Effect of tin substitution on the chemical composition and thermal expansion properties of Zr$_2$SP$_2$O$_{12}$

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**ABSTRACT**

Zr$_{1.8}$Sn$_{0.2}$P$_2$O$_{12.6}$ was prepared using a hydrothermal synthesis method, and its thermal expansion properties were evaluated. The solid solubility limit of Sn was found to be approximately $x = 0.6$, and the substitution of Sn influenced the formation of defects at S sites. All Sn-substituted Zr$_{1.8}$Sn$_{0.2}$P$_2$O$_{12.6}$ samples had smaller coefficients of thermal expansion($\alpha$) than Zr$_2$SP$_2$O$_{12}$. The lowest $\alpha$ value obtained was approximately $-125$ ppm/K for Zr$_{1.8}$Sn$_{0.2}$S$_{0.9}$P$_2$O$_{12.6}$ at 373–453 K. Rietveld analysis revealed that the values of polyhedral volume, bond angle variance, and quadratic elongation in the MO$_6$ octahedron of Zr$_{1.8}$Sn$_{0.2}$P$_2$O$_{12.6}$ were larger than those of Zr$_2$SP$_2$O$_{12}$. From these results, it was suggested that the increase in distortion caused by S vacancies can lead to increase in the lattice volume and control of CTEs.

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1. **Introduction**

Materials with negative coefficients of thermal expansion (CTEs) are widely studied because they can be used to control the thermal expansion of electrical or optical device components [1–7]. It is a commonly accepted theory that negative CTEs are aroused based on two mechanisms. One is a phase transition mechanism, inducing colossal volume shrinkage in a narrow temperature range. The other is a framework-type mechanism, which leads to continuous negative CTEs over a wide temperature range. Materials with negative CTEs can be used as fillers to be mixed with metal or resin with high CTEs [8–10], though for some, care must be taken that they are applied properly because of above-contrast characteristics.

Zr$_2$SP$_2$O$_{12}$ has been reported to have unique negative thermal expansion behavior involving both of the abovementioned mechanisms [11]. Zr$_2$SP$_2$O$_{12}$ has the Na super-ionic conductor (NaSICON) structure with the space group $R-3c$. It exhibits a framework-type mechanism at temperatures below 393 K or above 453 K and an isomorphic phase transition mechanism at 393–453 K. The volumetric CTE of $\alpha$-Zr$_2$SP$_2$O$_{12}$ is approximately $-70$ ppm/K from 393 to 773 K. In addition, its CTE value can be decreased by reducing the sulfur content that it contains by firing at a higher temperature. The CTE of $\alpha$-Zr$_2$S$_{0.9}$P$_2$O$_{12.6}$ is approximately $-108$ ppm/K, which is still a low value compared with that of conventional negative thermal expansion materials. Remarkably, this result suggests that the phase transition is related to the deformation of the ZrO$_6$ octahedron. To verify this hypothesis, the partial substitution of the Ti atoms for the Zr atoms was previously carried out [12]. In this previous study, Ti-substituted $\alpha$-Zr$_{2-x}$Ti$_x$S$_{0.9}$P$_2$O$_{12.6}$ was prepared, and the thermal expansion behavior was estimated. It was revealed that Ti substitution had two effects: the reduction of the lattice constant due to the difference in the ionic radius and the inhibition of lattice constant change during phase transition. However, these results do not necessarily lead to improvements in thermal properties, and the CTE value only changed from $-108$ to $-117$ ppm/K ($\alpha$-Zr$_{1.62}$Ti$_{0.38}$S$_{0.9}$P$_2$O$_{12.6}$).

The present paper reports a further attempt at improving the thermal properties of Zr$_2$SP$_2$O$_{12}$ based on the substitution of the Sn atom for the Zr atom instead of the Ti atom. This approach was chosen because Sn is adequate in terms of ionic radii as well as its valence and coordination number. The thermal expansion behavior of the obtained $\alpha$-Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12.6}$ was evaluated.

