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INCORPORATION OF CESIUM ION FROM $CsNO_3$ INTO $NH_4Zr_2(PO_4)_3$ STUDIED BY TG-IR SPECTROSCOPY AND POWDER XRD

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The incorporation mechanism of Cs^+ ions from $CsNO_3$ into $NH_4Zr_2(PO_4)_3$ was studied on a mixture of $CsNO_3$ and $NH_4Zr_2(PO_4)_3$ by powder X-ray diffraction analysis and by monitoring off-gases released from the mixture upon heating with a thermogravimetry analyzer connected to an infrared spectrometer. With increasing temperature, the decomposition of $CsNO_3$ first started, followed by the conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ with the release of NH_3. At around 500°C, the Cs $Zr_2(PO_4)_3$ phase started to appear as a result of the H^+/Cs^+ ion exchange. No Cs^+ ion loss was observed at thermal treatment temperatures of 900°C and lower.

Keywords: *$HZr_2(PO_4)_3$, immobilization of cesium, $NH_4Zr_2(PO_4)_3$, radioactive cesium, TG analyzer connected to IR spectrometer*

Introduction

Cesium-137, a β–emitter with the half life of 30.2 years, can cause risks not only from internal exposures, but also from external gamma exposure that is associated with the gamma ray from its decay product, barium-137m with the half-life of about 2.6 min. It is a major radionuclide in spent nuclear fuels; a high level radioactive waste from the reprocessing of spent commercial nuclear reactor fuels, and therefore must be immobilized and stored for a long time. At present, borosilicate glasses are the generally accepted first generation waste form [1]. A drawback of the immobilization of cesium with borosilicate glasses is the requirement of thermal treatment at over 1000°C, which can cause partial evaporation of radioactive cesium. In addition, they are not very stable against the attack by acids and alkalis.

A wide variety of synthetic inorganic compounds have been found to exhibit ion-exchange properties [2–4]. A promising alternative of borosilicates is ceramics, and zirconium phosphates are from among them; they require lower thermal treatment temperatures than borosilicates and, in addition, have great stability towards ionizing radiation, high temperatures and most chemical reagents [5]. There have been researches related to the immobilization of cesium by using sodium zirconium phosphate ($NaZr_2(PO_4)_3$; abbreviated hereafter as NZP) and zirconium phosphate ($HZr_2(PO_4)_3$; abbreviated hereafter as HZP) as immobilization matrix [6, 7]. Szirtes *et al.* carried out the thermal analysis on composite γ-zirconium phosphate-silica and found that the water loss process was very slow because of the placing of bilamellar species in the composite [8]. In this paper, incorporation process of cerium ions from cesium nitrate into ammonium zirconium phosphate ($NH_4Zr_2(PO_4)_3$; abbreviated hereafter as AZP), which has also been studied as lithium isotope separator [9, 10], is investigated by powder X-ray diffraction (XRD) analysis and by monitoring off-gases released from the mixture upon heating.

Experimental

Rhombohedral AZP, the host material of Cs^+ ion incorporation, and cesium nitrate ($CsNO_3$) were obtained from Daiichi Kigenso Chem. Ind., Co. A SEM photograph of AZP crystals is shown in Fig. 1.

The XRD patterns were recorded using a Rigaku RINT2100V/P X-ray diffractometer with the CuK_α radiation (λ= 1.54056 Å) in the 2θ range of 5 to 70° at room temperature. Each sample subjected to the XRD measurement was thermally treated at specified temperature for ten hours before measurement. The identification of the gases released during TG measurements (TG-IR analysis) was carried out with

Fig. 1 A SEM photo of AZP crystals

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an apparatus consisting of a PerkinElmer Spectrum 2000 IR spectrometer and a PerkinElmer TGA7 TG analyzer, in which gases released from a sample placed in the ceramics pan of the TG analyzer were directly introduced to the gas cell of the IR spectrometer by means of a N_2 flow without contacting the air. The TG-IR analysis was carried out on AZP, $CsNO_3$ and their mixtures between room temperature and 800°C. The heating rate was 50°C min^{-1} and the mass of a sample was around 5 mg. The scanning electron microscopy (SEM) analysis was carried out with a Hitachi S-4500 scanning electron microscope. IR spectra were recorded with a PerkinElmer 1650 IR spectrometer or the spectrum 2000 IR spectrometer using the KBr pellet technique.

