To resolve these problems, the following

immobilization method has been explored by subjecting the mixture of $\text{HZr}_2(\text{PO}_4)_3$ and $\text{M}(\text{NO}_3)_n$ aqueous solution to high pressure steam at high temperature with an autoclave [11,12].

$\text{HZr}_2(\text{PO}_4)_3$ has been known to be prepared by a thermal decomposition of ammonium-type zirconium phosphate $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at approximately 600 °C, where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ was obtained in advance by hydrothermal synthesis at 80 °C using a mixed solution of ZrOCl_2 , H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$. However, there is no detailed investigation about the processing time for the hydrothermal synthesis and the treatment temperature for the decomposition. In this study, we have investigated the characteristics of Sr immobilization by using an autoclave for $\text{HZr}_2(\text{PO}_4)_3$ prepared by the hydrothermal synthesis from 5 to 72 h and the thermal decomposition from 400 to 800 °C.

2. Experimental procedure

2.1. Synthesis of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ and its thermal decomposition

Reagent grades of zirconium oxychloride (ZrOCl_2), phosphoric acid (H_3PO_4) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) were dissolved in water and adjusted to pH 3 by aqueous ammonium. After hydrothermal synthesis at 80 °C for 5, 10, 15, 22 and 72 h, ammonium-type zirconium phosphate ($\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$) was filtered off, washed with plenty of pure water, and dried at 100 °C for 12 h in vacuum. The obtained $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ of approximately 6 g was put into alumina crucible (SSA-H, 25 cm³, Nikkato Co.) and calcined at 575 °C for 5 h to produce $\text{HZr}_2(\text{PO}_4)_3$. On the other hand, $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ synthesized hydrothermally at 80 °C for 22 h was calcined at 400, 450, 500, 550, 575, 600, 650, 700 and 800 °C for 5 h to produce $\text{HZr}_2(\text{PO}_4)_3$ or $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$.

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2.2. Immobilization and leachability of Sr

Five gram of $\text{HZr}_2(\text{PO}_4)_3$ or $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ was mixed with the aqueous solution of $\text{Sr}(\text{NO}_3)_2$ (20 ml) with the molar ratio of Sr against $\text{HZr}_2(\text{PO}_4)_3$ or $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ as 0.5. The mixture was thermally treated in an autoclave (TSC-006, Taiatsu Techno Co.) at 250 °C for 20 h to immobilize Sr to $\text{HZr}_2(\text{PO}_4)_3$ or $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$. The leachability performance of Sr^{2+} from the immobilized products was studied as follows; the immobilized product of 2 g was mixed with 1 M HCl aqueous solution of 16 cm^3 and placed in the autoclave (TVS-N2, Taiatsu Techno Co.) at 160 °C for 24 h (1 day). After cooling to the room temperature, the mixture was filtrated and the amount of or Sr^{2+} leached from the immobilized material into the filtrate was measured by atomic absorption

spectrophotometer (AA-6200, Shimadzu). The Sr leaching rate was evaluated as the weight of the leached Sr^{2+} divided by the surface area measured by the BET method.

2.3. Measurement

The crystal morphology was observed using a scanning electron microscope (JSM-6701F, JEOL Ltd.) and the surface area was determined by the BET method with N_2 adsorption (NOVE 3200, Quantachrome Instruments Co.). The crystalline structure was measured by powder X-ray diffraction (MiniFlex, Rigaku) carried out with $\text{Cu K}\alpha$ over the angles $2\theta = 20\text{--}40^\circ$. The weight loss of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ in the heating process with 5°C min^{-1} under the air flow at