2. **Materials and methods**

2.1. **Sample preparation**

$\alpha$-Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12.6}$ was synthesized from (NH$_4$)$_2$HPO$_4$ (FUJIFILM Wako Pure Chemical Corp., Japan), ZrOCl$_2$·8H$_2$O (FUJIFILM Wako Pure Chemical Corp., Japan), SnO$_2$ (Kanto Chemical Co., Inc., Japan), and H$_2$SO$_4$ (FUJIFILM Wako Pure Chemical Corp., Japan) using a hydrothermal reaction route. Initially, the abovementioned chemicals were stirred in deionized water for
90 min. The obtained precursor was then sealed in a Teflon-lined autoclave and reacted hydrothermally at 453 K for 12 h. The resulting product was calcined at 698–1,273 K for 4 h in air.

2.2. Characterization and evaluation

The chemical composition of the obtained substance was estimated by inductively coupled plasma optical emission spectroscopy (ICP-OES; 5100 VDV, Agilent Technologies Inc., United States). Stock solutions (100 mg/L) of zirconium, tin, sulfur, and phosphorus (FUJIFILM Wako Pure Chemical Corp., Japan) were used to produce the standards for the ICP-OES calibration curves. The obtained powders were dissolved in an acid mixture containing 0.5% HF and 5% HNO₃. Fourier transform infrared (FT-IR) spectra were obtained on an FT-IR spectrometer (FT/IR6100, Jasco Corp., Japan) with a spectral range of 4000–400 cm⁻¹ in the transmittance mode and resolution of 4 cm⁻¹. The KBr diluted pressed method was used. X-ray diffraction (XRD) patterns were collected at 303–773 K using a MiniFlex 600 diffractometer (Rigaku Corp., Japan) equipped with a BTS 500 heating stage (Anton Paar, Austria) and a CuKa radiation source. The NIST SRM 640c silicon standard was used as a peak position reference and temperature correction for the XRD studies. The crystal structural parameters were refined by Rietveld analysis using the RIETAN-FP program [13]. The valence of Sn was analyzed using X-ray photoelectron spectroscopy (XPS, model 5500 MT; PerkinElmer Inc.) using monochromated AlKα radiation. Particle morphology was observed using a field-emission scanning electron microscope (FE-SEM; JSM-7500F, JEOL, Japan), and transmission electron microscope (TEM) images as well as a selected range of electron diffraction were also observed (JEM-1010BS, JEOL, Japan). Differential scanning calorimetry (DSC; DSC-8230, Rigaku Corp., Japan) of the sample was conducted at 300–773 K (heating rate: 5 K/min) in air. Although samples calcined at various temperatures were used for ICP-OES and FT-IR measurements, the sample treated at 773 K was used for all other measurements.

3. Results

3.1. Synthesis of α-Zr₂ₓSnₓS₄P₂O₁₂₋₆

The chemical compositions estimated from ICP-OES measurements are listed in Table 1. The results indicated that Zr, Sn, and P loadings were in good agreement with the nominal composition. The XPS spectra indicate that Sn was tetravalent as shown in Fig. S1. The ionic radii of the coordination number of 4, 5 and 6 are approximately 55, 62 and 69 pm, respectively. These values are 3–4 times as large as the value of S (12 pm) or P (17 pm). It is considered that Sn⁴⁺ ions were substituted for Zr⁴⁺ ions. Nevertheless, the S content decreased with increasing Sn content at the same time. The S contents of the α-Zr₂ₓSnₓS₄P₂O₁₂₋₆ samples calcined at 673, 698, and 723 K imply that sulfur is gradually desorbed with calcination at higher temperatures. It is thought that sulfur is desorbed as SO₃ [11]. In addition, the relationship between the chemical composition and lattice constant as shown in Fig. S2 supports this consideration.

The crystal structure was determined by the XRD patterns shown in Figure 1. The samples with x = 0–0.6 were identified as α-Zr₂SP₂O₁₂ without any other phases. The diffraction peaks of the sample with x = 0.8 became broader, indicating low crystalline quality, and a very small peak attributed to Zr₄(PO₄)₄ was identified. Therefore, the solid solubility limit of Sn in Zr₂SnS₄P₂O₁₂₋₆ was found to be approximately 0.6. This value is comparable to the solubility limit of Ti in Zr₂₋ₓTiₓSP₂O₁₂₋₆ [12].