The Cs content of a thermally-treated product of an AZP/$CsNO_3$ mixture with the mole ratio of 1.0:0.4 was determined as follows: an aliquot of the product was first decomposed with HF solution, and then a saturated boric acid solution was added. The Cs concentration of the resultant solution, from which the Cs content of the thermally-treated product was calculated, was determined by flame photometry with a Daini Seikosha SAS-727 atomic absorption spectrometer after appropriate dilution with water.

Results and discussion

Conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$

The thermal conversion of rhombohedral AZP to rhombohedral HZP is expressed as $NH_4Zr_2(PO_4)_3 \rightarrow HZr_2(PO_4)_3 + NH_3$ [11, 12].

The results of TG-IR analysis on AZP is depicted in Fig. 2. The IR absorbance profiles of NH_3 (monitored by the absorbance at 966 cm^{-1}), NO (monitored by the absorbance at 1917 cm^{-1}), N_2O (monitored by the absorbance at 2241 cm^{-1}) and H_2O (monitored by the absorbance at 1597 cm^{-1}), and the mass loss of the AZP sample are given as functions of temperature. The release of NH_3 started being observed at around 350°C and continued till around 750°C, accompanied by the release of H_2O. The mass loss corresponding to the release of NH_3 and H_2O was observed nearly in the same temperature range. These observations indicated that the AZP phase survived up to around 750°C. No release of NO and N_2O was observed, which meant that no oxidation of NH_3 occurred under the adopted experimental conditions [13].

AZP was thermally treated at temperatures between 300 and 600°C for ten hours and subjected to XRD analysis. The XRD pattern of thermally treated product of AZP at each thermal treatment temperature, as well as that of AZP (JCPDS No. 38-0004), is shown in the 2θ range of 10 to 40° in Fig. 3. Although the XRD patterns of AZP and HZP (JCPDS No. 38-0004) were very similar to each other, they were distinguishable by the peak positions at around 2θ=19 and 30°; both the peaks slightly shifted to the larger degree side with the progress of the conversion of AZP to HZP. Practically the best and simplest way to trace the conversion was, in the present case, to check the differences in 2θ value of the peaks at around 2θ=19 and 20° and at around 2θ=28 and 30°; the former difference became smaller and the latter larger with progressing conversion of AZP to HZP. These data are listed in Table 1. Figure 3 and Table 1 show that the conversion of AZP to HZP has already started at 300°C and has continued up to 560°C. It has been over at 600°C.

