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Solid state synthesis and properties of monoclinic celsian

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Monoclinic celsian of $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ (BSAS-1) and $Ba_{0.85}Sr_{0.15}Al_2Si_2O_8$ (BSAS-2) compositions have been synthesized from metal carbonates and oxides by solid state reaction. A mixture of $BaCO_3$, $SrCO_3$, Al_2O_3, and SiO_2 powders was precalcined at ~900–940 °C to decompose the carbonates followed by hot pressing at ~1300 °C. The hot pressed BSAS-1 material was almost fully dense and contained the monoclinic celsian phase, with complete absence of the undesirable hexacelsian as indicated by X-ray diffraction. In contrast, a small fraction of hexacelsian was still present in hot pressed BSAS-2. However, on further heat treatment at 1200 °C for 24 h, the hexacelsian phase was completely eliminated. The average linear thermal expansion coefficients of BSAS-1 and BSAS-2 compositions, having the monoclinic celsian phase, were measured to be $5.28 \times 10^{-6}\,^{\circ}C^{-1}$ and $5.15 \times 10^{-6}\,^{\circ}C^{-1}$, respectively, from room temperature to 1200 °C. The hot-pressed BSAS-1 celsian showed room temperature flexural strength of 131 MPa, elastic modulus of 96 GPa and was stable in air up to temperatures as high as ~1500 °C.

1. Introduction

Monoclinic celsian $BaAl_2Si_2O_8$ (BAS) and $SrAl_2Si_2O_8$ (SAS) are refractory materials having melting points higher than 1700 °C. These are resistant to oxidation and reduction and also show reasonably good resistance to alkali attack. These materials are phase stable up to ~1600 °C and chemically compatible with alumina, mullite and silicon nitride (in inert or nitrogen atmospheres) at elevated temperatures. They show low values of dielectric constant and loss tangent which make them promising materials for electromagnetic windows/radome applications [1] at high temperatures, packaging for micro-electronics, high voltage condensers and other electric insulating products. Celsian is also being investigated as a matrix material for reinforcement with continuous ceramic fibres for high temperature structural composites [2–5] for applications in hot sections of the turbine engine.

BAS exists in three different polymorphs: the monoclinic, hexagonal, and orthorhombic phases. The monoclinic phase, commonly known as celsian, is the naturally occurring phase. The hexagonal, also known as hexacelsian, and the orthorhombic phases are found only in synthetic products. The hexacelsian phase is thermodynamically stable at temperatures between 1590 °C and the melting point whereas the celsian phase is stable at temperatures below 1590 °C. However, hexacelsian can exist as a metastable phase at all temperatures from 1590 °C to room temperature. At ~300 °C, hexacelsian undergoes a rapid, reversible structural transformation [6] into the orthorhombic form, accompanied with a large volume change of ~3%. Thus, hexacelsian is an undesirable phase.

In both BAS and SAS systems, the hexacelsian is always the first phase to form. However, on heat treatment at ~1200 °C or higher temperatures, its transformation into the monoclinic phase is very sluggish in BAS [7] and very rapid in SAS [8]. It is known that doping of BAS with SAS accelerates the hexacelsian to monoclinic celsian transformation [9]. Fortunately, BAS and SAS form solid solutions in the entire composition range [1, 9]. Starting compositions of $0.75BaO–0.25SrO–Al_2O_3–2SiO_2$ (BSAS-1) and $0.85BaO–0.15SrO–Al_2O_3–2SiO_2$ (BSAS-2) were used for the synthesis of monoclinic celsian in the present study.

Formation of celsian from clay–salt mixtures has been studied by others [10–13]. The objective of the present study was to develop a procedure for the synthesis of monoclinic celsian from solid state reaction of barium and strontium carbonates, alumina and silica. Room-temperature flexural strength, elastic modulus, and coefficient of linear thermal expansion of hot pressed celsian material have been measured. High temperature stability in oxidizing environment has also been examined.

2. Experimental procedures

The starting materials used were $BaCO_3$ (Alfa), $SrCO_3$ (Alfa), Al_2O_3 (Baikowski, high purity CR 30), and SiO_2 (Cerac, 99.9% purity, −325 mesh) powders.