Figure 2 shows the FE-SEM micrographs of the obtained powders. The sample without substitution (Zr₂SP₂O₁₂) exhibited 200–300 nm cube-like shapes that can be attributed to the rhombohedral lattice of the R-3c space group (#167) [11]. It is also considered that these particles are single crystals. In fact, the selected area diffraction pattern of these particles displayed spots, as shown in Figure 3. The FE-SEM micrographs of the samples with x = 0.2–0.6 also exhibited shapes similar to those of Zr₂SP₂O₁₂. However, the samples with x = 0.8 contained shapeless particles, thought to be the Zr₄(PO₄)₄ phase identified by the XRD pattern shown in Figure 1.

Figure 4 shows FT-IR spectra of the powders after hydrothermal treatment and heating at various temperatures ranging from 698 K to 1273 K. The spectra exhibit a peak at 3,450 cm⁻¹ that can be attributed to the OH stretching vibration of hydroxyl groups. A broad peak at around 3,230 cm⁻¹ was also detected because of water held in the crystal lattice. The peaks at 1,630 and approximately 1,400 cm⁻¹ correspond to the

| Table 1. Chemical compositions of Zr₂₋ₓSnₓS₄P₂O₁₂₋₆ estimated from ICP-OES. |
| Sample | Treatment temperature [K] | Expected chemical equation |
| x = 0  | 773  | Zr₂SP₂O₁₂⁻₆ |
| x = 0.2| 773  | Zr₁.₅Sn₀.₅S₄P₂O₁₂⁻₆ |
| x = 0.4| 773  | Zr₁Sn₀S₄P₂O₁₂⁻₆ |
| x = 0.6| 773  | Zr₁Sn₁₂S₄P₂O₁₂⁻₆ |
| x = 0.8| 673  | Zr₁Sn₁₂S₄P₂O₁₂⁻₆ |
| x = 0  | 773  | Z₁Sn₀S₄P₂O₁₂⁻₆ |
| x = 0.2| 698  | Z₁Sn₀.₅S₄P₂O₁₂⁻₆ |
| x = 0.4| 723  | Z₁Sn₀S₄P₂O₁₂⁻₆ |
vibrations of acidic –OH groups and the asymmetric stretching of S=O bonds, respectively. Peaks seen at 500–1200 cm\(^{-1}\) can be attributed to the asymmetric stretching vibrations of sulfate and phosphate groups [14–16]. This result implies that the samples heated at low temperatures maintained the sulfate, ammonium salts, and/or hydroxide from the starting materials. To summarize this section, Zr\(_2\)SP\(_2\)O\(_{12}\), Zr\(_{1.8}\)Sn\(_{0.2}\)S\(_{0.9}\)P\(_2\)O\(_{12-\delta}\), Zr\(_{1.6}\)Sn\(_{0.4}\)S\(_{0.7}\)P\(_2\)O\(_{12-\delta}\), and Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) were all obtained after heating at 773 K as single phases without impurity.

### 3.2. Thermal expansion behavior

Figure 5 shows the lattice constant and lattice volume of the obtained samples as functions of temperature. The refined crystallographic parameters and reliability factors are provided in the supplemental material (Fig. S3–18 and Table S1–16). The a-axis lattice constant of Zr\(_2\)SP\(_2\)O\(_{12}\) was approximately 0.8801 nm at 303 K. This value decreased slightly with increasing temperature up to 353 K, as shown in the black circle. Then, it increased to approximately 0.8853 nm from 373 to 473 K. At temperatures over 473 K, the lattice parameter also decreased with increasing temperature. The cooling behavior of Zr\(_2\)SP\(_2\)O\(_{12}\), shown in the gray circle, was in fair agreement with the heating behavior. The values of Zr\(_{1.8}\)Sn\(_{0.2}\)S\(_{0.9}\)P\(_2\)O\(_{12-\delta}\) and Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) are shown in the blue and red circles, respectively. The a-axis lattice constants of Zr\(_{1.8}\)Sn\(_{0.2}\)S\(_{0.9}\)P\(_2\)O\(_{12-\delta}\) and Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) at 303 K were approximately 0.8787 and 0.8771 nm, respectively, and both decreased from 303 to 353 K. Simultaneously, the a-axis lattice constants of the Sn-substituted samples increased. Remarkably, that of Zr\(_{1.6}\)Sn\(_{0.4}\)S\(_{0.7}\)P\(_2\)O\(_{12-\delta}\) was approximately 0.8853 nm at 473 K, same as the value of Zr\(_2\)SP\(_2\)O\(_{12}\). The a-axis lattice constant of Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) also increased from 373 to 453 K; however, the value was slightly low. The cooling behaviors of Zr\(_{1.8}\)Sn\(_{0.2}\)S\(_{0.9}\)P\(_2\)O\(_{12-\delta}\) and Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) are shown in the light blue and orange circles, respectively. These were almost in agreement with the heating behavior in the case of Zr\(_2\)SP\(_2\)O\(_{12}\).

