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# High thermal expansion $KAlSiO_4$ ceramic

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Orthorhombic kalsilite ($KAlSiO_4$) was prepared by solid-state reaction from $K_2CO_3$, $Al_2O_3$, and $SiO_2$. The axial thermal expansion coefficients of the orthorhombic kalsilite were $1.6 \times 10^{-5}\,°C^{-1}$ for the *a*-axis, $1.6 \times 10^{-5}\,°C^{-1}$ for the *b*-axis, $2.8 \times 10^{-5}\,°C^{-1}$ for the *c*-axis, and $2.0 \times 10^{-5}\,°C^{-1}$ for the average from room temperature to 1000 °C. A high thermal expansion ceramic consisting of the orthorhombic kalsilite was prepared by sintering. The densification was promoted by adding $Li_2CO_3$. The $KAlSiO_4$ ceramic sintered at 1200 °C for 2 h with 5 wt% $Li_2CO_3$ had a bending strength of 65 MPa and linear thermal expansion coefficient of $2.2 \times 10^{-5}\,°C^{-1}$ from room temperature to 600 °C.

## 1. Introduction

Although thermal expansions of ceramics are generally lower than those of metals, some framework silicates such as quartz ($SiO_2$), nepheline ($NaAlSiO_4$), sodalite ($Na_8Cl_2Al_6Si_6O_{24}$) and leucite ($KAlSi_2O_6$), show very high thermal expansions ($1.6$–$2.8 \times 10^{-5}\,°C^{-1}$) up to the α to β phase transformation [1–3]. Their high thermal expansions are interpreted as being due to the effect of the rotation of the framework (Si, Al)$O_4$ tetrahedra from a partially collapsed state towards the fully expanded state and/or the untwisting of the collapsed frameworks [1–3]. For bonding to metals, we have studied how to prepare high thermal expansion ceramics from framework silicates. Previously, we reported the preparation of a high thermal expansion polycrystalline nepheline ceramic ($1.6 \times 10^{-5}\,°C^{-1}$) for bonding to iron or stainless steel and leucite ceramic ($2.4 \times 10^{-5}\,°C^{-1}$) for bonding to aluminium [4–6]. In this study, a high thermal expansion ceramic has been prepared from kalsilite ($KAlSiO_4$) for bonding on copper ($1.8 \times 10^{-5}\,°C^{-1}$) or silver ($2.2 \times 10^{-5}\,°C^{-1}$).

The structure of kalsilite is based upon a tridymite-type framework similar to nepheline [7]. The hexagonal kalsilite inverts at approximately 850 °C to an orthorhombic phase, which has a melting point of $1686 \pm 5\,°C$ [7]. The inversion orthorhombic $\rightleftharpoons$ hexagonal is sluggish, and the high-temperature orthorhombic form can be preserved at normal temperatures by quenching [7]. Thus, the thermal expansion and sintering of the orthorhombic kalsilite have been investigated in this work.

## 2. Experimental procedure

Orthorhombic kalsilite was prepared by solid-state reactions from reagent-grade potassium carbonate, activated alumina, and silicon oxide. These raw materials were weighed to a 1:1:2 ratio of $K_2O:Al_2O_3:SiO_2$, dry-mixed in alumina mortar, calcined at 900 °C for 2 h, fired at 1300 °C for 48 h. The orthorhombic kalsilite powder was ground to an average particle size of approximately 1 μm, and in some runs 1–10 wt% of an alkali carbonate ($Li_2CO_3$, $Na_2CO_3$ or $K_2CO_3$) was added as a sintering aid. Test specimens were pressed at 100 MPa to form tablets of 16 mm diameter and ~3 mm height and rectangular bars of 60 mm × 5 mm. The specimens were then sintered at temperatures ranging from 1100–1400 °C for 2 h at a heating and cooling rate of $100\,°C\,h^{-1}$.

