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Note

Synthesis of Cubic $Cs_2FeSi_5O_{12}$ Powder in Ar Atmosphere and Its Thermal Expansion Property

Ikuo YANASE,† Hidehiko KOBAYASHI and Takashi MITAMURA*

Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255, Shimoohkubo, Urawa-shi, Saitama 338-8570
**Graduate School, Saitama Institute of Technology, 1690, Fusaiji, Okabe-machi, Ohsato-gun, Saitama 369-0293*

Ar 雰囲気中での立方晶 $Cs_2FeSi_5O_{12}$ 粉末の合成とその熱膨張特性

柳瀬郁夫† · 小林秀彦 · 三田村 孝*

埼玉大学工学部応用化学科，338-8570 埼玉県浦和市下大久保 255
*埼玉工業大学大学院，369-0293 埼玉県大里郡岡部町普済寺 1690

Cubic $Cs_2FeSi_5O_{12}$ powder with the space group *Ia*-3*d* was synthesized by heating the powder mixture of $Cs_2CO_3 \cdot 2H_2O$, Fe_3O_4 and amorphous SiO_2 with the molar ratio of Cs/Fe = 2 and Si/Fe = 5 at 1273 K for 20 h under Ar gas flow. The thermal expansion property of cubic $Cs_2FeSi_5O_{12}$ powder was investigated in the temperature range from 298 to 1273 K using high-temperature X-ray diffraction. The thermal expansion rate of cubic $Cs_2FeSi_5O_{12}$ was lower than that of cubic $CsFeSi_2O_6$. Consequently, increasing the molar ratio of Si/Fe was effective for decreasing the thermal expansion rate of Cs-Fe-leucite compounds. Cubic $Cs_2FeSi_5O_{12}$ showed a lower thermal expansion with the mean linear thermal expansion coefficient of 1.75×10^{-6} K^{-1} in the range from 573 to 1273 K.

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1. Introduction

Cubic Cs-leucite, $CsMSi_2O_6$ (M = B, Al, Fe, etc.) has a three-dimensional framework structure which consists of 48 (Si, M)O_4 tetrahedra having the molar ratio of Si/M = 32/16 with 16 Cs^+ ions occupying large 12-coordinate cavities in the unit cell.[1)-3)] The powder synthesis and the thermal expansion property of cubic $CsMSi_2O_6$ (M = B, Al, Fe), having the space group Ia-3d with the molar ratio of Si/M = 2, have been studied.[4)-7)] In particular, cubic $CsAlSi_2O_6$ has a low thermal expansion property with a mean linear thermal expansion coefficient of 2.2×10^{-6} K^{-1} in the temperature range from 473 to 1473 K.[4)-7)]

$Cs_2MSi_5O_{12}$ (M = Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn), Cs-leucite with the molar ratio of Si/M = 5, has also been synthesized by several methods, such as conventional solid-phase synthesis, hydrothermal synthesis and the melting method, and has several crystal structures such as cubic with *Ia*-3*d*, cubic with *Pa*3 and monoclinic with *Pbca*.[8)-13)] On the other hand, little is known about the effect of the chemical composition of Cs-leucite with the molar ratio of Si/M = 5 on the thermal expansion property. Therefore, it is important to investigate in detail the powder synthesis method for synthesizing Cs-leucite with the desired crystal structure and chemical composition. We have reported on the powder synthesis conditions of cubic $Cs_2MSi_5O_{12}$ (M = Cd, Mg, Ni, Zn) with the space group Ia-3d by a multistep heating method as the solid-state reaction method, and its thermal expansion property.[14),15)]

In this study, cubic $Cs_2FeSi_5O_{12}$ powder was synthesized by the solid-state reaction method under Ar gas flow. Then the thermal expansion property of the synthetic cubic $Cs_2FeSi_5O_{12}$ was compared with that of cubic $CsFeSi_2O_6$ to examine the influence of the molar ratio of Si/Fe on the thermal expansion property.

