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Solid-state synthesis of ceramics in the $BaO–SrO–Al_2O_3–SiO_2$ system

Yen-Pei Fu[a,*], Chin-Chung Chang[a], Cheng-Hsiung Lin[b], Tsung-Shune Chin[a]

[a]*Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu 300, Taiwan, ROC*
[b]*Department of Chemical Engineering, Wu-Feng Institute of Technology, Ming-Hsiung, Chiayi 621, Taiwan, ROC*

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Abstract

The solid-state reaction route was successfully used to prepare $(Ba,Sr)O–Al_2O_3–2SiO_2$ ceramics. Firstly, the mixed powder was characterized by differential thermal analysis and thermogravimetric analysis. The ceramics powder was obtained by calcining a $BaCO_3$, $SrCO_3$, Al_2O_3, and SiO_2 mixture at 950 °C for 4 h. Secondly, the calcined powder was pressed, sintered at 1040 °C for 4 h, Then the sintered samples were investigated by X-ray diffraction, scanning electron microscopy, density measurement, and thermal mechanical analyzer. In this work, the appropriate addition of SrO was observed to enhance the hexacelsian to celsian transformation. Additionally, the appropriate addition of SrO effectively reduced the thermal expansion coefficient of the $(Ba,Sr)O–Al_2O_3–2SiO_2$ ceramics.

Keywords: C. Thermal expansion; Barium aluminosilicate; Strontium aluminosilicate

1. Introduction

Barium aluminosilicate ($BaAl_2Si_2O_8$, BAS) exists primarily in three polymorphic forms; monoclinic, hexagonal, and orthorhombic [1]. Monocelsian, often called celsian, is the monoclinic form which is attractive as a substrate material for high-frequency electrical circuit boards, because it has a low dielectric constant (5–6 at 1MHz), a low dielectric loss, and a low coefficient of thermal expansion ($2.29\times10^{-6}/°C$)[2]. Hexacelsian is not a desired phase for this application because of its high thermal expansion coefficient ($8\times10^{-6}/°C$ in the range of 300–1000 °C)[3]. Hexacelsian is always metastable below 1590 °C and reversibly transforms to the orthorhombic form at approximately 300 °C undergoing a large volume change of 3–4%. This volume change may generate microcracks [4].

Strontium aluminosilicate ($SrAl_2Si_2O_8$, SAS) also exists in two polymorphic forms: monocelsian and hexacelsian. The monocelsian form has a high melting point (1650 °C) and a low coefficient of thermal expansion ($2.5\times10^{-6}/°C$). The hexacelsian form, a high-temperature metastable phase of strontium aluminosilicate, shows a high coefficient of thermal expansion ($8\times10^{-6}/°C$) and reversible phase transformations at 600–800 °C causing a volume expansion of approximately 3% [5]. In strontium aluminosilicate the hexacelsian phase may also exist metastably. The kinetics and mechanisms of the transformation from hexacelsian to monocelsian, with and without doping with mineralizers, have been reported, and the effects of mineralizers such as Li_2O, LiF, MoO_3, and TiO_2 have been identified [6,7]. Bansal et al. revealed that the addition of strontium oxide can promote the hexacelsian-monocelsian transformation in BAS glass fabricated by the melting route [8].

Several approaches to obtaining glass ceramics exist. They include glass processing (crystallized glass), the use of multiphase ceramics (glass + ceramic), and the sol-gel method. In the conventional melting method, which requires very high temperature (>1400 °C), chemical stoichiometric loss on ignition and phase separation are the primary problems in glass processing. For the multiphase ceramics, a low-softening temperature glass used as a sintering flux is added to crystalline ceramics and then fired at elevated temperature. In the multiphase

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[*] Corresponding author. Tel.: +886-3-571-4635; fax: +886-3-571-4635.

E-mail address: g887503@yahoo.com.tw (Y.-P. Fu).

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processing of ceramics, the preparation of these low-softening glasses temperature also requires a high temperature. The sol-gel process depends on special organic sources. These organic sources are usually expensive. However, the solid-state reaction route with low processing costs is normally used as a common industrial method for producing ceramics. This paper attempts to produce stoichiometric BAS ceramics by the solid-state reaction route and to study the influence of adding strontium oxide, by substituting Sr for Ba in the stabilization of the monocelsian.

