Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 399–404

www.elsevier.com/locate/jeurceramsoc

Preparation of reactive Sr-celsian powders by solid-state reaction and their sintering

Yuichi Kobayashi*, Miki Inagaki

Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, 1247 Yachigusa, Yakusa, Toyota, Aichi 470-0392, Japan

Abstract

In order to develop dense Sr-celsian ($SrO{\cdot}Al_2O_3{\cdot}2SiO_2$) and hexacelsian ceramics, thermal reactions between kaolin and strontium carbonate were investigated. Sintering characteristics of powders and phase transformation from hexacelsian to celsian were clarified. Reactive amorphous powder could be prepared by calcination of the mixtures at 800 °C. Dense hexacelsian and celsian ceramics with a relative density of about 97% were successfully obtained by heat-treatment between 950 and 1200 °C. Relative dielectric constant and dielectric loss of hexacelsian ceramics was measured to be 5.3 and 0.5×10^{-4} (1 MHz), respectively, showing possibility for electrical applications.

Keywords: Silicates; Sintering; Substrates; Thermal expansion; X-ray methods; Celsian; $SrAl_2Si_2O_8$

1. Introduction

Since Sr-celsian ($SrO{\cdot}Al_2O_3{\cdot}2SiO_2$) has a low thermal expansion coefficient and high melting temperature, it is known as a candidate material for the matrix of fiber-reinforced ceramic composites.[1] Sr-celsian, as well as Ba-celsian,[2] is expected to have a low dielectric constant and low dielectric loss, so that Sr-celsian is also a candidate material as the substrate for semiconductor packaging and multilayered ceramics substrate. One of the difficulties of Sr-celsian ceramics for these applications is that the metastable pseudo-hexagonal celsian phase (hereafter referred to as hexacelsian), which shows high thermal expansion coefficient,[3] appears in the beginning of heat treatment of raw materials in either glass-melting[1] or solid-state reaction,[4] and the heat-treatment above 1200 °C could not be avoided, in order to achieve complete transformation from hexacelsian to celsian.[4] Chinn et al.[5] studied the effect of addition of B_2O_3 on the formation and sintering of celsian polycrystals, but it was difficult to reconcile a sintering and a transformation at once. In our previous work, the preparation of dense celsian ceramics was tried by using kaolin and $SrCO_3$, but dense bodies of stoichiometric hexacelsian or celsian could not be obtained mainly because of its insufficient sinterability.

The purpose of this work is the preparation of sinterable powders, which can lead to either hexacelsian or celsian, from kaolin and strontium carbonate to obtain dense celsian ceramics through the acceleration of transformation from hexacelsian to celsian under the control of chemical composition and particle size of raw materials.

2. Experimental procedure

2.1. Sample preparations

$SrCO_3$ (reagent grade) and New Zealand kaolin (hereafter referred to kaolin) were used as starting materials. Kaolin was elutriated into the particle size below 1 μm by sedimentation in aqueous suspension. Chemical composition of elutriated kaolin is shown in Table 1, revealing that it has a molar ratio SiO_2/Al_2O_3 of 2.01, and almost ideal composition of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$). It contains few alkaline and alkaline–earth elements. $SrCO_3$ was milled into a mean particle size of 1.5 μm in order to achieve sufficient thermal reaction with kaolin.

Powder mixtures of $SrCO_3$ and kaolin in different compositions of $n SrO{\cdot}Al_2O_3{\cdot}2SiO_2$ ($n = 0.9–2.0$, n is also defined as SrO/Al_2O_3 in the present study) were calcined at 800 °C for several hours, and then milled again for 1–

---

* Corresponding author. Tel.: +81-565-48-8121; fax: +81-565-48-0076.

E-mail address: kobayasi@ac.aitech.ac.jp (Y. Kobayashi).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00215-2

Table 1
Chemical composition of New Zealand kaolin elutriated below 1 μm

Component	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Ig.loss	Total
mass%	45.72	38.09	0.25	0.08	0.01	0.08	0.01	0.02	14.64	98.9

20 h. The calcined powders were uniaxially compressed at 98 MPa to form a disk with the size of 16 mmϕ and 2 mm thick. The green disks thus prepared were heat-treated in air up to 1200 °C, with a heating rate of 5 °C/min from room temperature to 1000 °C and a rate of 2.5 °C/min above 1000 °C. Samples were kept at a respective temperature for 1 h, and then left to cool down by cutting the electric power for the furnace.