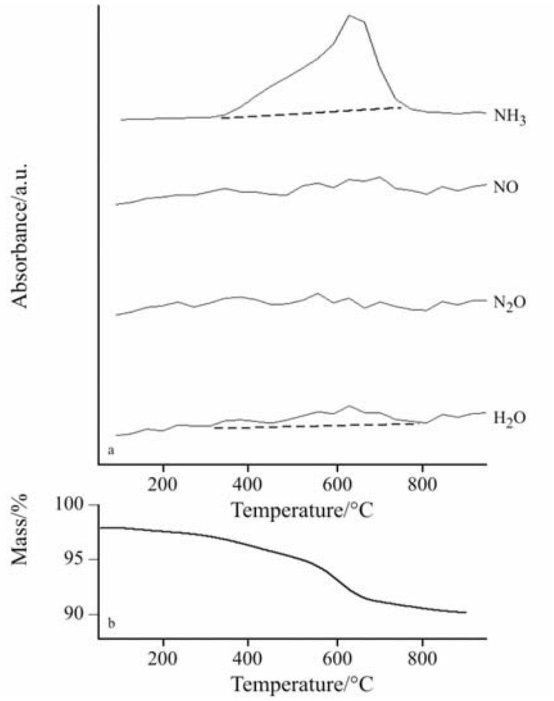

Fig. 2 a – IR absorbance profiles of off-gases and b – a TG graph of AZP

The temperature range in which the AZP phase survived is different between Figs 2 and 3. The XRD analysis showed that the AZP phase disappeared by 600°C, while the TG-IR analysis suggested that it survived up to around 750°C. This difference must be ascribed to the difference in the experimental condition; while the XRD measurements were carried out for the samples well thermally treated, the TG-IR analysis was performed at a fast heating rate of 50°C min^{-1}.

Incorporation of cesium into $NH_4Zr_2(PO_4)_3$

The results of TG-IR analysis on the mixture of AZP and $CsNO_3$ with the molar ratio of 1.0:0.4 is depicted in Fig. 4. With increasing temperature, NO_2 (monitored by the absorbance at 1629 cm^{-1}) and N_2O,

Table 1 Changes in peak position difference in XRD pattern upon heating $NH_4Zr_2(PO_3)_4$ powders

Temperature of thermal treatment/°C	$\Delta 2\theta_{20}{}^{*}$	$\Delta 2\theta_{30}{}^{**}$
none	1.58	2.26
300	1.54	2.34
400	1.36	2.40
500	1.26	2.52
560	1.10	2.66
600	1.08	2.62

*2θ value of the peak at around 2θ=20° minus that of the peak at around 2θ=19°
**2θ value of the peak at around 2θ=30° minus that of the peak at around 2θ=28°

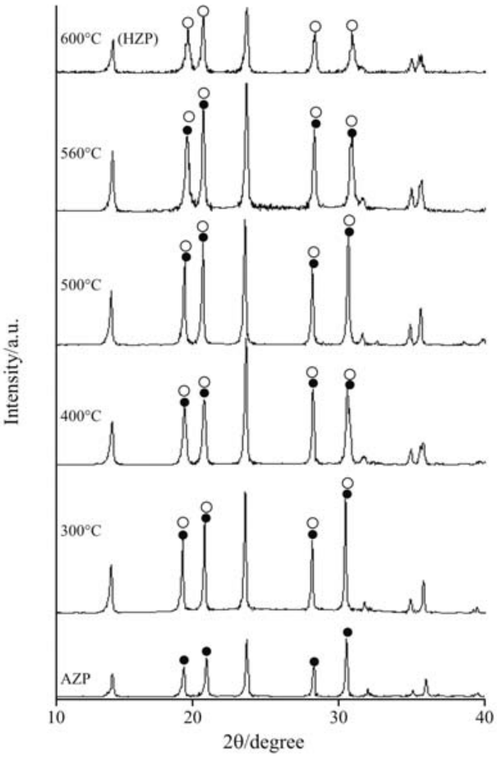

Fig. 3 XRD patterns of AZP and its thermally-treated products. Temperature attached to each XRD pattern is the one at which AZP was thermally treated for 10 h. ● – peaks ascribable to AZP; ○ – peaks ascribable to HZP

