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Short communication

Synthesis and thermal expansion of (V, P, Nb)-replaced pollucite

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Abstract

Pollucite compounds in which tetrahedral cations are partially replaced with V, P or Nb were synthesized by a solid-state reaction. An amorphous phase was recognized by X-ray diffractometry for all the above pollucite compounds when mixed raw powders were preliminarily heated at 600 °C to decompose $CsNO_3$ as a Cs source. Then V-replaced, Nb-replaced, and P-replaced pollucite compounds began to crystallize by heating at 550, 800, and 1000 °C, respectively. Finally, single phases of these compounds were synthesized at 700, 1000, and 1200 °C, respectively. The V-replaced pollucite compound $Cs_{0.7}V_{0.1}Al_{0.8}Si_{2.1}O_6$ exhibited the lowest thermal expansion in the range of 25–500 °C at which its thermal expansion coefficient was $0.7 \times 10^{-6}\,K^{-1}$, while the P-replaced pollucite compound $Cs_{0.7}P_{0.1}Al_{0.8}Si_{2.1}O_6$ and the Nb-replaced pollucite compound $Cs_{0.7}Nb_{0.1}Al_{0.8}Si_{2.1}O_6$ showed thermal expansion coefficients of $1.9 \times 10^{-6}\,K^{-1}$ and $1.4 \times 10^{-6}\,K^{-1}$ in the range of 25–500 °C, respectively. It was considered that such an excellent low thermal expansion coefficient of the synthesized V-replaced pollucite was due to the ionic radius of V^{5+} being between those of Al^{3+} and Si^{4+} in the aluminosilicate framework of pollucite compounds.
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Keywords: C. Thermal expansion; D. Silicate; Solid state reaction

1. Introduction

Pollucite, $CsAlSi_2O_6$, is an aluminosilicate compound with a cubic symmetry and a three-dimensional framework structure composed of 48 $(Si,Al)O_4$ tetrahedra with 16 Cs^+ ions occupying large 12-coordinated cavities in the unit cell [1–3]. From the viewpoint of the immobilization of Cs^+ ions in materials, pollucite-related compounds [4,5] have been noted as good candidates for trapping radioactive Cs isotopes in nuclear waste. Pollucite has a melting point of ca. 1900 °C [6] and maintains its cubic structure up to higher temperatures, which means that pollucite has excellent thermal stability for Cs immobilization. On the other hand, pollucite with a stoichiometric chemical composition inhibits rapid thermal expansion up to 200 °C of which the thermal expansion coefficient (TEC) is ca. $1.0 \times 10^{-5}\,K^{-1}$ [1,3,7,8], suggesting that thermal expansion causes Cs leaching from pollucite owing to the enlargement of cages consisting of an aluminosilicate framework in which Cs is trapped despite its TEC in the range of 200–500 °C being nearly zero [1,3,7,8].

As for their other applications, low thermal-expansion-pollucites are attractive candidates for thermal-shock-resistance materials [6] because of their high melting point and cubic symmetry. For instance, a pollucite sintered body [9–11] does not produce microcracks owing to thermal stress from anisotropic thermal expansion on heating and cooling as does cordierite [12,13] with a hexagonal symmetry, which is known as a low-thermal-expansion material. However, lowering the rapid thermal expansion of pollucite in the range of RT-200 °C is necessary for the development of low-thermal-expansion materials. Our previous study revealed that the Cs-deficient pollucite $Cs_{0.9}Al_{0.9}Si_{2.1}O_6$ synthesized by decreasing Cs^+ ion concentration and increasing Si/Al ratio has a low TEC of ca. $2.0 \times 10^{-6}\,K^{-1}$ in the wide temperature range from RT to 1000 °C [7,8,14,15], which means that the chemical composition of pollucite strongly affects its thermal expansion property [16–18].