† Now with National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba-shi, Ibaraki 305-0044
現在：無機材質研究所，305-0044 つくば市並木 1-1

2. Experimental procedure

2.1 Powder synthesis, phase identification and chemical composition

$FeCl_2$ (99.9% purity; Koujundo Chem. Co.) was dissolved in distilled water, and the solution of 1 mol·dm^{-3} was prepared. Oxalic acid (reagent grade, $H_2C_2O_4 \cdot 2H_2O$; Wako Pure Chem. Ind. Ltd.) solution of 1 mol·dm^{-3} was then added dropwise to the $FeCl_2$ solution with constant stirring. The mixed solution was stirred for 24 h to obtain Fe-oxalate, $FeC_2O_4 \cdot 2H_2O$, precipitate.[16)] The Fe-oxalate was decomposed in the temperature range from 673 to 1073 K for 1 h under Ar gas flow. Phase identification of the heat-treated samples was carried out by powder X-ray diffraction (XRD; Rigaku, Rad-C, Cu Kα, 40 kV, 30 mA).

$Cs_2CO_3 \cdot 2H_2O$ powder (99.9% purity; Koujundo Chem. Co.), Fe_3O_4 powder derived from the calcination of Fe-oxalate, and amorphous SiO_2 powder[14)] derived from SiO_2 sol (Nissan Chem. Co., Snowtex-O) were used as the starting materials. First, Fe_3O_4 and amorphous SiO_2 powders were mixed for 24 h by wet ball-milling in the presence of ethanol using alumina balls in a plastic bottle in a molar ratio of Si/Fe = 5. After milling, the powder mixture was dried by removing the solvent. Then, the $Cs_2CO_3 \cdot 2H_2O$ powder was added to the dried powders stoichiometrically, where the molar ratio was Cs : Fe : Si = 2 : 1 : 5. The powder, which consists of three components, was mixed manually for 3 h in air using an agate mortar. The synthesis conditions of the single phase of $Cs_2FeSi_5O_{12}$ were investigated in the temperature range from 873 to 1273 K for 1 to 20 h in air or Ar atmosphere. The single phase of $Cs_2FeSi_5O_{12}$ powder was synthesized by heat treatment of the powder mixture at 1273 K for 20 h under Ar gas flow.

A single phase of cubic $CsFeSi_2O_6$ powder was synthesized by the two-stage heat treatment of the powder mixture of $CsNO_3$, Fe_2O_3 and amorphous SiO_2, which had molar ratios of Cs/Fe = 1.0/1.0 and Fe/Si = 1.0/2.0. The powder mixture was calcined at 973 K for 24 h in air, followed by heating at 1573 K for 10 h in air.[15)]

The phase composition of the powder was determined by powder XRD in the scanning range $2\theta = 20$-$60°$ and at a

scanning speed of 4° min^{-1}. The product ratio (α) of crystal phases in the calcined powder was estimated using powder X-ray diffraction. In detail, the X-ray diffraction peak area corresponding to the (100) plane for α-Fe, the (200) plane for FeO, the (311) plane for Fe_3O_4, and the (104) plane for α-Fe_2O_3 was divided by the sum of these peak areas. Chemical compositions of synthetic $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ were examined by fluorescent X-ray diffraction (XRF; Philips, Japan, PW2400) and inductively coupled plasma (ICP) emission spectroscopic analysis.

2.2. Thermal expansion property

The thermal expansion properties of the synthetic cubic $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ were studied as to the change of the lattice constant with temperature in the range from 298 to 1273 K using high-temperature X-ray diffraction (HTXRD; Mac Science, MXP18VA, Cu Kα, 40 kV, 200 mA). The lattice constants of the synthetic $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ of each temperature were calculated by the least-squares method with the six peaks of (332), (521), (440), (611), (651) and (721) planes, which were corrected using the Si powder as the external standard at a scanning speed of 1° min^{-1} and in the scanning range from 20 to 60°. The sample was set in a Pt holder in contact with the thermocouple.