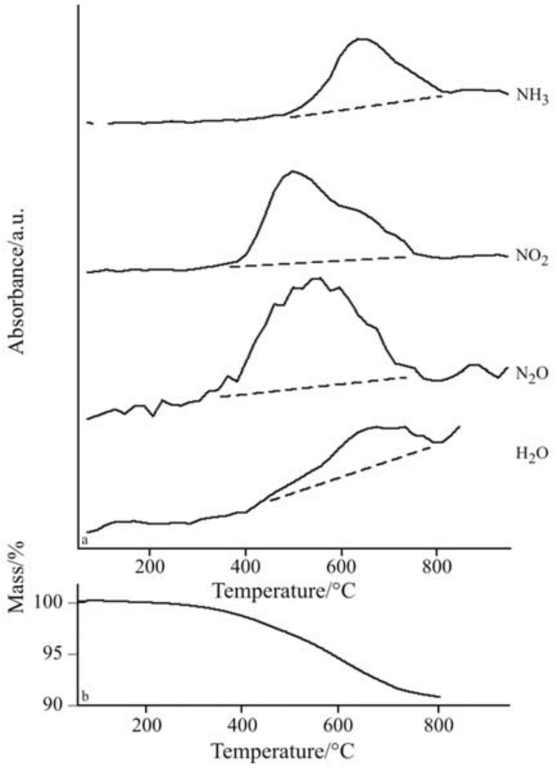

Fig. 4 a – IR absorbance profiles of off-gases and b – a TG graph of a mixture of AZP and $CsNO_3$ with the molar ratio of 1.0:0.4

the decomposition products of $CsNO_3$, started being released at around 400°C and their release continued till around 750°C, which indicated that the decomposition of $CsNO_3$ started at around 400°C. The release of NH_3 and H_2O from AZP was observed in the temperature range of around 450 to 800°C. The observation that the release of NO_2 and N_2O started and ended earlier than that of NH_3 and H_2O indicated that the decomposition of $CsNO_3$ started at lower temperature than the commencement of the conversion of AZP to HZP and that it ended at lower temperature than the completion of the conversion. Comparison of Figs 2 and 4 reveals that the start of the NH_3 and H_2O release occurred at a lower temperature on pure AZP than on the mixture of AZP and $CsNO_3$, indicating the obstruction of the AZP-to-HZP conversion by $CsNO_3$.

A mixture of AZP and $CsNO_3$ with the molar ratio of 1.0:0.4 was thermally treated at temperatures between 300 and 750°C for 10 h. The selected XRD patterns of the mixture treated between 420 and 580°C are shown in the 2θ range of 5 to 40° in Fig. 5. The peaks ascribable to $CsNO_3$ are observed at around 2θ=20, 29 and 35° (JCPDS No. 09-0403). With increasing temperature, these peaks became smaller. Figure 5 shows that the $CsNO_3$ crystal survived up to 500 or 510°C in the AZP/$CsNO_3$ mixture in spite of its reported melting point of 414°C. The XRD patterns of AZP, HZP and $CsZr_2(PO_4)_3$ (JCPDS No. 34-0196; abbreviated hereafter as CsZP) are very similar to each other and difficult to distinguish. A small shoulder observed on the larger 2θ side of the peak at around 2θ=19° at the thermal treatment temperature of 480°C is probably due to the existence of the HZP phase in the mixture that was converted from the AZP phase with the release of NH_3. It is thus suggested that the conversion of AZP to HZP started at around 480°C. That is, it started at a higher temperature in the AZP/$CsNO_3$ mixture than in pure AZP. A practical way to know the formation of the CsZP phase, which