The c-axis lattice constants increased with increases in Sn loading, and the values for Zr\(_2\)SP\(_2\)O\(_{12}\), Zr\(_{1.8}\)Sn\(_{0.2}\)S\(_{0.9}\)P\(_2\)O\(_{12-\delta}\), and Zr\(_{1.4}\)Sn\(_{0.6}\)S\(_{0.5}\)P\(_2\)O\(_{12-\delta}\) at 303 K were approximately 2.327, 2.343, and 2.351 nm, respectively. The values decreased slightly from 303 to 393 K and then decreased more intensely as the temperature increased from 393 to 453 K. Upon further increase in temperature, the c-axis lattice constant remained constant. The
c-axis lattice constants of the abovementioned Sn-substituted samples at 453 K were the almost same as that of Zr$_2$SP$_2$O$_{12}$. On the basis of these results, it can be determined that the lattice volume decreased over the studied temperature range. The lattice volumes of the Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12-δ}$samples were larger than the volume of Zr$_2$SP$_2$O$_{12}$ below 373 K and were smaller above 453 K. The volumetric CTEs estimated from Figure 5(c) are listed in Table 2. The values of Zr$_{1.8}$Sn$_{0.2}$S$_{0.9}$P$_2$O$_{12-δ}$, Zr$_{1.6}$Sn$_{0.4}$S$_{0.7}$P$_2$O$_{12-δ}$, and Zr$_{1.4}$Sn$_{0.6}$S$_{0.5}$P$_2$O$_{12-δ}$ during the phase transition were $-125$, $-122$, and $-116$ ppm/K, respectively. These values were larger than the value of the prepared Zr$_2$SP$_2$O$_{12}$ ($-95$ ppm/K) at this time. Overall, the results tended to be nearly the same as those obtained in previous reports [11,12]. However, a number of details were slightly different. Strictly speaking, the value of Zr$_2$SP$_2$O$_{12}$ calculated in this paper was between those of the previously reported Zr$_2$SP$_2$O$_{12}$ and Zr$_2$S$_{0.9}$P$_2$O$_{12-δ}$. It is considered that the amount of sulfur in the Zr$_2$SP$_2$O$_{12}$ synthesized for this study was slightly lower than that of the stoichiometric composition, which cannot be detected by ICP-OES. Finally, it was confirmed that the obtained samples exhibited negative CTEs with the framework-type and phase transition mechanisms, and the Sn-substituted samples showed more negative CTEs during phase transition.

4. Discussion

To understand the relationship between CTE and crystal deformation, the crystal structures of the samples obtained at each temperature were evaluated by Rietveld analysis. The refinement process of each XRD pattern was carried out individually. The obtained atomic coordination was visualized, and the quadratic elongation, bond angle variance, and polyhedral volume of the MO$_6$ (M = Zr, Sn)
octahedron and the AO₄ \( (A = S, P) \) tetrahedron were measured using VESTA 3[17]. Here, quadratic elongation and bond angle variance were calculated as follows[18]:

\[
\langle \lambda \rangle = \sum_{j=1}^{n} \frac{l_j}{l_0 n}, \tag{1}
\]

\[
\sigma^2 = \frac{\sum_{j=1}^{m} (\psi_j - \psi_0)^2}{m - 1}, \tag{2}
\]

where \( n \) is the coordination number of the centered atom, \( l_j \) is the distance between the centered and cornered atoms, and \( l_0 \) is the distance between the centered and cornered atoms of the regular polyhedron (which has the same volume as the analyzed one). Further, \( m \) is the number of bond angles, \( \psi_j \) is the bond angle, and \( \psi_0 \) is the bond angle of the abovementioned regular polyhedron.

Figure 6 shows the polyhedral volumes of Zr₂SP₂O₁₂ and Zr₁.₈Sn₀.₂S₀.₉P₂O₁₂-₆. The MO₆ volume was larger with Sn substitution even though the ionic radii of Zr
Figure 4. FT-IR spectra of the powders after hydrothermal treatment and heating at various temperatures ranging from 698 K to 1273 K.