2.2. Measurements

Mean particle size r_{50} of calcined powders was determined by using a centrifugal sedimentation size analyzer (model SA-CP3, Shimazu, Kyoto, JAPAN). The specific surface area was determined by BET method using nitrogen gas adsorption at 77 K. The crystalline phase was identified by using X-ray diffractometry (XRD, model RAD-B, Rigaku Denki, Tokyo, Japan). DTA and TG measurements were carried out using a DTA–TG apparatus (Rigaku Denki, TAS-100, Tokyo, Japan) at a heating rate of 10 °C/min. The thermal expansion coefficient measurement was performed with a thermomechanical analysis apparatus (TMA, Model TAS-100, Rigaku, Denki). The bulk density and apparent porosity were determined by using the Archimedes immersion technique. The microstructure of heat-treated specimens was observed at polished and HF-etched sections under scanning electron microscope (JSM-35, Nippon Denshi, Tokyo, JAPAN).

3. Results and discussion

3.1. Thermal analysis

The results of the DTA–TG measurements for the mixtures with $n = 1.0$ and $n = 2.0$ are shown in Fig. 1. The weight loss in TG curves from 350 to 600 °C was reasonably supposed to be due to the dehydration of kaolin, which corresponds to the endothermic peaks in DTA curves in the same temperature range. The second weight loss from 600 to 950 °C mainly due to the decomposition of $SrCO_3$ to SrO and CO_2. Just after the decomposition was completed, the DTA curve shifts to exothermic side. In the case of the reaction of kaolin with $CaCO_3$, sudden shift to the exothermic side above 900 °C was found to correspond to the abrupt shrinkage of the powder sample.[6] Therefore, the exothermic shifts observed on the present samples were also due to the shrinkage of samples. Two small exothermic peaks above 1000 °C, which probably relate to crystallizations, will be discussed at a later section.

3.2. Characterization of calcined mixtures

In our previous paper,[4] sintering characteristics were examined for the mixtures of $SrCO_3$ and kaolin without calcination, but sufficiently dense hexacelsian and celsian ceramics could not be obtained. The densification of the compacts was inhibited by CO_2 release due to the decomposition of $SrCO_3$, because the densification starts at a temperature close to the decomposition temperature. In consequence, preliminary calcination of the mixtures seems to be effective for full densification of the Sr-celsian ceramics.

Powder mixture with $n = 0.9–2.0$ were calcined at 800 °C for 1–5 h in order to remove CO_2 gas. The calcining temperature of 800 °C was selected by referring to the DTA–TG curves in Fig. 1. X-ray diffraction patterns of calcined powders were shown in Fig. 2. For mixtures with $n = 1.0$, decomposition reaction was almost completed after 5 h calcinations, as shown in Fig. 2(a). For the mixtures with $n > 1.0$, however, decomposition reaction of $SrCO_3$ was insufficient even at 800 °C. The decomposition product SrO was sup-

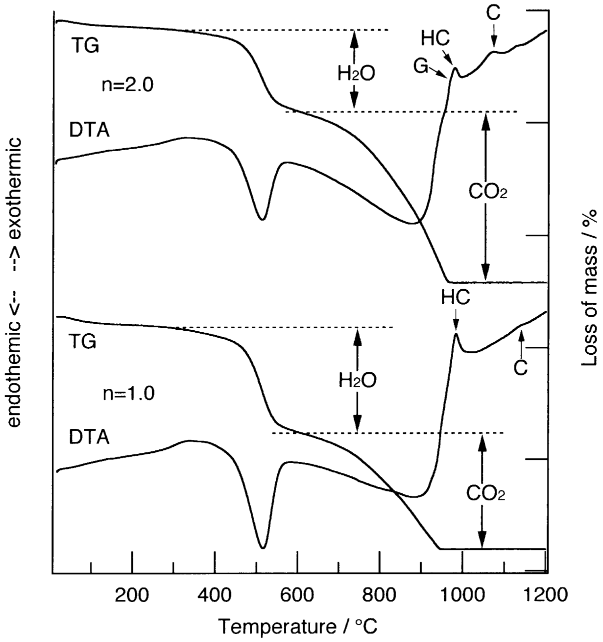

Fig. 1. DTA and TG curves of mixtures with molar ratio n (SrO/Al_2O_3) of 1.0 and 2.0. G: Crystallization of $2SrO{\cdot}Al_2O_3{\cdot}SiO_2$. HC: Crystallization of hexacelsian. C: Transformation from hexacelsian to celsian.