2. Experimental procedures

Powder stoichiometric celsian compositions were prepared by a solid-state reaction. In this investigation, forms of $(Ba_{1-x}Sr_x)O–Al_2O_3–2SiO_2$ with compositions given by $x = 0$, 0.125, 0.250, 0.375, 0.475, 0.500, 0.750, and 1 were compared. The aim of adding SrO is to study its ability to stabilize the monocelsian form of the stoichiometric celsian. Samples were prepared from reagent-grade powders of $BaCO_3$, SiO_2, Al_2O_3, and $SrCO_3$. The size and specific surface area of the particles are important factors in the solid-state reactions for the densification of ceramics. Table 1 lists the size and surface area of the particles of the starting materials for preparing $BaO–SrO–Al_2O_3–SiO_2$ ceramics. Mixtures were ball-milled for 4 h in distilled water, dried, and calcined at 950 °C for 4 h. Subsequently the powder was remilled, granulated, and pressed into pellet under a uniaxial pressure of 100 MPa. Pellets were sintered at 1140 °C for 4 h with 3 °C/min rate of temperature increase.

A computer-interfaced X-ray powder diffractometer (XRD, Rigaku D/Max-II) with CuK_α radiation was used to identify the crystalline phases in sintered $(Ba,Sr)O–Al_2O_3–2SiO_2$ ceramics. The hexacelsian to monocelsian transition ratio, f, was determined using the following equation:

$$f = \frac{I_{\mathrm{mono}}}{I_{\mathrm{hexa}} + I_{\mathrm{mono}}} \times 100\% \qquad (1)$$

Here I_{hexa} represents the integral intensity corresponding to the (101) peak for the hexacelsian phase and I_{mono} is the integral intensity corresponding to the (130) peak for the monocelsian phase.

The densities and porosities of sintered ceramics were measured by the Archimendean method. Differential thermal analysis and thermogravimetry (DTA/TG, Rigaku Thermalplus TG 8120) were used to determine the exo-endo temperature of the initial mixture of $BaCO_3 + SrCO_3 + Al_2O_3 + SiO_2$ powders. A heating rate of 10 °C/min was used to take both the DTA and the TG measurements up to 1000 °C in air. The microstructure of the polished and etched specimens was observed using a scanning electron microscope (SEM, JEOL JSM-6500F). The linear thermal expansion coefficient from room temperature to 400 °C was measured in air at a heating rate of 10 °C/min using a thermal mechanical analyzer (TMA, SEIKO TMA 320).

Table 1
Particle size and surface area of starting materials

Starting materials	$BaCO_3$	$SrCO_3$	Al_2O_3	SiO_2
Particle size (μm)	5.67	3.35	0.62	0.08
Surface area (m^2/g)	0.43	0.78	5.32	45.38

3. Results and discussion

Phase transformations of the initial mixture of $BaCO_3 + SrCO_3 + Al_2O_3 + SiO_2$ powders were examined using a differential thermal analyzer and thermogravimetry. The DTA/TG results are very important in

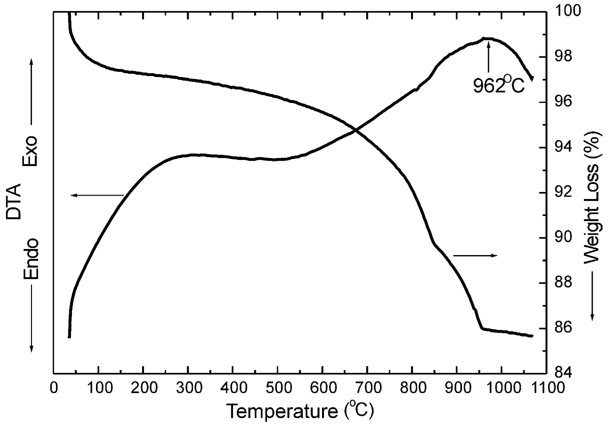

Fig. 1. TG/DTA curves of $(Ba,Sr)O–Al_2O_3–2SiO_2$ powder.