Therefore, from the viewpoint of Cs^+ ion concentration, the replacement of cations in $(Si,Al)O_4$ tetrahedra of the aluminosilicate framework of pollucite with a pentavalent metal is expected to lower the TEC of pollucite. This is because the replacement of a pentavalent metal produces positively charged tetrahedra, resulting in a decrease in the Cs^+ ion concentration of pollucite. Until now, there has been no report on the thermal expansion properties of pollucite compounds

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with pentavalent metal as tetrahedral cations. In this study, we aim to synthesize pollucite compounds in which tetrahedral cations are partially replaced with V, P or Nb and to investigate the thermal expansion behavior of the synthesized pollucite compounds.

2. Experimental procedure

Commercially available Al_2O_3 sol (Nissan Chemical, Aluminum sol 200, Japan), SiO_2 sol (Nissan Chemical, Snotex O, Japan), NH_4VO_3 powder (Wako Chemical, Japan), $NH_4H_2PO_4$ powder (Wako Chemical, Japan), $NbCl_5$ powder (Wako Chemical, Japan), and $CsNO_3$ powder (High Purity Chemical, Japan) were used as starting raw materials. NH_4VO_3 and $NH_4H_2PO_4$ powders were dissolved in distilled water, and the pH of the resulting solutions was adjusted to 5.4 by adding NH_3 water. The pH of both the of Al_2O_3 and SiO_2 sols was also adjusted to 5.4 [8]. $NbCl_5$ powder was dissolved in ethanol. Then, the prepared solutions were mixed and stirred at RT for 20 h, followed by solvent removal using a rotary evaporator to obtain a dried gel mixture. Here, the mixing molar ratio of Al:Si:V or P or Nb was 0.8:2.1:0.1. The prepared gel mixture was calcined in an Al_2O_3 crucible at 600 °C in air for 20 h. Then, the prepared fine powders were mixed with $CsNO_3$ powder by ball milling in ethanol for 24 h. Ethanol from the obtained sol mixture was then removed by evaporation. Here, the mixing molar ratio of Cs:Al:Si:V or P or Nb was 0.7:0.8:2.1:0.1. The mixed powders were heated at 550–700 °C for 2–20 h in the case of the V-replaced pollucite, at 600–1200 °C in the case of the P-replaced pollucite, and at 600–1000 °C in the case of the Nb-replaced pollucite for 10–20 h.

X-ray diffractometry (XRD; Rad-C, Cu Kα, Rigaku, Japan) was used to identify crystalline phases. Fourier transform infrared spectroscopy (FT-IR; IRPrestige-21, Shimadzu, Japan) with the KBr method was used to examine IR absorption spectra after 256 scans at 2 cm^{-1}. The thermal expansion properties of the synthesized compounds from 30 to 500 °C were determined by high-temperature XRD (HTXRD; MXP18VA, Cu Kα, Mac Science, Japan). A powder sample for measurement was set in a Pt holder in contact with the thermocouple in the HTXRD apparatus. The sample was measured at 30, 100, 200, 300, 400 and 500 °C at a heating rate of 5 °C min^{-1}, and then the measurement was performed at each temperature after holding for 5 min. The lattice parameters at each temperature of the synthesized pollucite compounds were refined by the least-squares method, using the five diffraction peaks of the (3 3 2), (4 4 0), (6 1 1), (7 2 1) and (6 5 1) planes referring to the JCPDS card of 29-0407, which were collected at a scanning rate of 1° min^{-1}. The diffraction peak positions were corrected using Si powder as the external standard, and then the lattice parameters at each temperature were used to calculate the thermal expansion ratio of the synthesized pollucite compounds.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Cs_{0.7}V_{0.1}Al_{0.8}Si_{2.1}O_6$ (hereafter, 71CVAS) powders obtained by multistep heat treatment at 600 °C for 20 h (b) for the decomposition of $CsNO_3$, at 550 °C for 20 h (c) after the heat treatment (b), at 700 °C for 10 h (d) and at 700 °C for 2 h (e), and of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a). The broad peak due to an amorphous phase (a) shifted to a higher 2θ angle when the mixed powder with $CsNO_3$ was heated at 600 °C for 20 h (b). The amorphous phase of the heated powder (b) began to crystallize by heating at 550 °C for 20 h (c). Furthermore, the residual amorphous phase in the heated powder (c) disappeared by repeating the heat treatment at 700 °C for 2–10 h, which led to the production of a single phase of 71CVAS.