3. Results and discussion

3.1 $Cs_2FeSi_5O_{12}$ powder synthesis

3.1.1 Preparation of Fe_3O_4 powder as source material of FeO

The Fe-oxalate is decomposed at 1173 K for 15 h under Ar gas flow through Reaction (1) and FeO is formed.[17]

$$FeC_2O_4 = FeO + CO + CO_2 \quad (1)$$

Thus, the Fe-oxalate prepared was decomposed in the temperature range from 673 to 1073 K for 1 h under Ar gas flow, and then the phase composition of the resultant powder was determined by powder XRD. The results are shown in Fig. 1. A single phase of Fe_3O_4 was formed at 673 K, Fe_3O_4 and α-Fe at 773 K, and FeO and α-Fe above 973 K. FeO was recognized above 873 K, and the intensity of the FeO phase signal was maximum at 973 K and then decreased in the range from 973 to 1073 K. The tendency of increase or decrease of FeO was affected by the amounts of Fe_3O_4 and α-Fe formed. The product ratio (α) of FeO was thought to increase by reaction (2), with increasing temperature in the range from 673 to 973 K.

$$Fe_3O_4 + \alpha\text{-}Fe = 4FeO \quad (2)$$

On the other hand, FeO was decomposed to Fe_3O_4 and α-Fe because FeO was unstable below 843 K.[17] Above 973 K, since FeO decreased and α-Fe increased, as shown in Fig. 1, a single phase of FeO was not obtained.

To prepare the single phase of FeO, it is necessary to modify the calcination of the Fe-oxalate powder. First, the Fe-oxalate was decomposed at 673 K for 1 h under Ar gas flow. Second, the powder was ground manually for a few hours in air using an agate mortar and then the powder was sonicated in ethanol. After the resultant powder was dried, it was calcined at 673–1073 K for 1 h under Ar gas flow. Figure 2 shows the relation between the product ratio (α) of crystal phases of the resultant powder and the calcination temperature. Although α-Fe was formed with Fe_3O_4 at 773 K, α-Fe disappeared at 873 K. FeO was formed at 873 K and its single phase was obtained above 973 K. Thus the Fe_3O_4 powder was used as the souce material of FeO for synthesizing the single phase of $Cs_2FeSi_5O_{12}$.

3.1.2 Synthesis of $Cs_2FeSi_5O_{12}$ powder

For the synthesis of Cs–Fe-leucite powder, $CsNO_3$, $Cs_2CO_3 \cdot 2H_2O$ and CsCl are usually used as Cs sources. Considering the results presented in the section above, the thermal decomposition of the Cs component must be checked under Ar gas flow. $CsNO_3$ and $Cs_2CO_3 \cdot 2H_2O$ powders were mixed to have the stoichiometric chemical composition of the molar ratio (Cs : Fe : Si = 2 : 1 : 5), and the thermal decomposition behavior of the mixed powder was investigated by TG–DTA under Ar gas flow.

Figure 3 shows the TG–DTA curves of the powder mixture containing $Cs_2CO_3 \cdot 2H_2O$ under Ar gas flow. Endothermic peaks were observed at 419 K and 451 K in the DTA curve, owing to the loss of crystal water present in $Cs_2CO_3 \cdot 2H_2O$. In the TG curve, a decrease in mass corresponding to these peaks was observed in the temperature range from 390 to 470 K. An exothermic peak in the range from 550 to 750 K, associated with a mass loss (ΔW_1) due to the thermal decomposition of Cs_2CO_3, was observed in the DTA curve.

The TG–DTA curve of the powder mixture containing $CsNO_3$ under Ar gas flow is shown in Fig. 4. The endothermic peaks in the DTA curve were due to the structural phase transition of $CsNO_3$ from hexagonal to cubic at 430 K, the fusion at 674 K and the thermal decomposition of $CsNO_3$ in the range from 720 to 860 K, respectively. The mass loss (ΔW_2) in the TG curve, due to the thermal decomposition of $CsNO_3$, was observed in the temperature range from 720 to 860 K.