Monoclinic celsian of compositions 0.75BaO–0.25SrO–Al_2O_3–$2SiO_2$ (BSAS-1) and 0.85BaO–0.15SrO–Al_2O_3–$2SiO_2$ (BSAS-2) were synthesized by the solid-state reaction method. Appropriate quantities of the powders were slurry mixed in acetone and ball milled for ∼24 h using alumina milling media. Acetone was then evaporated and a part of the mixture was subjected to thermogravimetric analysis (TGA) in air. Based on the TGA results, the mixed powder was calcined at ∼900–910 °C for 24 h for decomposition of the carbonates followed by cooling to room temperature and grinding. The calcined powder was loaded into a graphite die and hot pressed at 1300 °C for 2–3 h under 27.5 MPa pressure into ∼5 × 2.5 cm or 11.25 × 5 cm plates. The surface of the hot-pressed plate was polished. The plates were sliced into bars for thermal expansion and bend strength measurements.

TGA was carried out at a heating rate of 5 °C min^{-1} under flowing air (∼60 ml min^{-1}) from room temperature to 1500 °C using a Perkin-Elmer TGA-7 system which was interfaced with a computerized data acquisition and analysis system. X-ray diffraction (XRD) patterns were recorded at room temperature using a step scan procedure (0.02°/2θ step, time per step 0.5 or 1 s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing CuK_α radiation. Coefficient of thermal expansion was measured from room temperature to 1200 °C on a 2.5-cm long bar using a Netzsch differential dilatometer model 402 ED. Alumina was used as the standard material. Room temperature flexural strengths were determined using ∼5 × 0.625 cm bend bars. Stress–strain curves were recorded using a four-point bend fixture having 40 mm support span and 20 mm loading span. An Instron machine at a crosshead speed of 0.127 cm min^{-1} was used. Microstructures of the polished cross-sections were observed in a JEOL JSM-840A scanning electron microscope (SEM). X-ray elemental analyses of the phases were carried out using a Kevex Delta thin window energy dispersive spectrometer (EDS) and analyzer. A thin carbon coating was evaporated onto the SEM specimens for electrical conductivity prior to analysis.

3. Results and discussion

The TGA curve of the mixed powder of BSAS-1 composition consisting of metal carbonates and oxides is shown in Fig. 1. Minor weight loss near room temperature is caused by evaporation of the residual moisture and acetone. A major event showing a large weight loss, a result of the decomposition of barium and strontium carbonates into oxides, is observed between ∼750 and 1000 °C. A calcination temperature of 900–940 °C was chosen for decomposition of the carbonates. The mixed powder was calcined at this temperature for 20–24 h in air. TGA analysis of this calcined powder showed no further weight loss indicating complete decomposition of the metal carbonates during the calcination step.

The XRD pattern of the mixed powder, calcined at ∼915 °C for 20 h in air, is presented in Fig. 2. SiO_2 (α-quartz) and $BaAl_2O_4$ were the major phases present. Small amounts of Ba_2SiO_4, α-Al_2O_3, and $Ba_2Sr_2Al_2O_7$ were also identified. Fig. 3. shows the XRD pattern taken from the surface of a BSAS-1 monolithic plate made by hot pressing the precalcined powder at 1300 °C for 2 h under 27.5 MPa. All the XRD peaks correspond to the monoclinic celsian phase with complete absence of the undesirable hexacelsian phase. Hot pressing a powder of BSAS-2 composition, synthesized using the same procedure as above, at 1300 °C for 3 h at 27.5 MPa, resulted in the formation of monoclinic celsian along with a small amount of the hexacelsian phase (Fig. 4a). However, on further heat treatment at 1200 °C for 24 h in air, the undesirable hexacelsian phase was completely eliminated as seen in the XRD pattern in Fig. 4b.