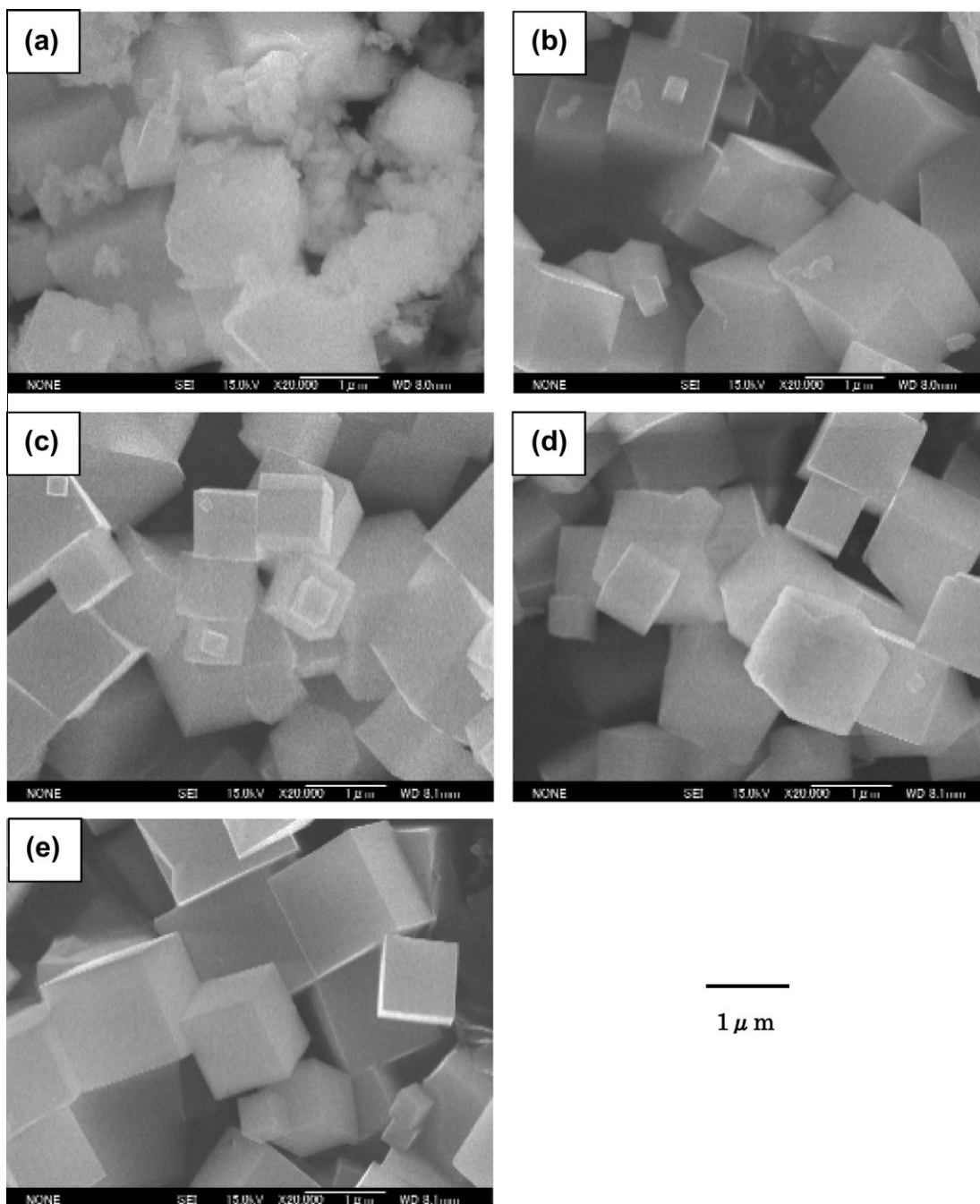


Fig. 1. Scanning electron micrographs of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by a hydrothermal synthesis in the processing time (a) 5 h, (b) 10 h, (c) 15 h, (d) 22 h and (e) 72 h.

$20 \text{ cm}^3 \text{ min}^{-1}$ was measured by thermo gravimetric analysis (TG8110, Rigaku). The amounts of Sr and Zr of the Sr immobilized $\text{HZr}_2(\text{PO}_4)_3$ or $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ were quantitatively analyzed by X-ray fluorescence spectroscopy (EDX-700, Shimadzu).