Bulk density was calculated from the weight and volume of the sintered body. Fracture strength was measured by the three-point bending method with a test span of 20 mm at a loading rate of $0.5\,mm\,min^{-1}$. The fracture surface was observed with a scanning electron microscope (JSM-T20, Nihon Denshi Co., Tokyo, Japan). The thermal expansion of ceramics was measured from room temperature to 600 °C at a heating rate of $10\,°C\,min^{-1}$ using a dilatometer (TMA DT-30, Shimazu Corp., Kyoto, Japan). The sintered samples were characterized by an X-ray powder diffraction, and the lattice parameters up to 1000 °C were determined using an X-ray diffractometer attached to a high-temperature apparatus (RINT1100, Rigaku Co., Tokyo, Japan). Platinum powder was employed as an internal standard. The diffraction patterns were measured in a 2θ range of 20°–55° using Cu$K_\alpha$ radiation with a scanning rate of $2°\,2\theta\,min^{-1}$. The lattice parameters at each elevated temperature were calculated by using a least-squares computer program (UNICS RSLC-3) from eight major peaks, (0 0 2), (2 2 1), (0 4 1), (2 3 0), (2 0 2), (1 3 2), (3 1 1), and (2 4 1).

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## 3. Results and discussion

Fig. 1 shows the thermal expansion of the crystal lattice parameters for the orthorhombic kalsilite. The *a*- and *b*-axes expanded almost linearly with increasing temperature up to 1000 °C. The *c*-axis had a thermal expansion which abruptly changed at 400–600 °C, conceivably resulting from the α to β phase transformation. The linear thermal expansion coefficients from room temperature to 1000 °C were $1.6 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$ for the *a*-axis, $1.6 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$ for the *b*-axis, and $2.8 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$ for the *c*-axis. The calculated average thermal expansion coefficient of the unit cell was $2.0 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$, which was intermediate between nepheline and leucite [4, 6].

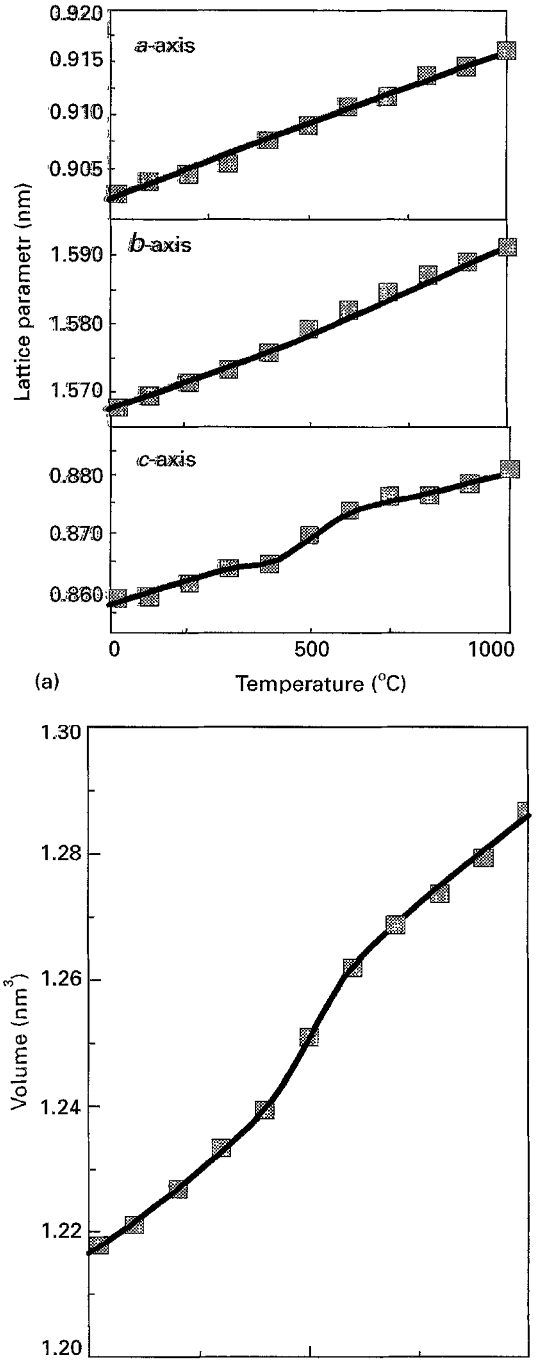

*Figure 1(a, b)* Lattice parameters versus temperature for orthorhombic kalsilite.