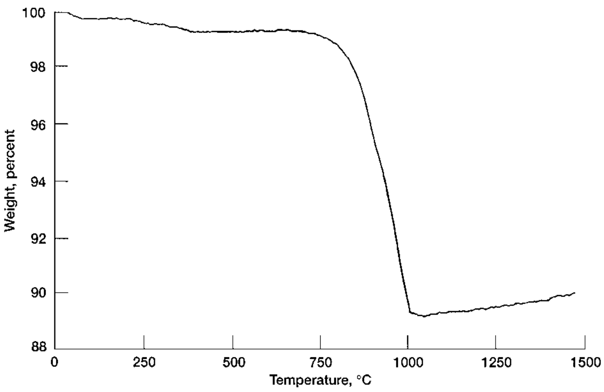

Figure 1 TGA curve of 0.75$BaCO_3$–0.25$SrCO_3$–Al_2O_3–$2SiO_2$ mixed powder at a heating rate of 5 °C min^{-1} in air.

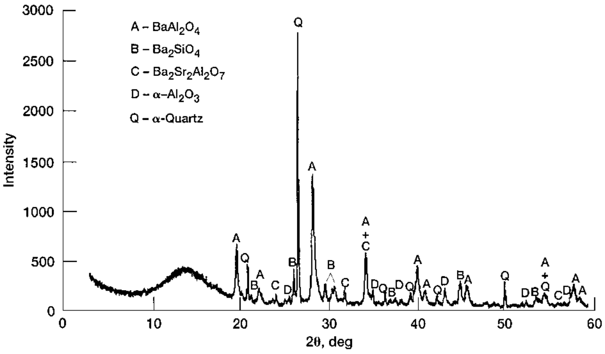

Figure 2 Powder X-ray diffraction pattern of the mixed 0.75$BaCO_3$–0.25$SrCO_3$–Al_2O_3–$2SiO_2$ powder after calcination at 915 °C for 20 h in air.

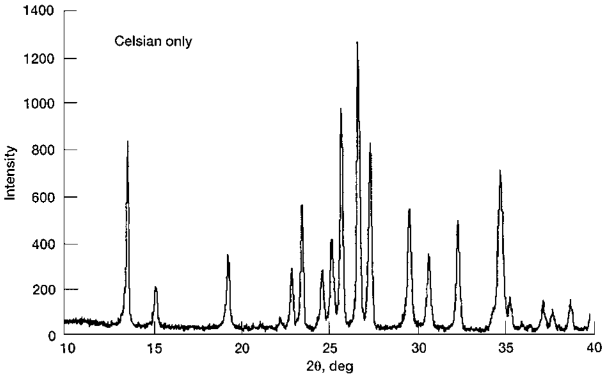

Figure 3 X-ray diffraction spectra from the surface of a $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ plate hot pressed at 1300 °C for 2 h at 27.6 MPa. All the diffraction peaks match with the monoclinic celsian phase.

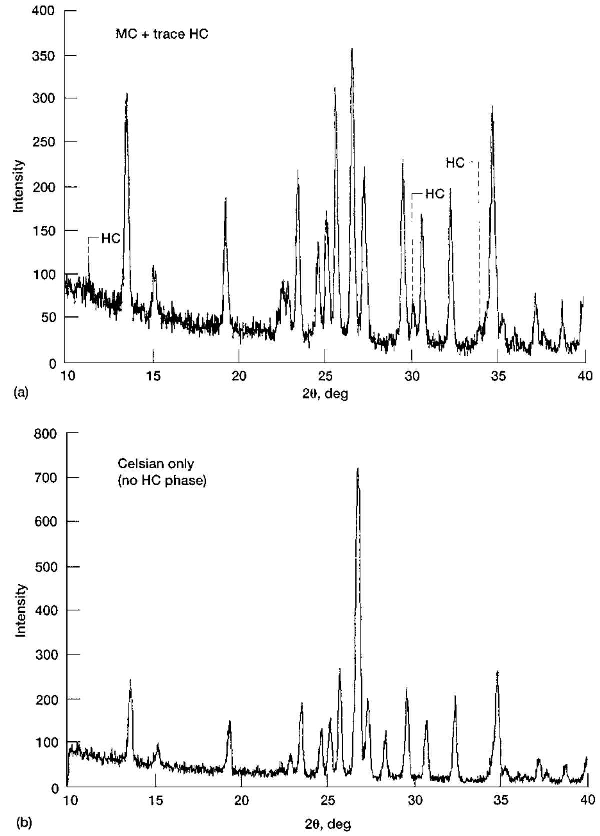

Figure 4 XRD spectra from the surface of a $\mathrm{Ba_{0.85}Sr_{0.15}Al_2Si_2O_8}$ plate hot pressed at 1300 °C for 3 h at 27.6 MPa: (a) as hot pressed; (b) after heat treatment for 24 h at 1200 °C in air.