3. Results and discussion

3.1. Processing time effect in the hydrothermal synthesis of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$

3.1.1. Formation of $\text{HZr}_2(\text{PO}_4)_3$

The precursor of $\text{HZr}_2(\text{PO}_4)_3$, $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ was produced by the hydrothermal synthesis of aqueous solutions of ZrOCl_2 , H_3PO_4 and $\text{H}_2\text{C}_2\text{O}_4$ at different processing times in the range from 5 to 72 h. The SEM photographs of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ obtained at different processing times are shown in Fig. 1. The shape of crystal is apparently cubic from 10 to 72 h except for 5 h. The surface area of

$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ measured by the BET method are 17.9, 2.0, 2.0, 1.8 and $2.0 \text{ m}^2 \text{ g}^{-1}$ for processing times 5, 10, 15, 22 and 72 h, respectively. It is considered that the reason why the only surface area for 5 h is quite large is due to fine crystals as shown in Fig. 1a. The surface area is almost constant at approximately $2 \text{ m}^2 \text{ g}^{-1}$ when the time is longer than 10 h and their corresponding crystals are cubic and has almost the same size.

Fig. 2 shows the thermo gravimetric curve of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by the hydrothermal synthesis at 22 h. The weight loss of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ decreases with increasing temperature in two steps.

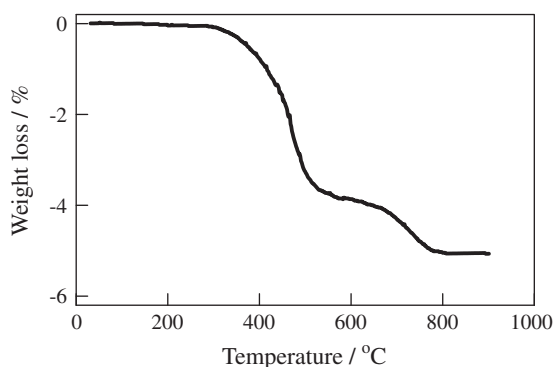


Fig. 2. Thermo gravimetric curve of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by a hydrothermal synthesis for 22 h.

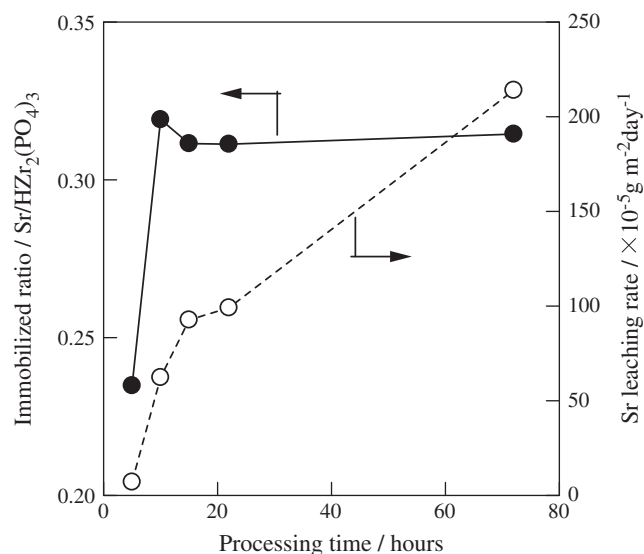


Fig. 4. Relationship between Sr immobilized ratio and processing time (●) and relationship between Sr leaching rate and processing time (○) for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by a hydrothermal synthesis in the processing time range of 5–72 h.

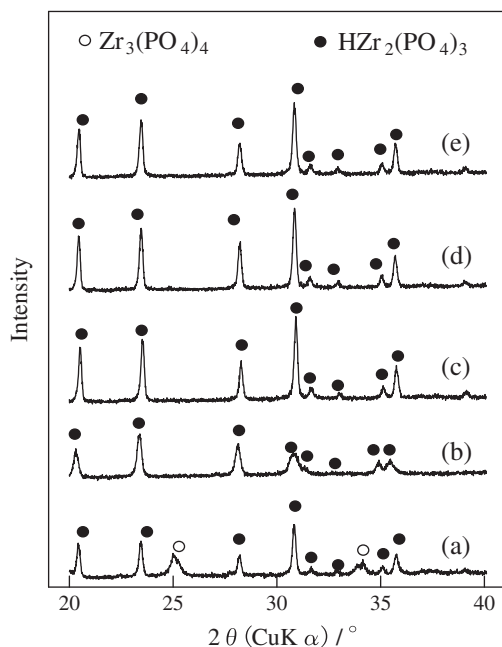


Fig. 3. XRD patterns for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ thermally treated at 575°C , where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ is produced by a hydrothermal synthesis at different processing times (a) 5 h, (b) 10 h, (c) 15 h, (d) 22 h and (e) 72 h.