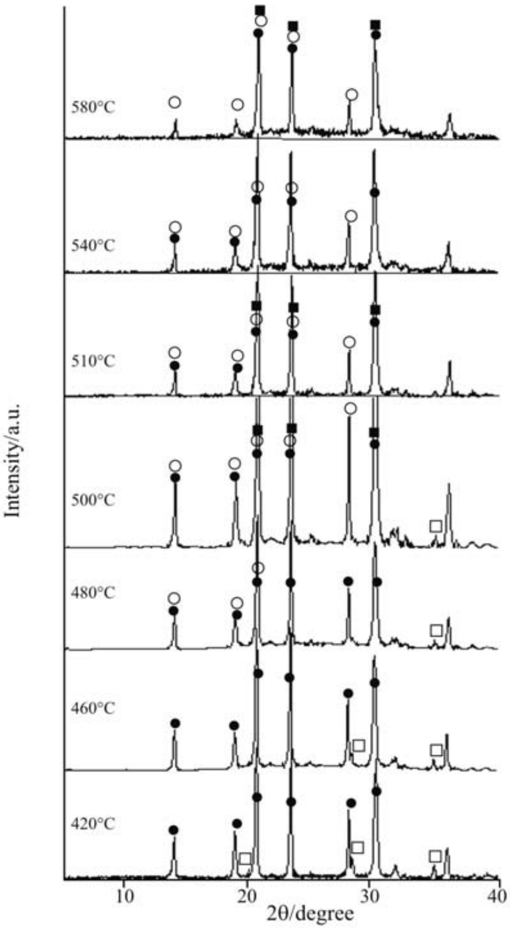

Fig. 5 XRD patterns of a 1.0:0.4 mixture of AZP and $CsNO_3$. Temperature attached to each XRD pattern is the one at which the mixture was thermally treated for 10 h. ● – peaks ascribable to AZP; ○ – peaks ascribable to HZP; □ – peaks ascribable to $CsNO_3$; ■ – peaks ascribable to CsZP

is converted from HZP through the H^+/Cs^+ ion exchange, is to compare the relative peak height at around 2θ=21 and 23°; the peak height at around 2θ=21° is about the same as or higher than that of the peak at around 2θ=23° for AZP and HZP, while the former peak is lower than the latter for CsZP under the present experimental conditions. According to this criterion, the CsZP phase started to appear in the XRD pattern at 500°C. The AZP phase survived even at 580°C, which was confirmed by the IR measurement of the AZP/$CsNO_3$ mixture thermally treated at 580°C shown in Fig. 6.

Table 2 summarizes the amounts of Cs found in the thermally-treated products relative to those of the AZP/$CsNO_3$ mixtures before the thermal treatment, i.e., the degrees of Cs solidification. As can be seen in the table, no Cs loss is observed upon thermal treatment up to 900°C within experimental uncertainty. At 1000°C, a small portion of Cs may be lost by thermal treatment. We also would like to note that XRD analysis revealed the existence of the $Zr_2P_2O_7$ phase (JCPDS No. 24-1490) in addition to those of HZP and CsZP in the thermally-treated products at 900°C or higher. Thus, it is recommended that AZP/$CsNO_3$ mixtures should be thermally treated at temperatures between 600 and 900°C for the effective solidification of Cs with AZP.

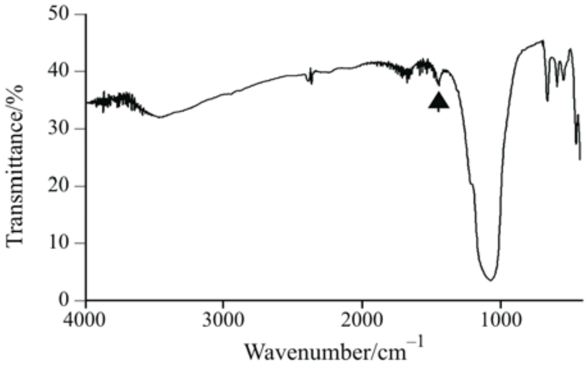

Fig. 6 An IR spectrum of the AZP/$CsNO_3$ mixture thermally treated for 10 h at 580°C. The peak at around 1420 cm^{-1} indicated by an arrow shows the existence of NH_4^+

Table 2 The degree of Cs solidification

Temperature of thermal treatment/°C	The degree of Cs solidification/%
600	99.7
750	99.8
900	99.9
1000	98.6

Conclusions

To summarize, we make the following statements: With heating a 1.0:0.4 mixture of AZP/$CsNO_3$ crystals, the decomposition of $CsNO_3$ started first, followed by the commencement of the conversion of AZP to HZP. The CsZP phase then started to be formed from the HZP phase through the H^+/Cs^+ ion exchange at around 500°C. Cs^+ ions were thus incorporated into the crystal lattices of HZP, forming the CsZP phase. No Cs^+ ion loss was observed at thermal treatment temperatures of 900°C and lower within the experimental uncertainty.

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