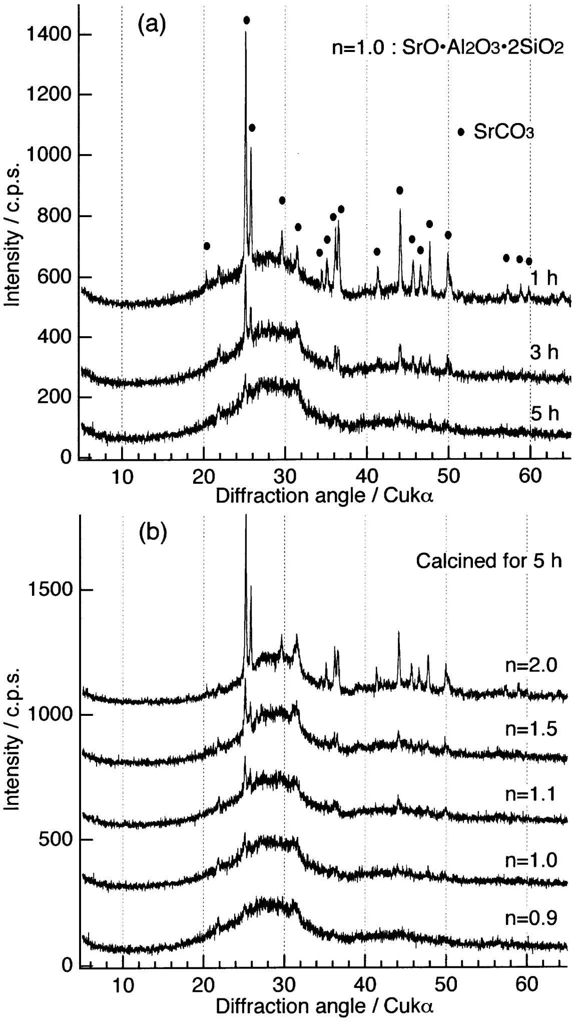

Fig. 2. XRD patterns of specimens calcined at 800 °C.

posed to react with dehydrated kaolin to form voluminous amorphous phase, because of the presence of only a broad band at 28° in 2θ. Calcined powder from the mixture with $n = 1.0$ was then milled for 1–20 h using ethanol and zirconia (ZrO_2) beads. Mean particle size r_{50} measured by particle size analyzer, specific surface area (SSA) and particle size r_{SSA} calculated from SSA are plotted against milling time in Fig. 3. Mean particle size r_{50} reached to about 0.4 μm in a short time. On the other hand, SSA and r_{SSA} showed almost constant values of 25 m^2/g and 0.1 μm, respectively, in this experimental condition. Therefore, the amorphous powders probably consisted of agglomerates with primary particles about 0.1 μm and milling caused only deagglomeration of the particles, but it was not completed.

3.3. Sintering and crystallization characteristics of calcined powders

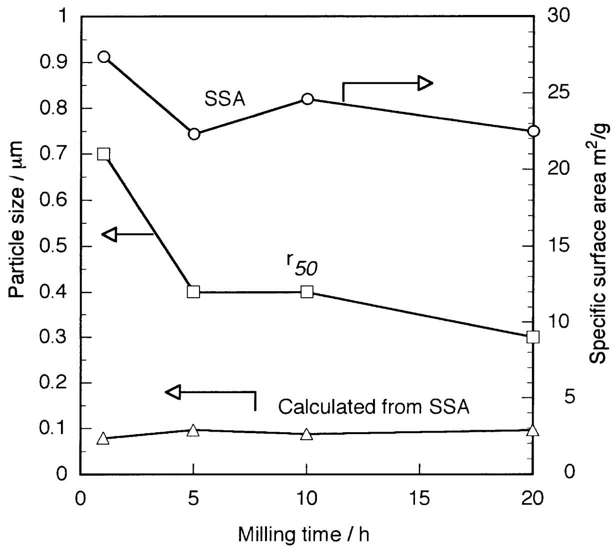

Fig. 3. Effect of milling time on specific surface area and particle size of the powders with $n = 1.0$, which were calcined at 800 °C for 5 h.