Figure 5. (a) $a$-axis lattice constant, (b) $c$-axis lattice constants, and (c) lattice volumes of the obtained $\text{Zr}_2.8\text{Sn}_x\text{S}_y\text{P}_2\text{O}_{12-\delta}$ powders.
and Sn were 0.72 and 0.69 Å, respectively. By contrast, the AO₄ volume was smaller with Sn substitution. Given the results on chemical composition, this implies that sulfur vacancy causes MO₆ to become unstable. In addition, it may be corresponded that the reduced connectivity in the framework structure that destabilizes the framework and leads to a reduction of the AO₄ tetrahedral size. Figure 7 presents the bond angle variance and quadratic elongation. The distortion index of the MO₆ octahedron of Zr₁.₈Sn₀.₂S₀.₉P₂O₁₂₋₅

Table 2. CTE values of ZrₓSn₂S₀.₉P₂O₁₂₋₅ calculated from high-temperature XRD.

| Composition            | a₀ [ppm/K] 303–373 K | a₀ [ppm/K] 373–453 K | a₀ [ppm/K] 453–773 K |
|------------------------|-----------------------|-----------------------|-----------------------|
| Zr₂SP₂O₁₂              | −23                   | −95                   | −14                   |
| Zr₁₆Sn₀.₂S₀.₉P₂O₁₂₋₅   | −29                   | −125                  | −14                   |
| Zr₁₆Sn₀.₄S₀.₁P₂O₁₂₋₅   | −19                   | −122                  | −11                   |
| Zr₁₆Sn₀.₆S₀.₇P₂O₁₂₋₅   | −26                   | −116                  | −15                   |

Figure 6. Polyhedral volumes in (a) the MO₆ octahedron and (b) the AO₄ tetrahedron of ZrSP₂O₁₂ and Zr₁₆Sn₀.₂S₀.₉P₂O₁₂₋₅.
was larger than that of Zr$_2$SP$_2$O$_{12}$ at 303 K. However, the values sharply decreased during heating, and those of the bond angle variance and quadratic elongation approached 0 and 1.000, respectively, at 433 K. This result implies that the crystal phase transitions of Zr$_2$SP$_2$O$_{12}$ and Zr$_{2-x}$Sn$_x$SP$_2$O$_{12}$ are triggered by order-disorder transformation and the high temperature phase of the MO$_6$ polyhedron was almost identical to a regular octahedron. Above 453 K, both of the above values increased gradually. It is assumed that this trend occurred on account of oxygen vacancies. Meanwhile, the values of the AO$_4$ tetrahedron changed non-monotonously, and it can thus be speculated that the AO$_4$ tetrahedron cannot affect phase transitions directly. Further, the distortion was found to increase with Sn substitution. From the DSC plots shown in Figure 8, the enthalpies of Zr$_2$SP$_2$O$_{12}$, Zr$_{1.8}$Sn$_{0.2}$S$_{0.9}$P$_2$O$_{12}$, Zr$_{1.6}$Sn$_{0.4}$S$_{0.7}$P$_2$O$_{12}$, and Zr$_{1.4}$Sn$_{0.6}$S$_{0.5}$P$_2$O$_{12}$ were calculated as 41.41, 128.2, 149.0, and 124.5 mJ/mol respectively. The results revealed that a greater Sn content leads to a larger transition enthalpy from the low-temperature to the high-temperature phase. The slightly lower enthalpy of Zr$_{1.4}$Sn$_{0.6}$S$_{0.5}$P$_2$O$_{12}$ occurs on account of low crystallinity. Considering the above results, it can be concluded that sulfur was desorbed in the form of SO or SO$_2$ by Sn substitution, causing the crystal structure to become unstable and leading to a larger volume.