When compacts of pure orthorhombic kalsilite powder were sintered at 1200–1400 °C, they did not densify. In order to prepare a dense ceramic, an alkali carbonate was added as a sintering aid. When

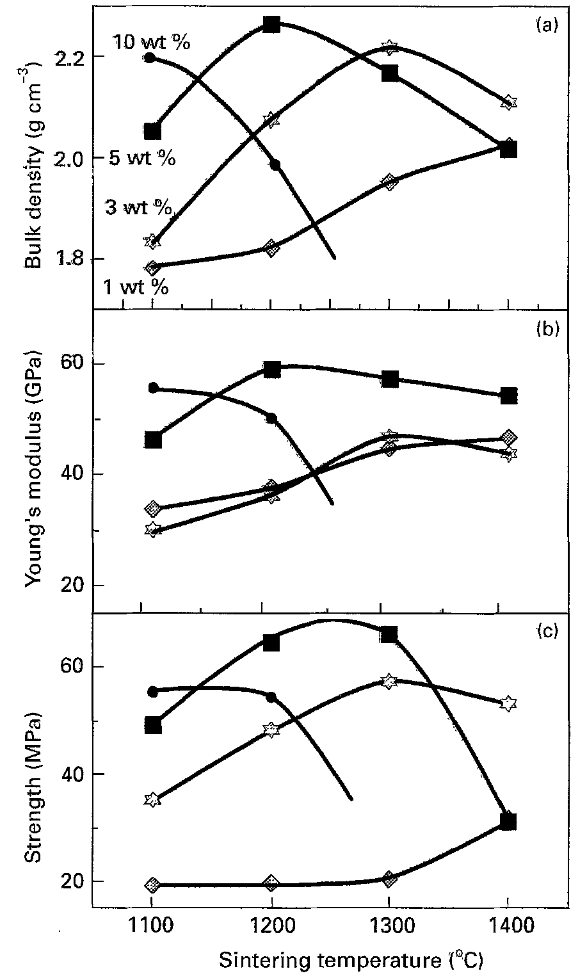

*Figure 2* Variations of (a) bulk density, (b) Young's modulus and (c) bending strength with the amount of $Li_2CO_3$ and sintering temperature.

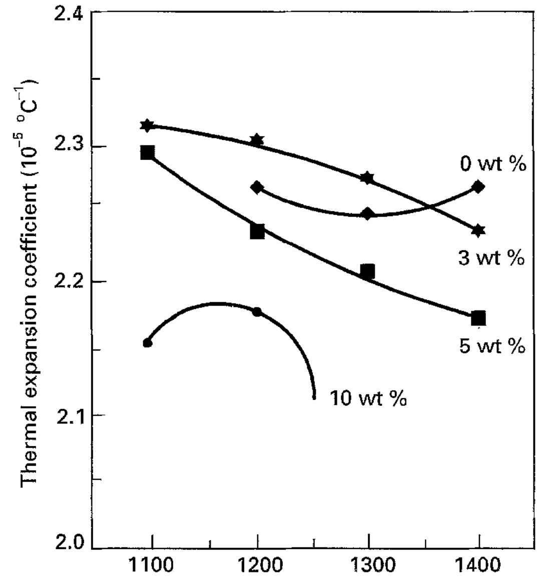

*Figure 3* Variations of thermal expansion coefficient with the amount of $Li_2CO_3$ and sintering temperature.

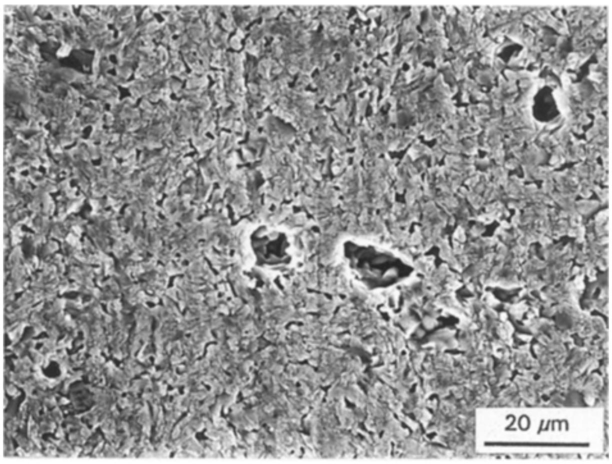

*Figure 4* Scanning electron micrograph of a fracture surface of the orthorhombic kalsilite ceramic sintered at 1200 °C with 5 wt % $Li_2CO_3$.

$Na_2CO_3$ or $K_2CO_3$ was added to the orthorhombic kalsilite powder, the specimens did not densify. On the other hand, when $Li_2CO_3$ was added, the specimens densified at lower temperatures in a manner similar to that of the nepheline ceramic [5]. A relative density of about 90% was achieved by sintering at 1200 °C for 2 h with 5 wt % $Li_2CO_3$. At higher sintering temperatures, the specimens partly melted and then the relative density showed a downward trend.