Fig. 4 shows the effect of milling time and heat-treatment temperature on the sintering characteristics of calcined powders with $n = 1.0$. The bulk density and porosity of specimens heat-treated below 900 °C were not shown in Fig. 4, because any shrinkage was not observed. Bulk density of sintered bodies increased with the increase in milling time and heat-treatment temperature. For powders milled for longer than 5 h, bulk density of higher than 2.9×10^3 kg/m^3 was reached by a heat treatment above 950 °C.

Fig. 5 shows the effect of molar ratio n (SrO/Al_2O_3) on the sintering characteristics of powders calcined at 800 °C for 5 h and then milled for 20 h. Abrupt increase in bulk density and decrease in apparent porosity shift to the lower temperature for the powder with the higher molar ratio n. Bulk density and porosity of all the specimens with $n = 0.9 - 1.2$ showed almost constant values

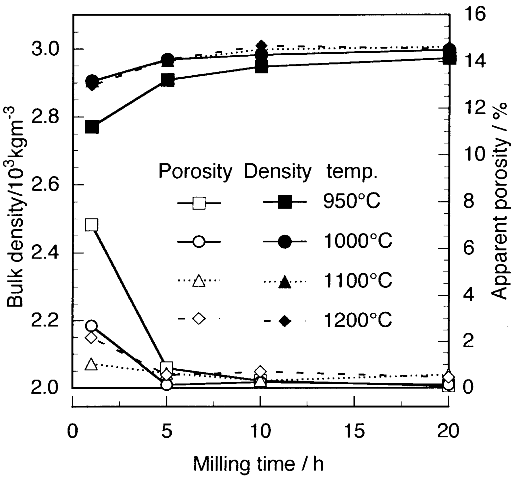

Fig. 4. Effect of milling time on the sintering characteristics of calcined powders. The powders with $n = 1.0$ were calcined at 800 °C for 5 h and then milled.

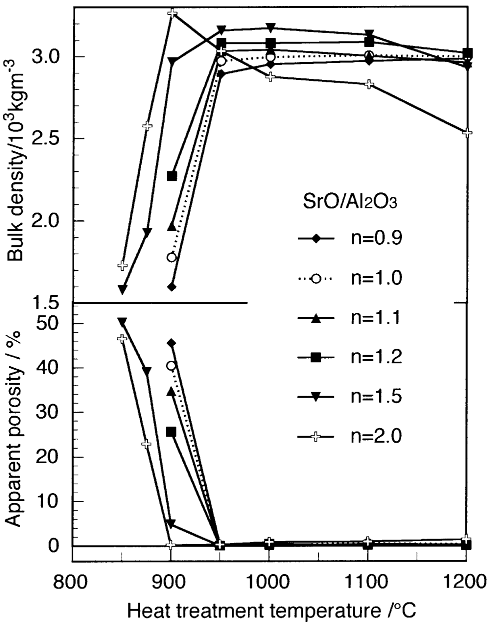

Fig. 5. Sintering characteristics of powders calcined at 800 °C for 5 h and then milled for 20 h.

above 950 °C. Specimen with $n=2.0$ exhibits a decrease in bulk density above 950 °C, which seems to be due to the evolution of CO_2 from $SrCO_3$ remained by insufficient decomposition shown in Fig. 2.

Fig. 6 shows the phase change of the powder with $n=1.0$ calcined for 5 h with heat-treatment temperature above 900 °C. At 900 °C, any crystalline phase was not observed at all. Sudden densification was found, which seemed to be promoted by viscous flow of the amorphous materials above 900 °C. Rapid crystallization of hexacelsian occurred at 950 °C, and its transformation to celsian started at 1100 °C. At 1200 °C, the phase transformation from hexacelsian to celsian was completed. This crystallization of hexacelsian and its transformation to celsian was observed as small exothermic peaks in DTA curve (Fig. 1).