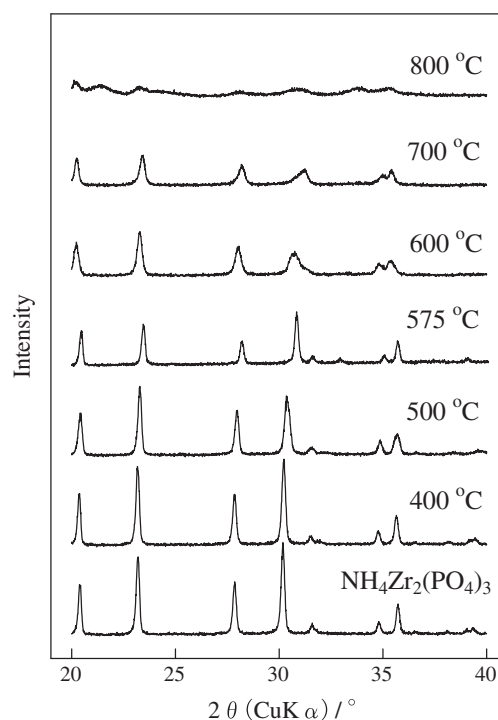
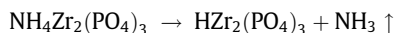


Fig. 5. XRD patterns for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ and $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ thermally treated at several temperatures from 400 to 800°C , where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ is produced by a hydrothermal synthesis for 22 h.

The 1st step from 350 to 575 °C with a rapid decrease 3.5 wt.% is considered as the following change from $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ to $\text{HZr}_2(\text{PO}_4)_3$ as



It is noted that not only crystal morphology but also surface area did not change before and after the thermal decomposition of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at 575 °C with any processing time (even 5 h). It has been considered that $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ is completely decomposed to $\text{HZr}_2(\text{PO}_4)_3$ at 575 °C. The 2nd step at around 700 °C will be due to the change from $\text{HZr}_2(\text{PO}_4)_3$ to ZrP_2O_7 .

Fig. 3 shows the XRD patterns for thermally decomposed $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at 575 °C, where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ was produced by hydrothermal synthesis at different processing times in the range from 5 to 72 h. The XRD bands are due to not only $\text{HZr}_2(\text{PO}_4)_3$ but also $\text{Zr}_3(\text{PO}_4)_4$ for 5 h, while the bands due to $\text{Zr}_3(\text{PO}_4)_4$ disappears for more than 10 h. The bands due to $\text{HZr}_2(\text{PO}_4)_3$ become stronger for more than 15 h and it indicates that the degree of crystallinity becomes larger.

3.1.2. Performance of immobilization ratio and leaching rate of Sr

The mixture of $\text{HZr}_2(\text{PO}_4)_3$ and the aqueous solution of $\text{Sr}(\text{NO}_3)_2$ with the molar ratio of Sr against $\text{HZr}_2(\text{PO}_4)_3$ as 0.5 was treated in the autoclave at 250 °C for 20 h. Fig. 4 shows the plot of the

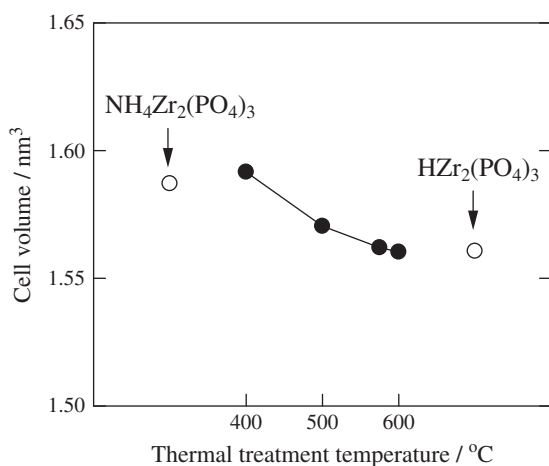


Fig. 6. Relationship between cell volume and thermal treatment temperature for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by a hydrothermal synthesis for 22 h.