Figure 7. Distortion indices of ZrSP$_2$O$_{12}$ and Zr$_{1.8}$Sn$_{0.2}$S$_{0.9}$P$_2$O$_{12-\delta}$: (a) bond angle variance in the MO$_6$ octahedron, (b) bond angle variance in the AO$_4$ octahedron, (c) quadratic elongation in the MO$_6$ octahedron, and (d) quadratic elongation in the AO$_4$ octahedron.
5. Conclusion

α-Zr$_2$SP$_2$O$_{12}$ samples with Sn partially substituted for Zr (α-Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12-δ}$) were prepared, and their thermal expansion values were evaluated. Compared with α-Zr$_2$SP$_2$O$_{12}$, the volume of α-Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12-δ}$ was larger below 393 K and smaller above 453 K, resulting in smaller negative CTEs from 393 to 453 K compared with those of previously reported α-Zr$_2$SP$_2$O$_{12}$ and α-Zr$_{2-x}$Ti$_x$S$_{0.9}$P$_2$O$_{12-δ}$. The sulfur content was also found to decrease as the Sn content increased. It is estimated that this vacancy made the crystal structure unstable, leading to a larger volume for the low-temperature phase. Considering its huge negative CTEs and its availability, Zr$_{2-x}$Sn$_x$S$_y$P$_2$O$_{12-δ}$ can be used for various applications in industrial fields, such as electrical or optical devices.

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References

[1] Barrera GD, Bruno JAO, Barron THK, et al. Negative thermal expansion. J Phys Condens Matter. 2005;17:R217–R252.

[2] Miller M, Smith CW, Mackenzie DS, et al. Negative thermal expansion: a review. J. Mater. Sci. 2009;44 (5441–5451):5441–5451.

[3] Jakubinek MB, Whitman CA, White MA. Negative thermal expansion materials: thermal properties and implications for composite materials. Journal of Thermal Analysis and Calorimetry. 2010;99 (1):165–172.

[4] Takenaka K. Negative thermal expansion materials: technological key for control of thermal expansion. Sci. Technol. Adv. Mater. 2012;13(13001):013001.

[5] Chen J, Hu L, Denga J, et al. Negative thermal expansion in functional materials: controllable thermal expansion by chemical modifications. Chem. Soc. Rev. 2015;44(3522–3567):3522–3567.

[6] Dove MT, Fang H. Negative thermal expansion and associated anomalical physical properties: review of the lattice dynamics th12eoretical foundation. Rep Prog Phys. 2016;79(6):066503.

[7] Isobe T, Houtsuki N, Hayakawa Y, et al. Preparation and properties of Zr2MoP2O12 ceramics with negative thermal expansion. Mater. Des. 2016;112(11–16):11–16.

[8] Yamashina. N, Isobe T, Ando S. Low thermal expansion composites prepared from polyimide and zrw2o8 particles with negative thermal expansion.

J. Photopolym. Sci. Technol. 2012;25(385–388):385–388.

[9] Zhang Z, Sun W, Liu H, et al. Synthesis of Zr2WP2O7/ZrO2 composites with adjustable thermal expansion. Front Chem. 2017;5(105). DOI:10.3389/fchem.2017.00105

[10] Yanase I, Sakai H, Kobayashi H. Fabrication of Zr2WP2O12 /Zr0.6P1.4O7 composite with a nearlyzero-thermal-expansion property. Mater Lett. 2017;207:221–224.

[11] Isobe T, Hayakawa Y, Adachi Y, et al. Negative thermal expansion in α-Zr2SP2O12 based on phase transition- and framework-type mechanisms. NPG Asia Mater. 2020;12 (1):80.

[12] Isobe T, Adachi Y, Matsushita S, et al. Effect of titanium substitution for the improvement of thermal expansion properties of Zr2S0.9P2O12. Ceram. Int. 2021;47 (7):10197–10200.

[13] Izumi F, Momma K. Three-dimensional visualization in powder diffraction. Solid State Phenom. 2007;130(15–20):15–20.

[14] Acetylation of Glycerol over Mixed Zirconium Phosphate-Sulphate Catalysts?. 2017 International Renewable and Sustainable Energy Conference (IRSEC), Tanger, 1-4 (2017).

[15] Lai Z, Qian J, Lu Z, et al. Rapid synthesis of ditmarite by microwave-assisted hydrothermal method. Adv Mater Sci Eng. 2012;85:71–73.

[16] Qian J, Cui G, Jing M, et al. Hydrothermal synthesis of nitrogen-doped titanium dioxide and evaluation of its visible light photocatalytic activity. Int J Photoenergy. 2012;2012:1–6.

[17] Momma K, Izumi F, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J Appl Crystallogr. 2011;44:1272–1276.

[18] Robinson K, Gibbs GV, Ribbe PH. Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. Science. 1971;172:567–570.