Effect of molar ratio n on the transformation from hexacelsian to celsian was shown in Fig. 7. In the specimen having $n=1.2$, celsian starts to crystallize already at 1000 °C. In the specimens having $n=1.1$ and 1.2, diffraction peaks corresponding to hexacelsian disappeared completely above 1100 °C, and a small amount of $SrSiO_3$, together with $Sr_2Al_2SiO_7$, was observed at 1200 °C. In the specimen with $n=0.9$, neither mullite nor cristobalite was identified at every temperatures, even though their formation was expected from the chemical composition of the sample. Although the detailed mechanism is not known, phase transformation of hexacelsian to celsian was accelerated with the increase in molar ratio n.

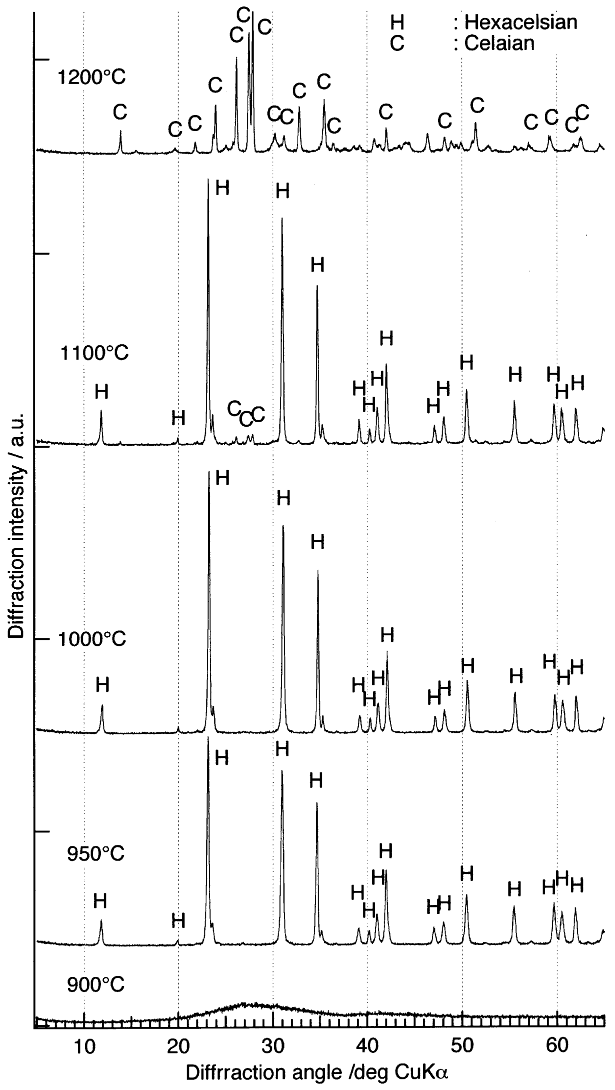

Fig. 6. X-ray powder patterns of specimen with $n=1.0$, heat-treated at different temperature for 1 h.

3.4. Properties of sintered specimens

Relative density of larger than 97% was accomplished for the specimens with $n=1.0-1.2$ at a heat-treatment temperature between 1000 and 1100 °C. SEM photographs of the polished and HF-etched sections of the specimen with $n=1.0$ are shown in Fig. 8. Only a small amount of tiny pores was observed in the polished section of specimens heat-treated at 1000 and 1100 °C. Occasionally, dendrites of hexacelsian were observed on the HF-etched section of specimens heat-treated at 1000 °C, which suggested that a small amount of glass remains. On the other hand, no character except small pores was detected on the HF-etched section of specimens heat-treated at 1100 °C, suggesting that a metastable glass was hardly remaining at this temperature.