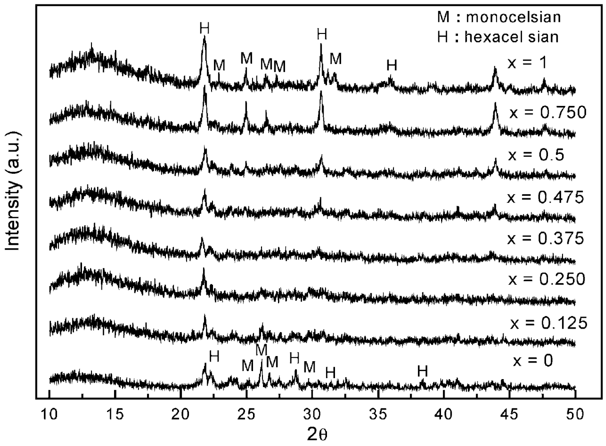

Fig. 2. XRD patterns of the $(Ba_{1-x}Sr_x)O–Al_2O_3–2SiO_2$ samples with different SrO amounts heated at 1040 °C for 4 h.

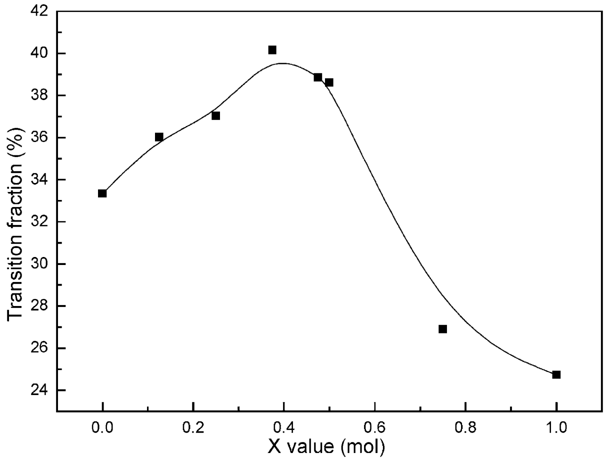

Fig. 3. Hexacelsian → monocelsian phase transition of the samples with different SrO amounts heated at 1040 °C for 4 h.

determining the reaction temperatures of the sample. Fig. 1 presents the differential thermal analysis and thermogravimetric curves for 0.625BaO–0.375SrO–Al_2O_3–$2SiO_2$ powder. The weight of 0.625BaO–0.375SrO–Al_2O_3–$2SiO_2$ powder appears to be constant for temperature above 960 °C, and the exothermic peak appears around 960 °C, which is attributed to the crystallization of a phase confirmed by XRD analysis.

XRD studies reveal some important information regarding the phase evolution of the specimens. Fig. 2 presents the XRD patterns of all specimens sintered at 1040 °C for 4 h. Hexacelsian and monocelsian are present in all the samples. Interestingly, the ratio of the amount of monocelsian to that of hexacelsian increases with the addition of SrO. Fig. 3 plots the transition ratio of hexacelsian to monocelsian for different amounts of added SrO in the samples heated at 1040 °C for 4 h. The transition ratio of hexacelsian to monocelsian was calculated according to Eq. (1). It increases gradually with the amount of added SrO. After the maximum transition rate (40.1%) is reached when 0.375 mol SrO is added, the transition rate decreases drastically, indicating that adding the appropriate amount of SrO enhances the transition degree of hexacelsian to monocelsian.

The thermal expansion coefficient of material depends on its crystalline phases, and additives. Fig. 4(a) and (b) show the thermal expansion curves for BaO–Al_2O_3–$2SiO_2$ and SrO–Al_2O_3–$2SiO_2$ ceramics, respectively, sintered at 1040 °C for 4 h. The orthorhombic-to-hexacelsian transformation of BaO–Al_2O_3–$2SiO_2$ occurs in