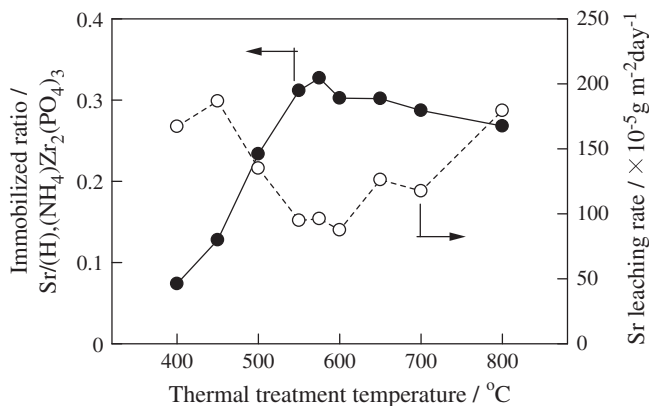


Fig. 7. Relationship between Sr immobilized ratio and thermal treatment temperature (●) and relationship between Sr leaching rate and thermal-treated temperature (○) for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ prepared by a hydrothermal synthesis for 22 h.

immobilization molar ratio of Sr to $\text{HZr}_2(\text{PO}_4)_3$, $\text{Sr}/\text{HZr}_2(\text{PO}_4)_3$ as a function of the processing time. The value of $\text{Sr}/\text{HZr}_2(\text{PO}_4)_3$ is exceeded as 0.5 when all Sr^{2+} ions are immobilized to $\text{HZr}_2(\text{PO}_4)_3$. The immobilization ratio of Sr to $\text{HZr}_2(\text{PO}_4)_3$ rapidly increases from 5 to 10 h and becomes constant over 0.31 for more than 10 h. The fact that the immobilization ratio is small as 0.23 at 5 h is considered to be related to the formation of $\text{Zr}_3(\text{PO}_4)_4$ as pointed in Fig. 3.

Fig. 4 also shows the leaching rate of Sr from its immobilized $\text{HZr}_2(\text{PO}_4)_3$ as a function of the processing time. The leaching rate is the weight of Sr leached from its immobilized $\text{HZr}_2(\text{PO}_4)_3$ divided by the surface area, where the Sr immobilized $\text{HZr}_2(\text{PO}_4)_3$ was kept with 1 M HCl in an autoclave for 24 h at 160 °C. The leaching rate of Sr linearly increases with increasing the processing time from 10 to 72 h. The value of the leaching rate for 5 h relatively departs from the linear relationship in the range from 10 to 72 h, and it would be due to the immobilization ratio for 5 h itself is small as 0.23% and 25% less than that for more than 10 h as 0.31. The linear relationship except for 5 h datum suggests that the immobilization site size becomes slightly larger with longer processing time. However, the size change of sites does not reflect the cell volume change, where the cell volume was calculated by XRD measurement and could be considered as constant in the range from 1.558 to 1.562 nm^3 for any processing time.

3.2. Temperature effect in the thermal decomposition of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$

3.2.1. Formation of $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$

Fig. 5 shows the XRD results for $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ and thermal treatment $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at different temperatures from 400 to 800 °C, where $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ is produced by a hydrothermal synthesis for 22 h. Considering that the thermal treatment of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ promotes the change from $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ to $\text{HZr}_2(\text{PO}_4)_3$, the product may be better regarded as $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$. The peak intensities at 400 and 500 °C are almost the same as that of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ with no thermal treatment. Then, the peak intensity decreases above 600 °C and almost disappears at 800 °C. It indicates that the crystal structure of zirconium phosphate becomes disordered with increasing the treatment temperature.