The phase composition of the mixed powder calcined at 1173 K for 1 h under Ar gas flow was determined by powder XRD. The results are shown in Fig. 5. The XRD patterns

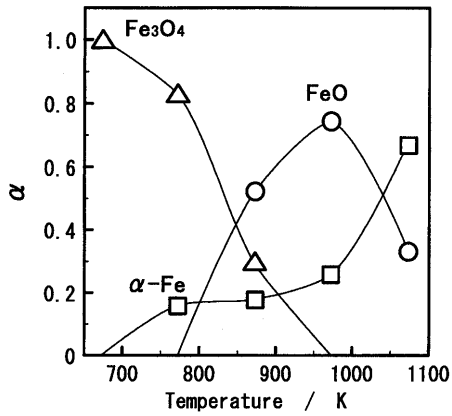

Fig. 1. Change in the product ratio (α) of crystal phases upon calcination of Fe-oxalate at each temperature for 1 h under Ar gas flow.

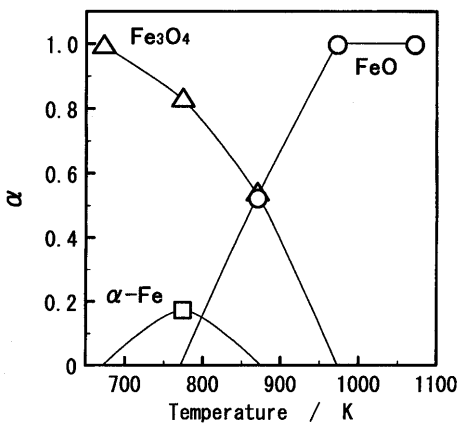

Fig. 2. Change in the product ratio (α) of crystal phases by calcination of Fe-oxalate at each temperature for 1 h under Ar gas flow after ultrasonic treatment.

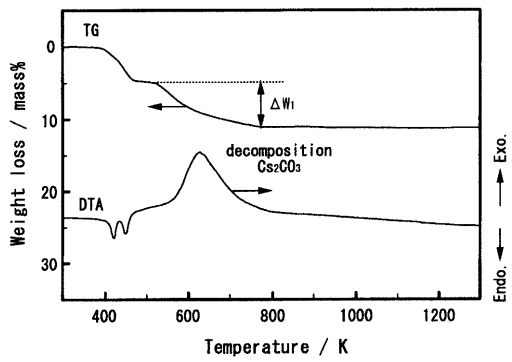

Fig. 3. Thermal decomposition behavior of the powder mixture of $Cs_2CO_3 \cdot 2H_2O$, Fe_3O_4 and amorphous SiO_2 under Ar gas flow.

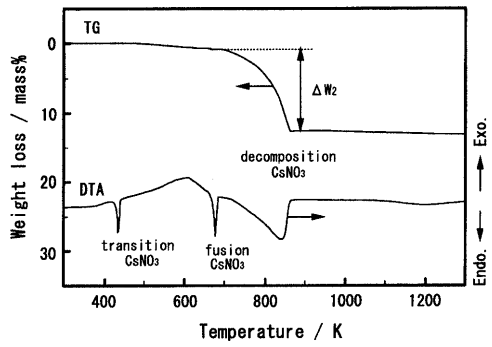

Fig. 4. Thermal decomposition behavior of the powder mixture of $CsNO_3$, Fe_3O_4 and amorphous SiO_2 under Ar gas flow.

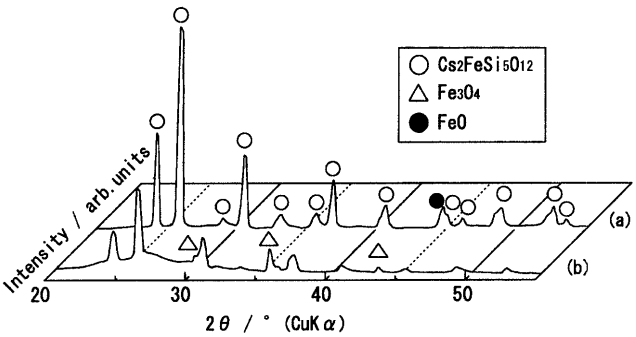

Fig. 5. XRD patterns of the resultant powders calcined at 1173 K for 1 h under Ar gas flow. Starting materials: (a) $Cs_2CO_3 \cdot 2H_2O$, Fe_3O_4 and amorphous SiO_2, (b) $CsNO_3$, Fe_3O_4 and amorphous SiO_2.