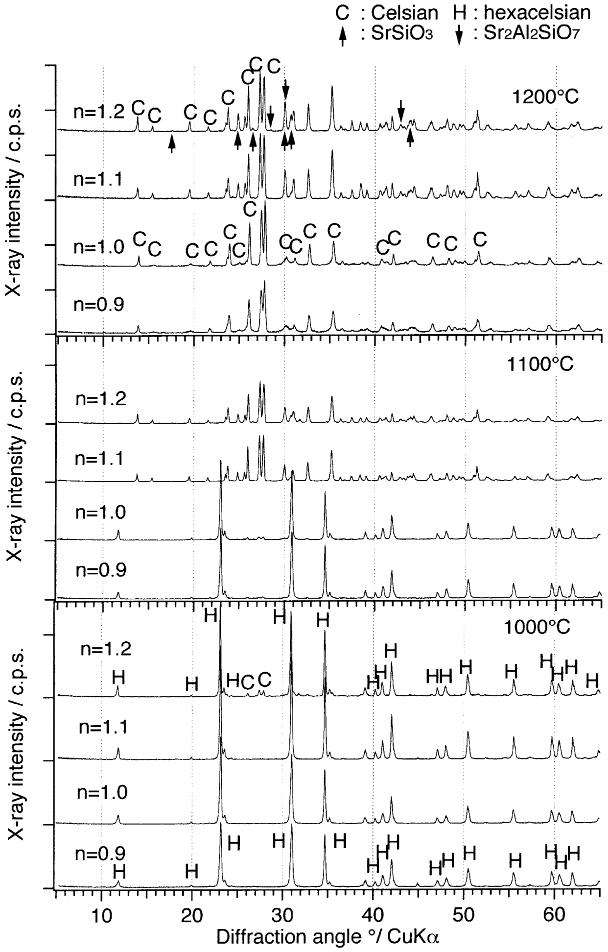

Fig. 7. Effect of molar ratio n on the transformation from hexacelsian to celsian.

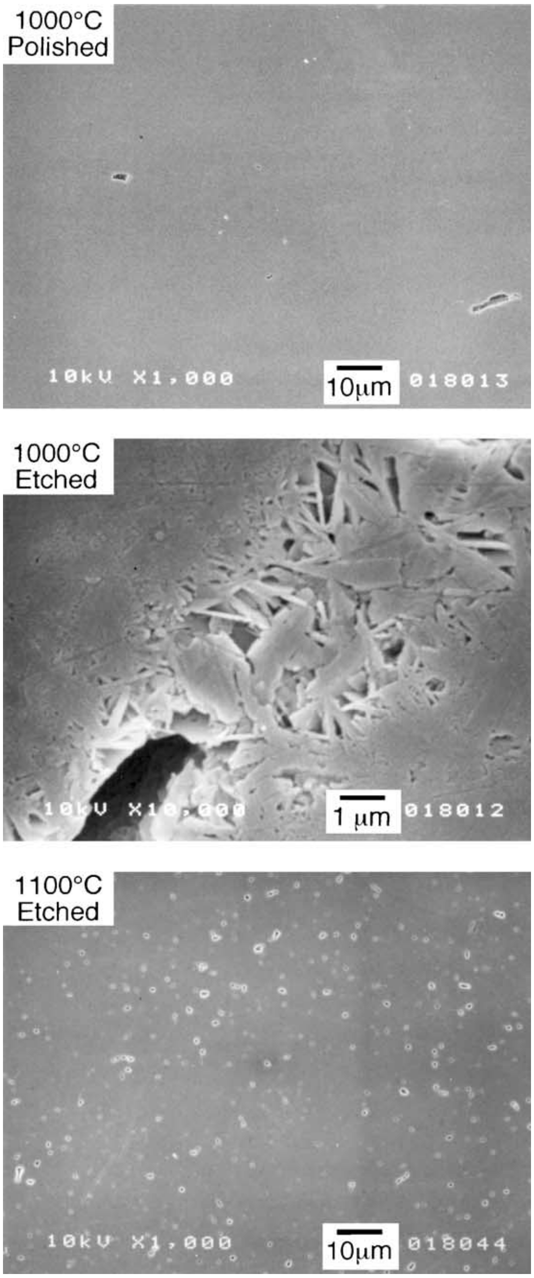

Fig. 8. SEM photographs of polished and HF-etched sections of specimens with $n = 1.0$ heat-treated at 1000 and 1100 °C.

Fig. 9 shows thermal expansion curves of celsian and hexacelsian bodies sintered at 1000 and 1200 °C with the relative density of 96 and 97%, respectively. Thermal expansion coefficient of hexacelsian calculated from the curve in Fig. 9 is about 11×10^{-6}/K. Such a high thermal expansion coefficient of hexacelsian is quite useful for multilayered substrate, which must meet the requirements of thermal matching with lower-resistance conductors or dielectric substances. The expansion curve of hexacelsian suggests the existence of low-high displacive transformation around 700 °C. Such a low-high transformation was observed for Ba-hexacelsian[3] having the same crystal structure as Sr-hexacelsian. From Fig. 9, the thermal expansion coefficient of celsian is about 4.2×10^{-6}/K, which is very similar to that of silicon. Therefore, Sr-celsian ceramics can be used as substrate materials for polycrystalline silicon thin-film in solar cells.[7]

Relative dielectric constant and dielectric loss of hexacelsian heat-treated at 1100 °C was measured to be 5.3 and 0.5×10^{-4} (1 MHz), respectively, by impedance analyzer HP-4194A. Both values are low enough to be used as substrate materials for semiconductor packaging or multilayered ceramic substrate for high frequency electronic circuits.