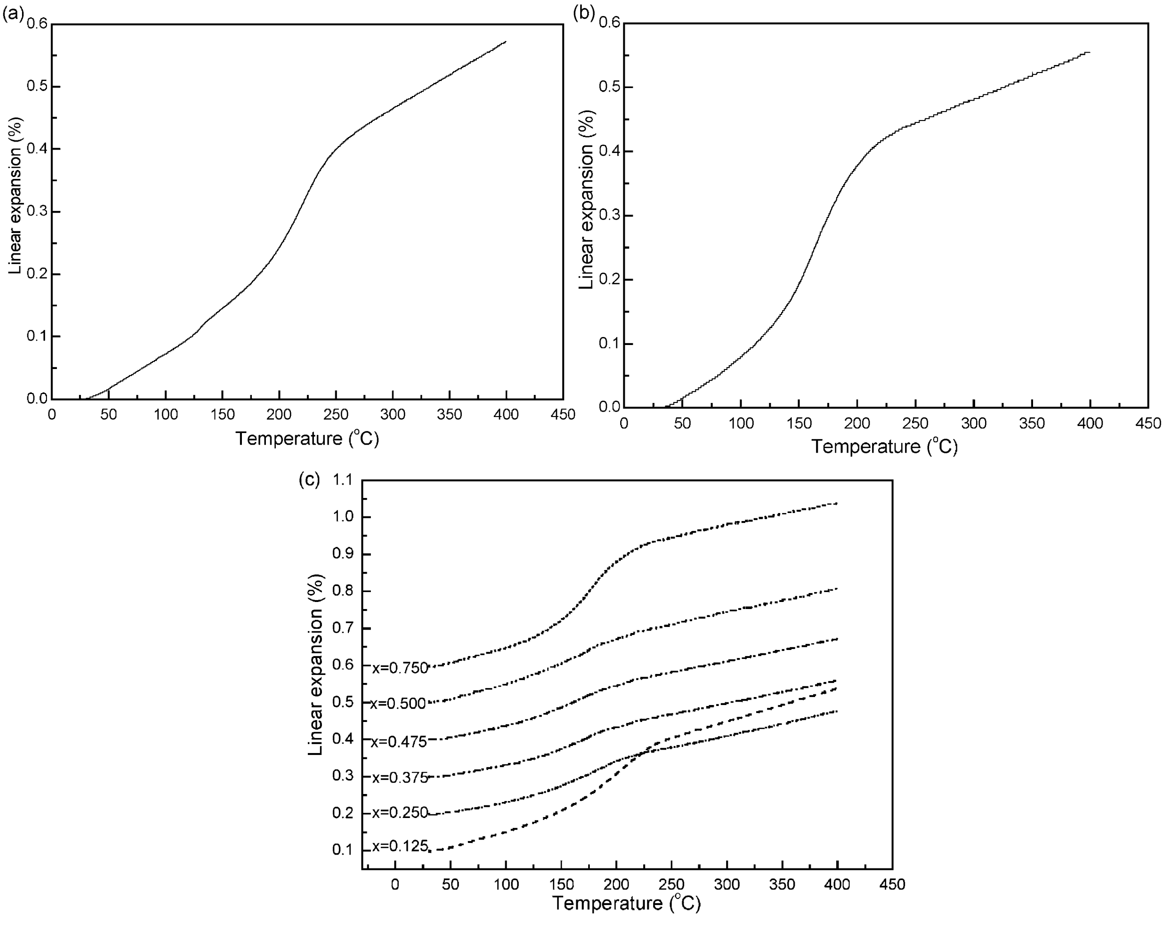

Fig. 4. TMA curves of (a) BaO–Al_2O_3–$2SiO_2$, (b) SrO–Al_2O_3–$2SiO_2$, (c) $(Ba_{1-x}Sr_x)O$–Al_2O_3–$2SiO_2$.

the temperature range of 200–250 °C, causing a large volume change. The metastable phase of hexacelsian is formed at a temperature above 250 °C. The orthorhombic-to-hexacelsian transformation temperature of SrO–Al_2O_3–$2SiO_2$ is between 150 and 220 °C. The average linear thermal expansion coefficients in the range 25–400 °C were calculated to be 15.48×10^{-6}/°C and 15.00×10^{-6}/°C for the two compositions, respectively. These high thermal expansion coefficients may be associated with the presence of the hexacelsian phase in the BaO–Al_2O_3–$2SiO_2$ and SrO–Al_2O_3–$2SiO_2$ ceramics. Fig. 4(c) plots the thermal expansion curves of (Ba,Sr)O–Al_2O_3–$2SiO_2$ ceramics with various SrO contents. The curves show that replacing an appropriate amount of BaO with SrO in (Ba,Sr)O–Al_2O_3–$2SiO_2$ ceramic can effectively reduced the thermal expansion coefficient.

Fig. 5 plots the average thermal expansion coefficient in the 25–400 °C range with different SrO amounts of added. The average thermal expansion coefficients of $(Ba_{1-x}Sr_x)O$–Al_2O_3–$2SiO_2$ ceramic with 0.250, 0.375, 0.475, and 0.500 mol were 7.47×10^{-6}/°C, 6.99×10^{-6}/°C, 7.37×10^{-6}/°C, and 8.32×10^{-6}/°C (25–400 °C), respectively. Notably, adding an appropriate concentration of SrO in the range 0.250–0.475 mol can effectively reduce the average thermal expansion coefficient, implying that the appropriate addition of strontium oxide promotes the transformation form hexacelsian to celsian. The average thermal expansion coefficient is minimum for the sample with 0.375 mol SrO. These results are strongly consistent with transition rate and confirm that the SrO additive can promote the hexacelsian to monocelsian transition up to a amount of around 0.375 mol, while an inhibitory effect was observed at higher SrO amount.