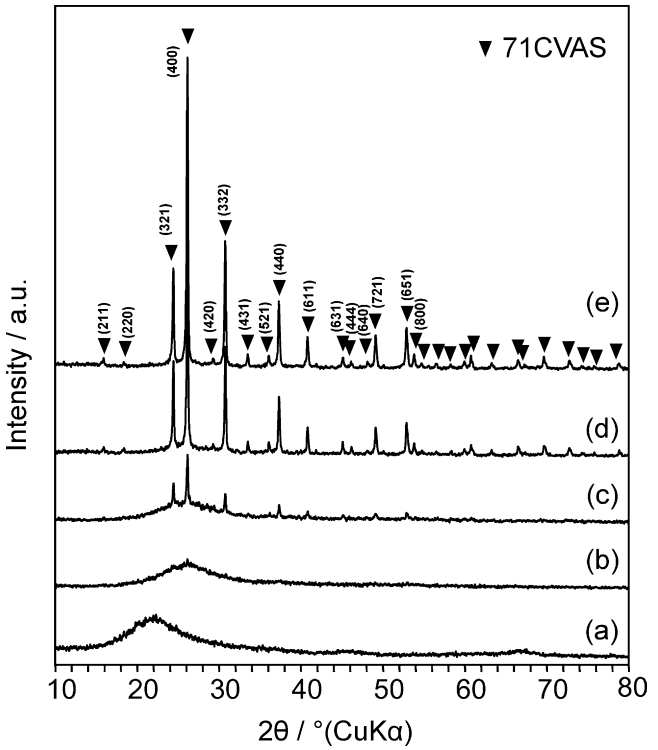

Fig. 1. XRD patterns of 71CVAS powders heated at 600 °C for 20 h (b), 550 °C for 20 h (c), 700 °C for 10 h (d), and 700 °C for 2 h (e), and XRD pattern of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a).

The FT-IR spectra of the powder heated at 600 °C for 20 h (b), 550 °C for 20 h (c) and 700 °C for 2 h (d), and of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a), were investigated. The results are shown in Fig. 2. As for the absorption peaks of the FT-IR spectra for the 71CVAS single-phase powder, the peaks at around 1050 cm^{-1} were assigned to the Si–O–Si(Al) asymmetric stretching vibration ν_{as} [19,20]. The peaks at around 780 and 740 cm^{-1} were assigned to the Si–O–Si and Si–O–Al symmetric stretching vibrations ν_s [19,20], respectively. Both peaks at around 620 and 430 cm^{-1} were assigned to the Si–O–Si(Al) bending vibration ν_d [19,20]. The absorption peak of the Si–O–Si asymmetric stretching vibration ν_{as} at around 1100 cm^{-1} due to SiO_2 [21] shifted to the lower-frequency side from around 1100 to 1050 cm^{-1} when the mixed raw powder with $CsNO_3$ was heated at 600 °C for 20 h, as shown in Fig. 2(b). The peak shift means that $(Si,Al)O_4$ tetrahedra were produced [22] via the thermal decomposition of the mixed powder including $CsNO_3$,

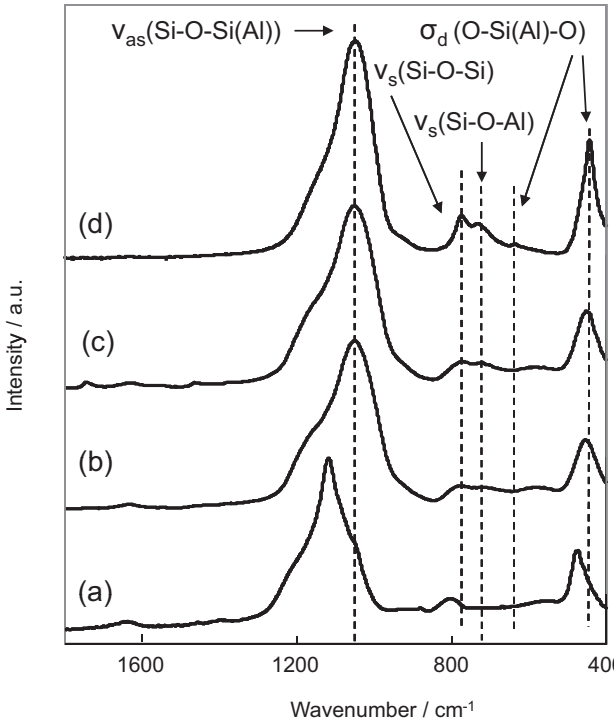

Fig. 2. FT-IR spectra of 71CVAS powders heated at 600 °C for 20 h (b), 550 °C for 20 h (c), and 700 °C for 2 h (d), and XRD pattern of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a).