Fig. 2 shows the variations of bulk density, Young's modulus, and bending strength with the amount of $Li_2CO_3$ and sintering temperature. They increased with increasing amount of $Li_2CO_3$ and sintering temperature. However, they decreased with a larger amount of $Li_2CO_3$ and/or at a higher sintering temperature. The specimen completely melted on sintering at 1300 °C with 10 wt % of $Li_2CO_3$. Fig. 3 shows the thermal expansion coefficients from room temperature to 1000 °C of the orthorhombic kalsilite ceramics. The thermal expansion coefficient decreased with increasing amount of $Li_2CO_3$ and sintering temperature. The specimen melted by sintering at 1300 °C with 10 wt % $Li_2CO_3$ had a lower thermal expansion coefficient of about $1.2 \times 10^{-5}\,°C^{-1}$. Consequently, it was considered that the lowering of density, Young's modulus, strength, and thermal expansion coefficient was due to the formation of a glass phase. Fig. 4 demonstrates that grains were surrounded by a glassy substance with some large pores.

In conclusion, the addition of $Li_2CO_3$ accelerated the formation of a liquid phase, resulting in faster densification at lower temperatures. The orthorhombic kalsilite ceramic obtained by sintering at 1200 °C for 2 h with 5 wt % $Li_2CO_3$ revealed a bending strength of 65 MPa, and a Young's modulus of 60 GPa; its high thermal expansion coefficient, $2.2 \times 10^{-5}\,°C^{-1}$, was almost equal to the average of the unit cell.

In addition, Fig. 5 shows the variation of the thermal expansion curves of the orthorhombic kalsilite crystal and ceramic with the addition of $Li_2CO_3$. When $Li_2CO_3$ was added to the orthorhombic kalsilite, the thermal expansion of both the crystal and ceramic altered very little. However, the abrupt expansion at 400–600 °C was somewhat smoothed. Consequently, it was considered that some $Li^+$ might be incorporated into the orthorhombic kalsilite crystal lattice.

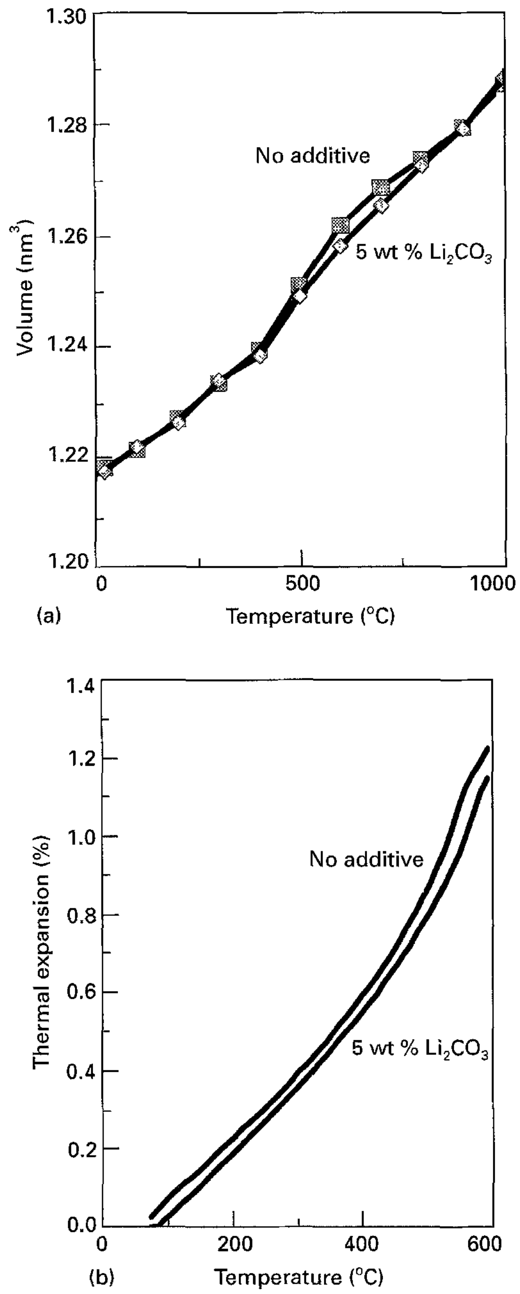

*Figure 5* Variation of the thermal expansion curves of (a) orthorhombic kalsilite crystal and (b) ceramic with the addition of $Li_2CO_3$.

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