Fig. 6 shows the relative density of the samples sintered at 1040 °C for 4 h. The relative density equals the bulk density of a sample divided by its theoretical density. The theoretical densities of stoichiometric BaO–Al_2O_3–$2SiO_2$ and SrO–Al_2O_3–$2SiO_2$ are 3.391 and 3.084 g/cm^3, respectively. The theoretical density of the studied composition can be obtained applied a simple rule of mixture approach [3]. The sample with $x = 0.500$ is the most dense, but increasing the amount of SrO may reduce the density. The porosity of (Ba,Sr)O–Al_2O_3–SiO_2 system was also measured. Fig. 7 plots the relative porosities of the samples against SrO content. Samples with 0.125–0.500 mol SrO are shown to have low porosity, which decreases almost to zero. A comparison of the density measurement and the porosity measurement reveals that samples with low porosity but have relative density not close to 100%, perhaps because of the formation of some closed pores before densification occurs during sintering. Fig. 8 presents SEM photographs of etched samples. The micrograph shows that the sample with moderate SrO content ($x = 0.5$ mol) has a much less porous than the other samples. The microstructures of BaO–Al_2O_3–$2SiO_2$ and SrO–Al_2O_3–$2SiO_2$ ceramics

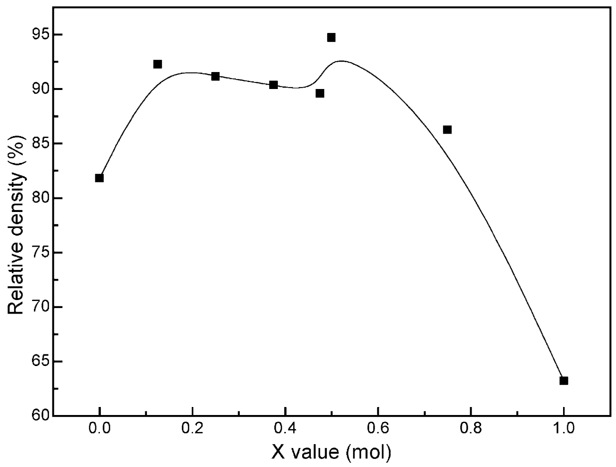

Fig. 6. Relative density of the samples with different SrO amounts heated at 1040 °C for 4 h.

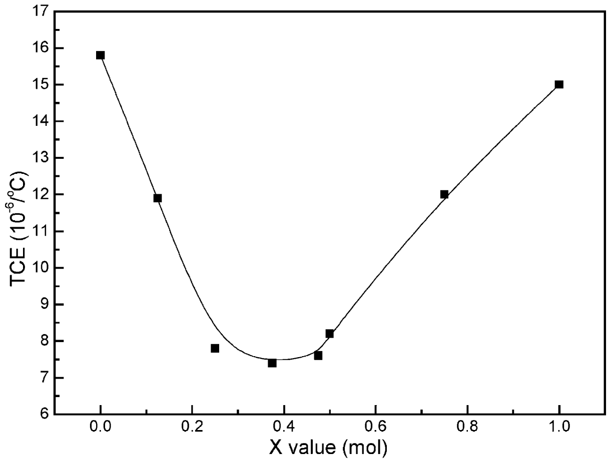

Fig. 5. The average thermal expansion coefficient of the samples with different SrO amounts in the range of 25–400 °C.

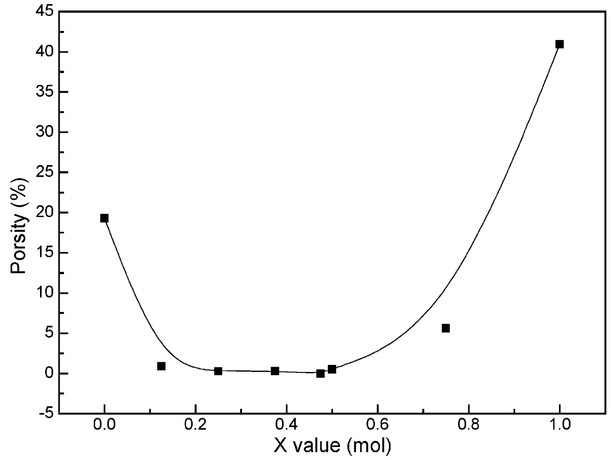

Fig. 7. Relative porosity of the samples with different SrO amounts heated at 1040 °C for 4 h.