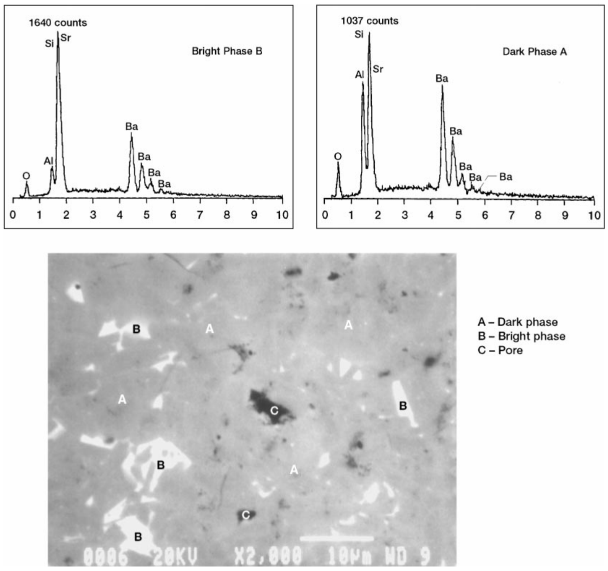

Figure 5 Back-scattered electron micrograph of the polished cross-section of $\mathrm{Ba_{0.75}Sr_{0.25}Al_2Si_2O_8}$ specimen hot pressed at 1300 °C for 2 h at 27.6 MPa. EDS compositional spectra of the dark (A) and bright (B) phases are also given.

SEM micrographs of polished cross-sections of BSAS-1 monoliths, as hot-pressed and after annealing at 1200 °C for 24 h in argon, are shown in Figs 5 and 6, respectively. A bright phase B in the bulk celsian dark phase A, along with some pores C, are present in both samples. EDS compositional spectra taken from the bright and dark phases are also given in Figs 5 and 6. The bright phase B is richer in Si and Sr and deficient in A1 and Ba than the bulk celsian phase A. Approximate chemical composition of the bright phase B was determined to be $\mathrm{(Ba,Sr)AlSi_3O_8}$ with the hyalophane structure. Annealing at 1200 °C does not appear to have much effect on phase composition. The fraction of phase B should be low as it could not be detected from XRD analysis.

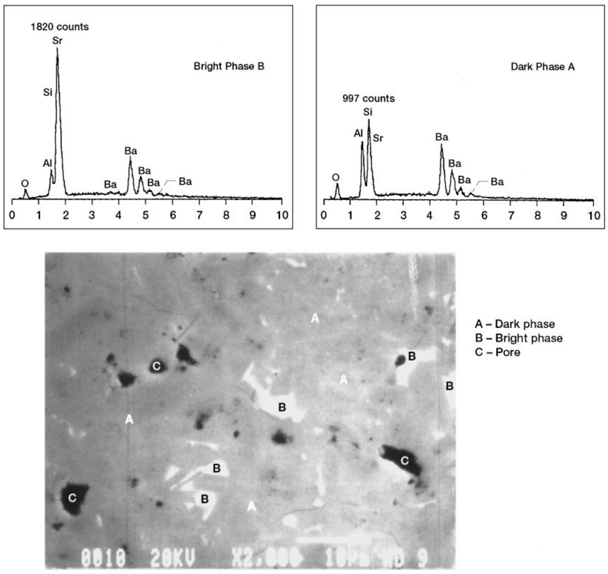

Figure 6 Back-scattered electron micrograph of the polished cross-section of $\mathrm{Ba_{0.75}Sr_{0.25}Al_2Si_2O_8}$ specimen hot pressed at 1300 °C for 2 h at 27.6 MPa and annealed at 1200 °C for 24 h in argon. EDS compositional spectra of the dark (A) and bright (B) phases are also given; the vertical scale has been normalized to 2000 counts maximum.