Al_2O_3 and SiO_2, which resulted in the production of the aluminosilicate framework structure of pollucite compounds [20]. Moreover, the above peak shift due to the production of the $(Si,Al)O_4$ framework structure also suggests that the amorphous phase shown in Fig. 1(b) consisted of very fine crystals of 71CVAS.

Fig. 3 shows the XRD patterns of $Cs_{0.7}P_{0.1}Al_{0.8}Si_{2.1}O_6$ (hereafter, 71CPAS). The 71CPAS phase began to crystallize by heating at 1000 °C for 20 h (c) and the residual amorphous phase in the heated powders disappeared with an increase in the heat-treatment temperature. Finally, a 71CPAS single phase was obtained at 1200 °C for 20 h (e). Fig. 4 shows the XRD patterns of $Cs_{0.7}Nb_{0.1}Al_{0.8}Si_{2.1}O_6$ (hereafter, 71CNbAS). A slight crystallization of the 71CNbAS phase occurred at 800 °C for 10 h (c), and the residual amorphous phase in the heated powders disappeared with an increase in heat-treatment temperature. Finally, a 71CNbAS single phase was obtained at 1000 °C for 10 h (e). Thus, both 71CPAS and 71CNbAS single phases were synthesized by multistep heat treatment, similarly to the 71CVAS phase. Of the synthesized 71CVAS, 71CPAS and 71CNbAS, 71CVAS had the lowest crystallization temperature and 71CPAS had the highest. Thus, it was shown that the crystallization temperatures of the synthesized 71CVAS, 71CPAS and 71CNbAS was not dependent on the ionic radius of the tetrahedral cations V^{5+}, P^{5+} and Nb^{5+}, namely, 0.355, 0.17 and 0.48 Å, respectively [23]. As the ionic radii of Al^{3+} and Si^{4+} were 0.39 and 0.26 Å [23], respectively, it was considered that the replacement of V^{5+} with a closer ionic radius to Al^{3+} and Si^{4+} than to P^{5+} and Nb^{5+}, facilitated the crystallization of the pollucite phase.

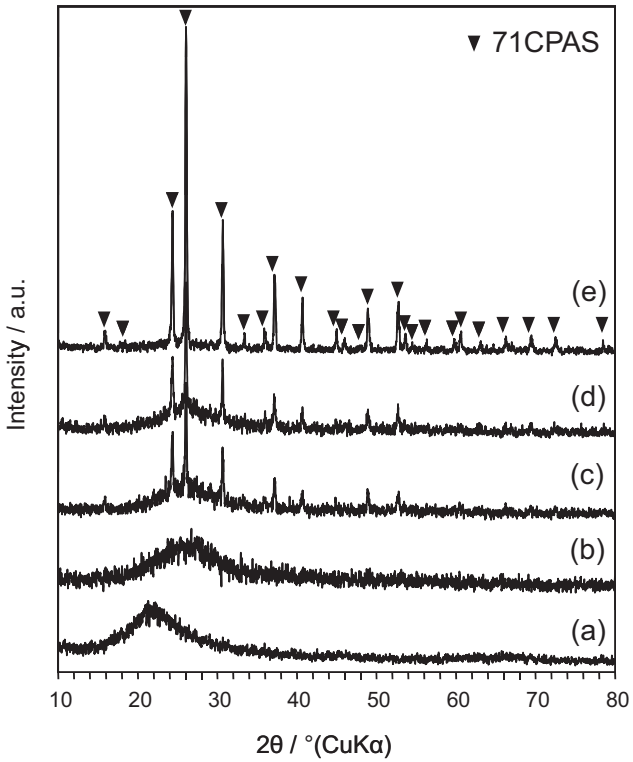

Fig. 3. XRD patterns of 71CPAS powders heated at 600 °C for 20 h (b), 1000 °C for 20 h (c), 1100 °C for 10 h (d), and 1200 °C for 20 h (e), and XRD pattern of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a).