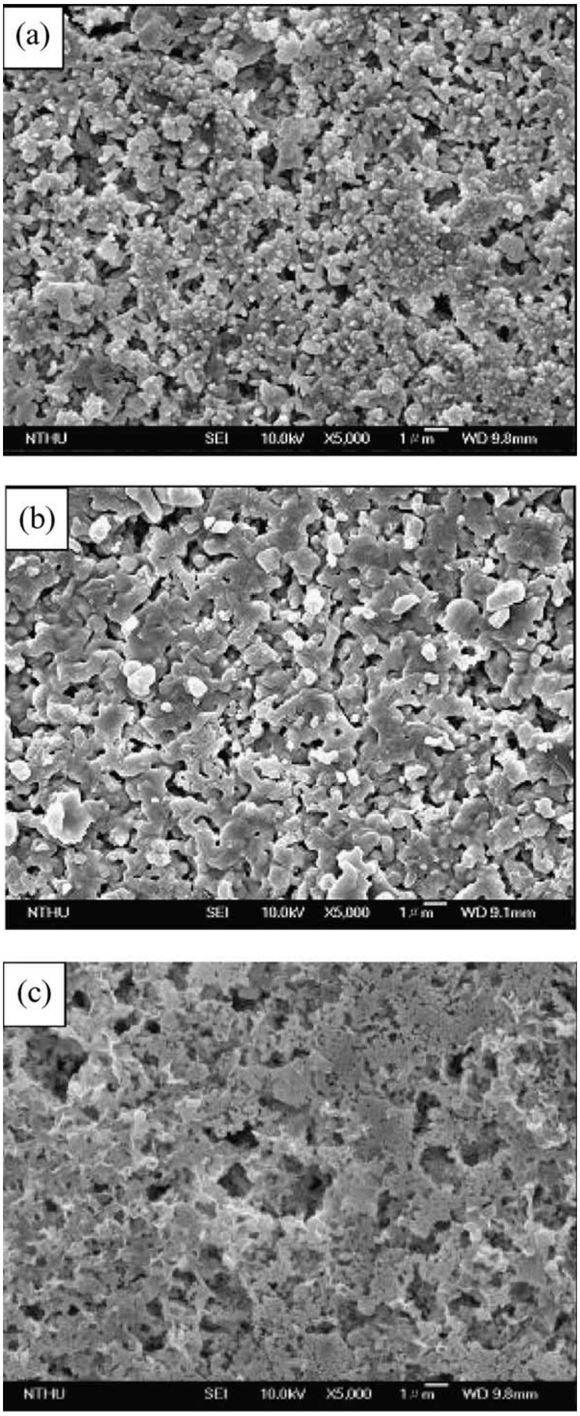

Fig. 8. SEM photographs of the etched samples with different SrO amounts sintered at 1040 °C for 4 h. (a) $x=0$ mol, (b) $x=0.5$ mol, (c) $x=1$ mol.

have relatively high porosity. The density measurements and SEM photographs showed that the appropriate addition of SrO can increase the densification of BaO–Al_2O_3–$2SiO_2$ ceramics.

4. Conclusions

Ceramics with the composition of (Ba,Sr)O–Al_2O_3–$2SiO_2$ were successfully synthesized by the solid-state reaction route. This approach has the potential to synthesize celsian ceramics at a low temperature, in contrast to the traditional melting route, which requires a high temperature. This study shows that the controlled addition of SrO can enhance the hexacelsian to celsian transformation. Moreover, adding SrO can effectively reduce the thermal expansion coefficient of the (Ba,Sr)O–Al_2O_3–$2SiO_2$ ceramics. The BaO–SrO–Al_2O_3–SiO_2 ceramics with 0.375 mol SrO has the lowest average thermal expansion coefficient (6.99×10^{-6}/°C) and the highest degree of transition (40.1%) from hexacelsian to monocelsian.

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