(a) and (b) were obtained from the starting powder mixtures containing $Cs_2CO_3 \cdot 2H_2O$ and $CsNO_3$, respectively. The $Cs_2FeSi_5O_{12}$ phase, the color of which was black, was mainly recognized, as well as a small amount of the α-Fe phase, in XRD pattern (a). On the other hand, $Cs_2FeSi_5O_{12}$ and Fe_3O_4 phases were recognized in XRD pattern (b), the color of which was crimson. Therefore, the use of $Cs_2CO_3 \cdot 2H_2O$ powders as a Cs source proved to be suitable for the synthesis of a single phase of $Cs_2FeSi_5O_{12}$.

$Cs_2CO_3 \cdot 2H_2O$, Fe_3O_4 and amorphous SiO_2 powders were used as starting materials for the synthesis of $Cs_2FeSi_5O_{12}$. The mixture of starting materials was heated at 873–1273 K for 1–20 h under Ar gas flow, and then the phase composition of the resultant powder was determined by powder XRD. The results are shown in Fig. 6. Although the reduction of Fe_3O_4 to FeO was not complete after the heat treatment at 873 K for 1 h (a), $Cs_2FeSi_5O_{12}$ was crystallized by the heat treatment at 1073 K for 1 h (b). However, divided peaks of $Cs_2FeSi_5O_{12}$ in the XRD pattern were observed in the range from 40 to 55°, apparently due to the existence of two kinds of $Cs_2FeSi_5O_{12}$ phases. The divided peaks of $Cs_2FeSi_5O_{12}$ became a nondivided peak after heating at 1273 K for 1 h (c). The $Cs_2FeSi_5O_{12}$ single phase with the chemical composition of $Cs_{2.06(4)}Fe_{1.00(1)}Si_5O_{12}$ was synthesized at 1273 K for 20 h (d), as shown in Fig. 6. Numbers in parentheses are standard deviations. Si and O contents in the chemical formula of $Cs_2FeSi_5O_{12}$ were fixed at 5 and 12.

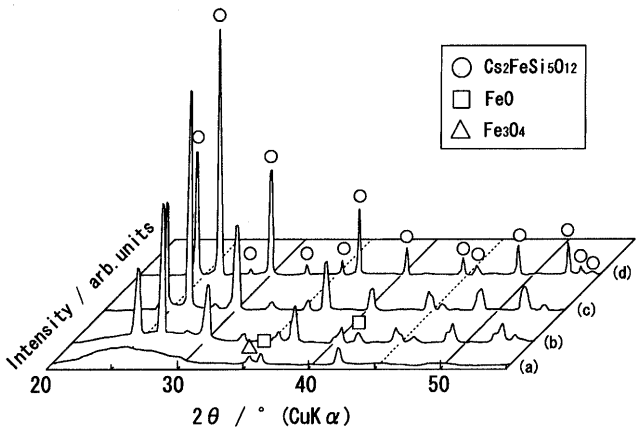

Fig. 6. XRD patterns of the resultant $Cs_2CO_3 \cdot 2H_2O$, Fe_3O_4 and amorphous SiO_2 powders with molar ratio of Cs : Fe : Si = 2 : 1 : 5 calcined (a) at 873 K for 1 h, (b) at 1073 K for 1 h, (c) at 1273 K for 1 h and (d) at 1273 K for 20 h.