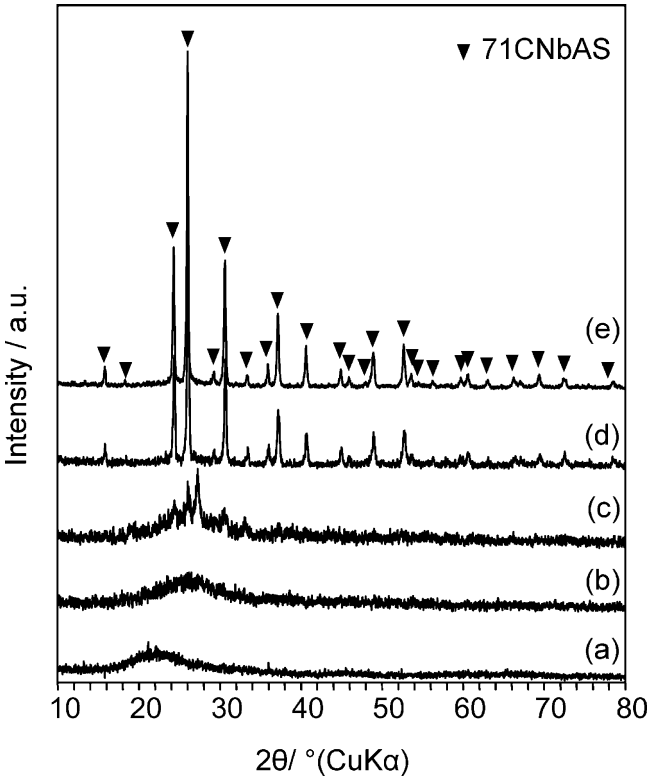

Fig. 4. XRD patterns of 71CNbAS powders heated at 600 °C for 20 h (b), 800 °C for 10 h (c), 900 °C for 10 h (d), and 1000 °C for 20 h (e), and XRD pattern of the powder heated at 600 °C for 20 h before mixing with $CsNO_3$ (a).

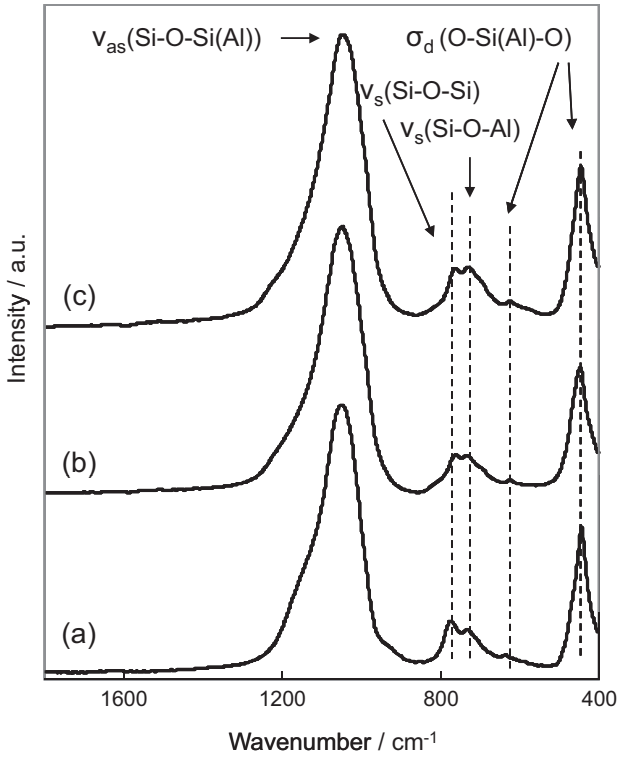

Fig. 5. FT-IR spectra of synthesized pollucite compounds: 71CVAS (a), 71CPAS (b), 71CNbAS (c).