Thermal expansion curves for BSAS-1 and BSAS-2 compositions having the monoclinic celsian phase, from room temperature to 1200 °C, are presented in Figs 7 and 8, respectively. The average values of linear thermal expansion coefficient, α, were calculated to be $5.28 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ and $5.15 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, respectively, for the two compositions. Thermal expansion coefficient of BAS celsian has been reported [14, 15] to be $2.3 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$. This implies that the replacement of a small fraction of BaO with SrO in BAS celsian has a pronounced effect on its thermal expansion coefficient. On further SrO additions, the α value

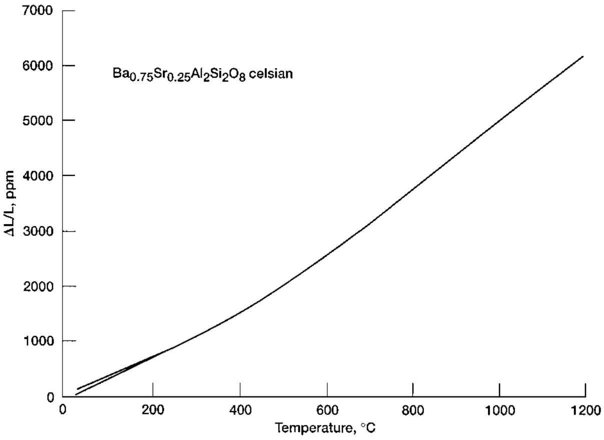

Figure 7 Dilatometric thermal expansion curve of $\mathrm{Ba_{0.75}Sr_{0.25}Al_2Si_2O_8}$ celsian hot pressed at 1300 °C for 2 h at 27.6 MPa.

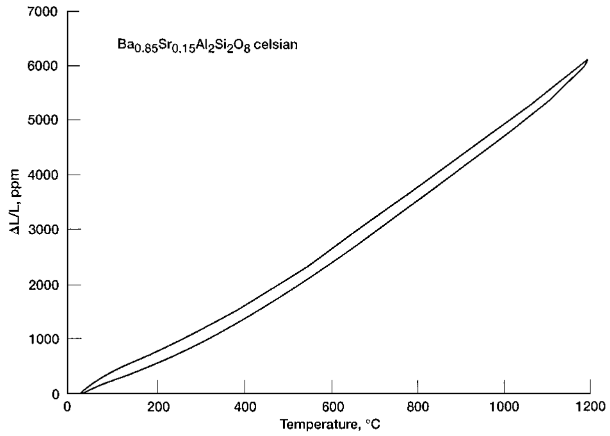

Figure 8 Dilatometric thermal expansion curve of $Ba_{0.85}Sr_{0.15}Al_2Si_2O_8$ celsian hot pressed at 1300 °C for 2 h at 27.6 MPa and annealed for 24 h at 1200 °C.

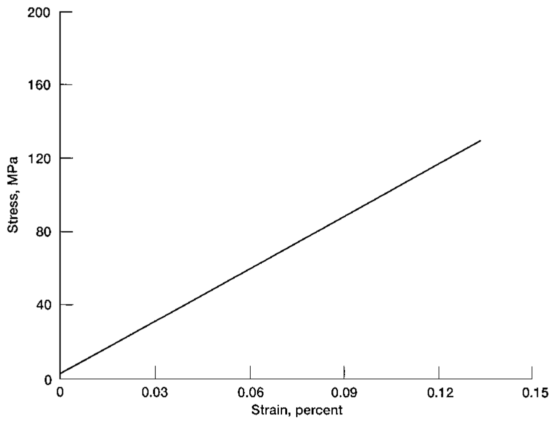

Figure 9 Room-temperature stress–strain curve of hot-pressed $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ celsian measured in four-point flexure.

increases only slightly. Another possibility could be that the thermal expansion coefficient of hyalophane, present as a minor phase, is much higher than that of monoclinic celsian. Values of α for monoclinic celsian of BAS and SAS compositions in the 100–150 °C range are reported to be 4.56×10^{-6} and $4.92 \times 10^{-6}\,°\mathrm{C}^{-1}$, respectively, by Talmy and Haught [16]. This high value of α for BAS celsian may be because of the presence of some hexacelsian phase in the BAS material.