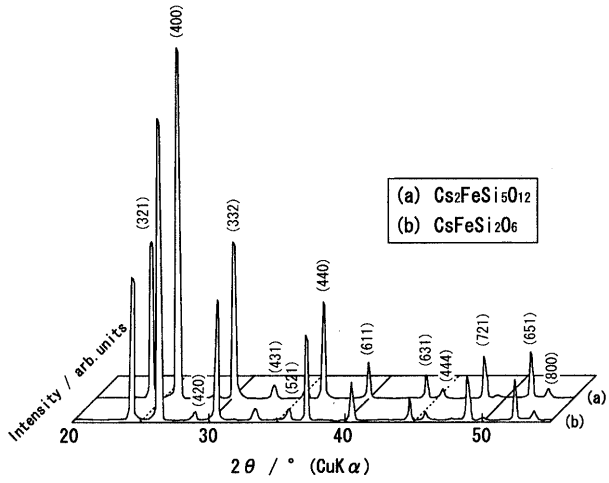

Fig. 7. XRD patterns of (a) $Cs_2FeSi_5O_{12}$ and (b) $CsFeSi_2O_6$ powders.

Figure 7 shows the XRD patterns of $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ synthesized by the solid-state reaction method. Since the XRD pattern of $Cs_2FeSi_5O_{12}$ closely corresponded with that of cubic $CsFeSi_2O_6$ having the space group *Ia*–3*d*, all the diffraction lines of $Cs_2FeSi_5O_{12}$ could be indexed as cubic with the space group *Ia*–3*d*, by comparison with the XRD pattern of cubic $CsFeSi_2O_6$. The colors of cubic $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ powders were black and crimson, respectively.

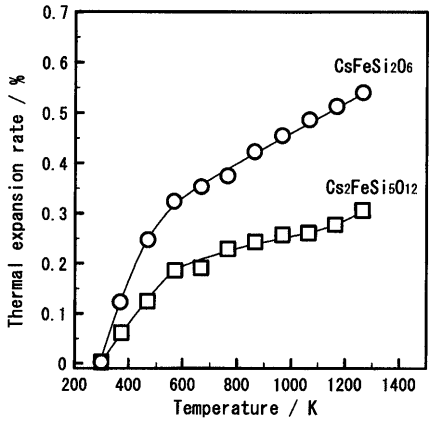

Fig. 8. Thermal expansion properties of $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ in the temperature range from 298 to 1273 K.

3.2 Thermal expansion properties of $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ powders

The lattice constants of $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ at 298 K were 1.3680 and 1.3834 nm, which are quite different. Figure 8 shows the thermal expansion properties of $Cs_2FeSi_5O_{12}$ and $CsFeSi_2O_6$ in the temperature range from 298 to 1273 K. The thermal expansion property of $Cs_2FeSi_5O_{12}$ was considerably different from that of $CsFeSi_2O_6$. The thermal expansion rate of $Cs_2FeSi_5O_{12}$ was smaller than that of $CsFeSi_2O_6$. $Cs_2FeSi_5O_{12}$ showed a high thermal expansion with the mean linear thermal expansion coefficient of $6.82\times10^{-6}\,K^{-1}$ in the range from 298 to 573 K, and it showed a low thermal expansion with the mean linear thermal expansion coefficient of $1.75\times10^{-6}\,K^{-1}$ in the range from 573 to 1273 K. This result suggests that $Cs_2FeSi_5O_{12}$ has the potential to be a lower-thermal-expansion material in the temperature range from 573 to 1273 K. Furthermore, increasing the molar ratio of Si/Fe decreases the thermal expansion rate of Cs–Fe-leucite compounds, based on the fact that the Si/M molar ratio of $Cs_2FeSi_5O_{12}$ (=5) was larger than that of cubic $CsFeSi_2O_6$ (=2).

4. Conclusions

Cubic $Cs_2FeSi_5O_{12}$ powder was synthesized by the solid-state reaction method under Ar gas flow, and then the thermal expansion property of synthetic $Cs_2FeSi_5O_{12}$ was compared with that of cubic $CsFeSi_2O_6$ to examine the influence of the molar ratio of Si/Fe on the thermal expansion property.