Fig. 5 shows the FT-IR spectra of the synthesized 71CVAS, 71CPAS and 71CNbAS single phases. All the compounds had a distinctive absorption spectrum for pollucite compounds [19]. However, the relative intensity of the absorption peak around 780 cm^{-1} of 71CVAS, which was assigned to the Si–O–Si symmetric stretching vibrations ν_s, was larger than those of 71CPAS and 71CNbAS. Considering that there was almost no difference in the peak intensity at around 780 cm^{-1} between 71CPAS and 71CNbAS, the peculiar peak intensity of 71CVAS should be noted. Since the ionic radius of V^{5+} is between those of Al^{3+} and Si^{4+}, it was considered that positively charged VO_4^+ tetrahedra could be adjacent to negatively charged AlO_4^- tetrahedra, which resulted in an increase of the Si–O–Si bond in pollucite compound only with the replacement of V^{5+}.

The thermal expansion behaviors of 71CVAS, 71CPAS and 71CNbAS are shown in Fig. 6. 71CVAS exhibits the lowest thermal expansion, and 71CPAS exhibits the highest. Additionally, 71CVAS had a nearly zero thermal expansion behavior up to around 200 °C. The mean thermal expansion coefficients of 71CVAS, 71CPAS and 71CNbAS in the range of RT to 500°C were approximately $0.7 \times 10^{-6}\,K^{-1}$, $1.9 \times 10^{-6}\,K^{-1}$ and $1.4 \times 10^{-6}\,K^{-1}$, respectively. It was considered that the ionic radius of V^{5+} (0.355 Å) being between those of Al^{3+} (0.39 Å) and Si^{4+} (0.26 Å) caused a smaller structural distortion in the $(Si,Al,V)O_4$ framework than in that of the $(Si,Al,P)O_4$ and $(Si,Al,Nb)O_4$ frameworks. It has been explained that the larger thermal expansion of pollucite compounds in the range of RT up to around 200 °C is due to a structural change from ''a collapsed form'' with a structural distortion to ''an expanded form'', which occurs with the rotation of $(Si,Al)O_4$ tetrahedra

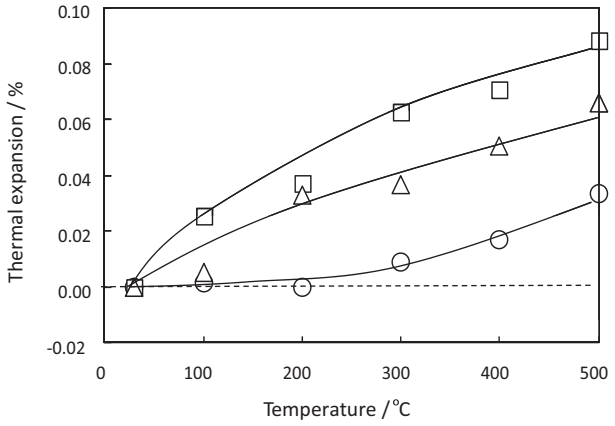

Fig. 6. Thermal expansion behaviors in the range of 30–500 °C of synthesized pollucite compounds: 71CPAS (square), 71CNbAS (triangle), 71CVAS (circle).

[1,3]. Therefore, in the case of 71CVAS, it seemed that a distortion of the framework structure was eased by the replacement of V, accompanied by an increase of the Si–O–Si bond, which results in an ultra low thermal expansion property.

4. Conclusions

V, P and Nb-replaced pollucite compounds were synthesized by multistep heat treatment. Of the synthesized compounds, the V-replaced pollucite 71CVAS had the lowest crystallization temperature and lowest thermal expansion coefficient. 71CVAS showed an almost zero thermal expansion behavior up to around 200 °C. The lower thermal expansion coefficient of 71CVAS was due to the ionic radius of V^{5+} being closer to those of Al^{3+} and Si^{4+} than to those of P^{5+} and Nb^{5+} in tetrahedra of the aluminosilicate framework of pollucite compounds. Thus, it was found that the replacement of V can be used to lower the thermal expansion coefficient of pollucite compounds.

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