A typical stress–strain curve for hot-pressed BSAS-1 tested in four-point flexure is given in Fig. 9. From the slope of the stress–strain curve, the value of elastic modulus was calculated to be 96 GPa. The flexure strength of BSAS-1 celsian was determined to be 131 MPa which compares well with the values reported by other researchers. Flexural properties of sintered 100% monoclinic celsian BAS material have been measured in four-point bend by Johnsen [17]. The room temperature flexural strength was 101 ± 16 MPa and the flexural modulus was 101 ± 7 GPa. Room temperature three-point bend strengths of BSAS ceramics of different compositions, sintered at various temperatures between 1500 and 1650 °C, were also measured by Talmy and Haught [16]. Materials sintered at 1600 °C showed the highest strengths. A specimen of $0.75BaO–0.25SrO–Al_2O_3–2SiO_2$ composition showed a strength of 127 MPa compared to 98 MPa and 78 MPa for BAS and SAS, respectively. Room temperature four-point flexural strengths of hot-pressed BAS and SAS glass-ceramics are reported [18] to be 100 and 90 MPa, respectively.

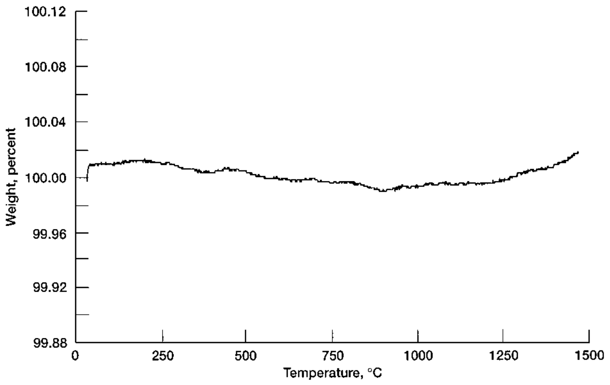

Figure 10 TGA curve of hot pressed $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ celsian at a heating rate of 5 °C min^{-1} in air.

The TGA curve of hot pressed BSAS-1, recorded at a heating rate of 5 °C min^{-1} in air from room temperature to 1500 °C, is shown in Fig. 10. Hardly any weight change is observed in the entire temperature range indicating stability of this material up to 1500 °C.

4. Summary of results

A procedure has been developed for solid state synthesis of monoclinic celsian. Hot pressing of mixed powder of $0.75BaO–0.25SrO–Al_2O_3–2SiO_2$ composition, obtained from calcination of metal carbonates and oxides, results in almost fully dense monoclinic celsian with complete absence of the undesirable hexacelsian phase. The hot pressed $0.85BaO–0.15SrO–Al_2O_3–2SiO_2$ still contained a small fraction of hexacelsian which was completely eliminated by further annealing at 1200 °C for 24 h. The hot-pressed $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ celsian showed a room-temperature flexural strength of 131 MPa, elastic modulus of 96 GPa, average coefficient of thermal expansion of $5.28 \times 10^{-6}\,°\mathrm{C}^{-1}$ from room temperature to 1200 °C, and was stable in air up to ∼1500 °C. Thermal expansion coefficient of the $Ba_{0.85}Sr_{0.15}Al_2Si_2O_8$ celsian was measured to be $5.15 \times 10^{-6}\,°\mathrm{C}^{-1}$.

5. Conclusions

It may be concluded that $Ba_{1-x}Sr_xAl_2Si_2O_8$ ($x = 0.15$, 0.25) monoclinic celsian can be obtained by solid state synthesis from a mixture of the metal carbonates and oxides. The hot-pressed celsian is stable in air up to 1500 °C. Replacement of a small fraction of BaO with SrO in $BaAl_2Si_2O_8$ monoclinic celsian results in a large increase in its thermal expansion coefficient.

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