The results can be summarized as follows.

(1) In synthesizing the single phase of $Cs_2FeSi_5O_{12}$, it was effective to use $Cs_2CO_3\cdot2H_2O$, Fe_3O_4 and amorphous SiO_2 powders. Cubic $Cs_2FeSi_5O_{12}$ with the space group *Ia*–3*d* was synthesized at 1273 K for 20 h under Ar gas flow.

(2) Synthetic cubic $Cs_2FeSi_5O_{12}$ exhibited high thermal expansion, with the mean linear thermal expansion coefficient of $6.82\times10^{-6}\,K^{-1}$, in the temperature range from 298 to 573 K, and low thermal expansion, with the mean linear thermal expansion coefficient of $1.75\times10^{-6}\,K^{-1}$, in the temperature range from 573 to 1273 K. The thermal expansion rate of cubic $Cs_2FeSi_5O_{12}$ was lower than that of cubic $CsFeSi_2O_6$. Consequently, increasing the molar ratio of Si/Fe was effective for decreasing the thermal expansion rate of Cs–Fe-leucite compounds, based on the fact that the Si/M molar ratio of $Cs_2FeSi_5O_{12}$ (=5) was larger than that of $CsFeSi_2O_6$ (=2).

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References

1) W. H. Taylor, *Z. Kristallogr.*, **99**, 283–91 (1938).
2) D. Taylor and C. M. B. Henderson, *Am. Mineral.*, **53**, 1476–89 (1968).
3) A. A. Kosorukov and L. G. Nadal, *Sov. Phys.-Crystallogr.* (*Eng. Transl.*), **31**, 252–57 (1986).
4) D. W. Richerson and F. A. Hummel, *J. Am. Ceram. Soc.*, **55**, 269–73 (1972).
5) I. Yanase, H. Kobayashi, Y. Shibasaki and T. Mitamura, *J. Am. Ceram. Soc.*, **80**, 2693–95 (1997).
6) H. Kobayashi, T. Terasaki, T. Mori, C. Ishihara, S. Saito, H. Yamamura and T. Mitamura, *J. Ceram. Soc. Japan* (*Seramikkusu Ronbunshi*), **99**, 686–91 (1991) [in Japanese].
7) H. Kobayashi, T. Terasaki, T. Mori, H. Yamamura and T. Mitamura, *J. Ceram. Soc. Japan*, **100**, 90–93 (1992) [in Japanese].
8) L. M. Torres-Martinez and A. R. West, *Z. Anorg. Allg. Chem.*, **573**, 223–30 (1989).
9) L. M. Torres-Martinez, J. A. Gard, R. A. Howie and A. R. West, *J. Solid State Chem.*, **51**, 100–03 (1984).
10) L. M. Torres-Martinez and A. R. West, *Z. Kristallogr.*, **175**, 1–7 (1986).
11) A. M. T. Bell, S. A. T. Redfern, C. M. B. Henderson and S. C. Kohn, *Acta Cryst.*, **B50**, 560–66 (1994).
12) A. R. Heinrich and Ch. Baerlocher, *Acta Cryst.*, **C47**, 237–41 (1991).
13) A. M. T. Bell and C. M. B. Henderson, *Acta Cryst.*, **C52**, 2132–39 (1996).
14) I. Yanase, N. Miyashita, H. Kobayashi, F. Noguchi and T. Mitamura, *J. Ceram. Soc. Japan*, **106**, 1099–103 (1998) [in Japanese].
15) I. Yanase, H. Kobayashi and T. Mitamura, *J. Ceram. Soc. Japan*, **108**, 26–31 (2000).
16) H. Kobayashi, T. Ikeda, T. Mitamura, K. Kakizaki and N. Hiratsuka, *J. Jpn. Soc. Powder Powder Metall.*, **43**, 89–94 (1996) [in Japanese].
17) "Jikken Kagaku Kouza 16, Mukikagobutsu," 4th ed., Ed. by Nippon Kagakukai (1993) p. 235 [in Japanese].