The cell volume of $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ was calculated by the XRD pattern and plotted as a function of thermal treatment temperature in Fig. 6 together with the cell volume data of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ and $\text{HZr}_2(\text{PO}_4)_3$ calculated by the lattice constants of JCPDS. The cell volume decreases with increasing temperature in the process from $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ to $\text{HZr}_2(\text{PO}_4)_3$. It indicates that $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ produced by a thermal decomposition of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at 575 °C and 600 °C becomes nearly equal to $\text{HZr}_2(\text{PO}_4)_3$. This is consistent with the result of the thermo gravimetric curve of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ in Fig. 2.

3.2.2. Performance of immobilization ratio and leaching rate of Sr

The mixture of $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ and aqueous solution of $\text{Sr}(\text{NO}_3)_2$ with the molar ratio of Sr against $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ as 0.5 was treated in the autoclave at 250 °C for 20 h. The immobilized rate of Sr to $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ was measured by X-ray fluorescence spectroscopy, where $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ was produced by the thermal treatment of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ at different temperatures in the range from 400 to 800 °C. The immobilization ratio of Sr increases with increasing temperature and becomes largest at 575 °C as shown in Fig. 7. $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ is produced by the thermal treatment of $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ from 450 to 550 °C, and the immobilization ratio of Sr becomes larger with decreasing the number of NH_4 sites of $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$. A small decrease in the immobilization ratio above 600 °C would be due to the disorder of the crystal structure of $\text{HZr}_2(\text{PO}_4)_3$ as shown in Fig. 5.

Fig. 7 also shows the leaching rate of Sr from its immobilized $\text{H}_x(\text{NH}_4)_{1-x}\text{Zr}_2(\text{PO}_4)_3$ or $\text{HZr}_2(\text{PO}_4)_3$ as a function of the decomposi-

tion temperature in the range from 400 to 800 °C. The leaching rate of Sr monotonically decreases from 450 to 550 °C and increases above 600 °C. $H_x(NH_4)_{1-x}Zr_2(PO_4)_3$ is produced by the thermal treatment of $NH_4Zr_2(PO_4)_3$ from 450 to 550 °C, and the leaching rate of Sr becomes smaller with decreasing the number of NH_4 sites of $H_x(NH_4)_{1-x}Zr_2(PO_4)_3$. It is considered that the immobilization site size of $H_x(NH_4)_{1-x}Zr_2(PO_4)_3$ becomes slightly smaller with decreasing the number of NH_4 site and increasing the number of H site. The ion radius of NH_4^+ , Sr^{2+} , H^+ is 0.145, 0.116 and 0.03 nm, respectively. The reason why the Sr leaching rate increases above 600 °C would be due to the disorder of the crystal structure of $HZr_2(PO_4)_3$.

4. Conclusions

- (1) $HZr_2(PO_4)_3$ is prepared by thermal decomposition of $NH_4Zr_2(PO_4)_3$ at 575 °C, where $NH_4Zr_2(PO_4)_3$ is obtained by hydrothermal synthesis with different processing times from 5 to 72 h. The XRD results show that only the bands due to $HZr_2(PO_4)_3$ are observed for more than 10 h and become stronger for more than 15 h. The immobilized ratio of Sr to $HZr_2(PO_4)_3$ is 0.23 for 5 h, then constant as 0.31 for more than 10 h. The leaching rate monotonically increases with increasing the processing time for the hydrothermal synthesis.

- (2) $H_x(NH_4)_{1-x}Zr_2(PO_4)_3$ is prepared by thermal decomposition of $NH_4Zr_2(PO_4)_3$ at different temperatures from 400 to 800 °C, where $NH_4Zr_2(PO_4)_3$ was obtained in advance by hydrothermal synthesis for 22 h. The XRD results show that the band peak is almost constant below 500 °C, then rapidly decrease above 600 °C and almost disappear at 800 °C. The cell volume of $H_x(NH_4)_{1-x}Zr_2(PO_4)_3$ decreases with increasing the decomposition temperature and becomes almost equal to that of $HZr_2(PO_4)_3$ above 575 °C. The performance of immobilization ratio of Sr and leaching rate is good when the decomposition temperature is 575 °C.

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