4. Conclusions

In this work, preparation process and sintering characteristics of reactive powders, which could lead to either hexacelsian or celsian, were investigated using kaolin and $SrCO_3$ as starting materials and following results were clarified.

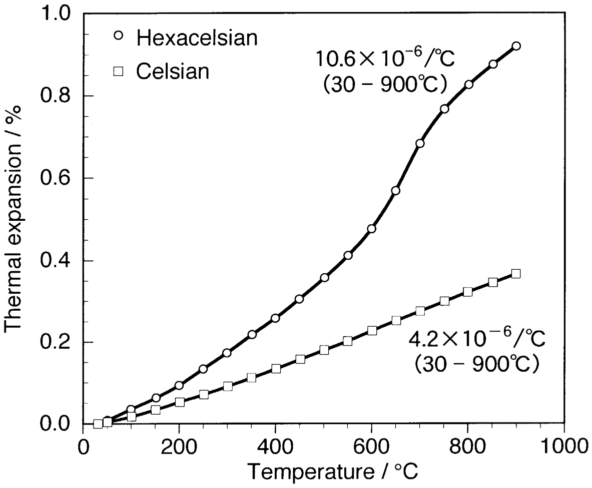

Fig. 9. Thermal expansion curves of hexacelsian and celsian ceramics prepared at 950 and 1200 °C, respectively.

1. Reactive amorphous powders having chemical composition of $SrO{\cdot}Al_2O_3{\cdot}2SiO_2$ could be obtained by calcination of the mixtures of kaolin and $SrCO_3$. The compacts of the powders sintered to hexacelsian and celsian ceramics with relative density of 96 and 97.5% at 1000 and 1100 °C, respectively.
2. An increase in molar ratio of n (SrO/Al_2O_3) accelerated the transformation from hexacelsian to celsian, and dense celsian ceramics could be obtained at a heat-treatment temperature below 1100 °C.
3. Dielectric properties of hexacelsian were suitable for substrate materials for semiconductor packaging or multilayered ceramics substrate for high-frequency electric circuits.

References

1. Bansal, N. P. and Hyatt, M. J., Crystallization and properties of Sr-Ba aluminosilicate glass–ceramic matrices. *Ceram. Eng. Sci. Proc*, 1991, **12**, 1222–1234.
2. Kobayashi, Y., Transformation kinetics from hexacelsian to celsian for powders having uniform particle size. *Ceramics International*, 2001, **27**, 179–184.
3. Bahat, D., Several metastable alkaline earth feldspar modifications. *J. Mater. Sci.*, 1972, **7**, 198–201.
4. Kobayashi, Y., Sumi, K., Asai, T. and Kato, E., Fabrication of dense celsian ceramics by reaction of kaolin with $SrCO_3$ and $BaCO_3$. *J. Ceram. Soc. Japan*, 1999, **107**, 657–661.
5. Chinn, R. E., Haun, M. J., Kim, C. Y. and Price, D. B., Low-temperature transient glass-phase processing of monoclinic $SrAl_2Si_2O_8$. *J. Am. Ceram. Soc.*, 1998, **81**, 2285–2293.
6. Kobayashi, Y., Sumi, K. and Kato, E., Reaction and sintering for the mixtures of kaolin and calcium carbonate below 1000 °C. *J. Ceram. Soc. Japan*, 1999, **107**, 657 -661.
7. Keitz, A., Roosmalen, J. A. M., Tool, C. J. J., Schiermeier, S. E. A., Zutphen, A. J. M. M., Fung, F. and Christie, G. M., Improvement of low cost ceramic substrates for use in thin film silicon solar cells. In *2nd World Conference on Photovoltaic Solar*. 1998, pp. 1829–1832.