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Nepheline gradient solid solutions

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Nepheline solid solutions having high thermal expansion coefficients ranging from 1.2 to $1.8 \times 10^{-5}\,°C^{-1}$ were prepared from the systems $NaAlSiO_4$–$LiAlSiO_4$ and $NaAlSiO_4$–$KAlSiO_4$. The thermal expansion coefficient decreased by substituting Li^+ for Na^+, and increased by substituting K^+ for Na^+. By forming a series of the nepheline solid solutions in a single ceramic body, a functionally gradient material with respect to thermal expansion was prepared. The thermal expansion coefficient should gradually vary with position according to the composition x in $Na_{1-x}M_xAlSiO_4$ (M = Li and K).

1. Introduction

Thermal expansions of ordinary ceramics such as alumina and zirconia are generally lower than those of metals. So, in composite materials composed of ceramic and metal, a stress is developed by the thermal expansion mismatch, and then the composite sometimes breaks up. In order to avoid this failure, we need a ceramic having a high thermal expansion coefficient equal to that of a metal. It is known that some framework silicates such as nepheline and leucite show very high thermal expansions, which is interpreted as due to the effect of the rotation of framework SiO_4 tetrahedra from a partially-collapsed state towards the fully-expanded state [1–3]. We have previously prepared the high thermal expansion ceramics from nepheline ($NaAlSiO_4$) and leucite ($KAlSi_2O_6$) [4–6].

Another technique of ceramic–metal joining is a way to use functionally gradient materials (FGM), where the ratio of ceramic and metal are gradually varied [7]. FGM is characterized by the material having a continuously varying property from one surface to the other. Such a material is prepared by forming a pile of composite layers composed of ceramic and metal, having the predetermined compositional distribution, with several methods such as chemical vapour deposition, spraying and sintering.

Recently, we prepared a FGM by forming a series of solid solutions in a single ceramic body, where a $KZr_{2-x}Ti_x(PO_4)_3$ solid solution having a different composition by the place was formed by heating $KZr_2(PO_4)_3$ and $KTi_2(PO_4)_3$ in contact with each other [8]. We call such a solid solution "a gradient solid solution" and an ordinary solid solution "a homogeneous solid solution". The thermal expansion coefficient of gradient $KZr_{2-x}Ti_x(PO_4)_3$ solid solution continuously increased from $0–3 \times 10^{-6}\,°C^{-1}$ with increasing x from one end to the other in a single ceramic body. In the present work, such a FGM was prepared from nepheline solid solutions ($Na_{1-x}M_xAlSiO_4$: M = Li or K) having high thermal expansion coefficients.

2. Experimental procedure

Nepheline homogeneous solid solutions ($Na_{1-x}M_xAlSiO_4$: M = Li or K) were prepared by the solid state reaction between nepheline ($NaAlSiO_4$) and eucryptite ($LiAlSiO_4$) or kalsilite ($KAlSiO_4$). Nepheline, eucryptite and kalsilite were synthesized from reagent-grade chemicals (Na_2CO_3, Li_2CO_3, K_2CO_3, Al_2O_3, and SiO_2) as follows: the starting chemicals were mixed in the molar ratio of $M_2O:Al_2O_3:SiO_2 = 1:1:2$ (M = Na, Li and K), calcined at 900 °C for 2 h, and fired at 1200 °C for 4 h, at 1300 °C for 6 h, and at 1300 °C for 48 h to obtain the single phases, respectively.

Gradient solid solutions were prepared by the following method. First, nepheline powder compacted into the shape of a 16-mm-diameter tablet by lower pressure (15 MPa), and then the mixed powder of nepheline and eucryptite or kalsilite, where the composition is the limit of each homogeneous solid solution, was formed on the nepheline compact by higher pressure (80 MPa). Next, this compact was sintered at an appropriate temperature for an appropriate time.

The lattice parameters and thermal expansion were measured by using a powder X-ray diffractometer (RIGAKU: RINT1100) equipped with a heating unit. The lattice parameters were calculated by a least squares method from the positions of eight larger peaks in the range of $2\theta = 15°$ to 50° (CuK_α). Platinum was used as an internal standard. The microstructures were observed and analysed by scanning electron microscopy (SEM) (NIHON DENSHI: JSM-T20, JSM6100 and JED2001).

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3. Results and discussion

3.1. Preparation and thermal expansion of nepheline homogeneous solid solutions

Since there is a difference in crystal structure between $NaAlSiO_4$ (nepheline) and $LiAlSiO_4$ (eucryptite) or $KAlSiO_4$ (kalsilite), the solid solution cannot be formed in the range of whole compositions. So, to begin with, we confirmed the limits of solid solution between them. The single phase of nepheline solid solution was formed up to $x = 0.15$ in the system of $Na_{1-x}Li_xAlSiO_4$ by firing at 1200 °C for 2 h, and up to $x = 0.43$ in the system of $Na_{1-x}K_xAlSiO_4$ by firing at 1250 °C for 2 h, respectively. Fig. 1 shows the variation of lattice parameters of nepheline solid solutions with composition x in $Na_{1-x}M_xAlSiO_4$ (M = Li and K). Both the a and c parameters increased linearly up to the limits of their solid solutions with increasing x.

Fig. 2 shows the lattice parameters of $Na_{1-x}M_xAlSiO_4$ (M = Li and K) plotted against temperature. Both the a-axis and the c-axis expanded for all compositions with rising temperature. With increasing x, the magnitude of the expansion decreased in the system of $Na_{1-x}Li_xAlSiO_4$, and increased in the system of $Na_{1-x}K_xAlSiO_4$. From the expansion curves in Fig. 2, the linear thermal expansion coefficients from room temperature to 600 °C were calculated as shown in Fig. 3. The thermal expansion coefficients for the a axis and c axis decreased by substituting smaller Li^+ for Na^+, and increased by substituting K^+ for Na^+. As a result, the average thermal expansion coefficient of nepheline solid solution decreased from $1.6 \times 10^{-5}\,°C^{-1}$ to $1.2 \times 10^{-5}\,°C^{-1}$ in the system of $Na_{1-x}Li_xAlSiO_4$, and increased from $1.6 \times 10^{-5}\,°C^{-1}$ to $1.8 \times 10^{-5}\,°C^{-1}$ in the system of $Na_{1-x}K_xAlSiO_4$ with increasing x.

3.2. Preparation of nepheline gradient solid-solution ceramics

Green-compact layers composed of $NaAlSiO_4$ nepheline powder and ($0.85NaAlSiO_4 + 0.15LiAlSiO_4$) or ($0.57NaAlSiO_4 + 0.43KAlSiO_4$) mixed powder were sintered for 10 min to 16 h at 1200 °C in the case of M = Li and at 1250 °C in the case of M = K. Then,

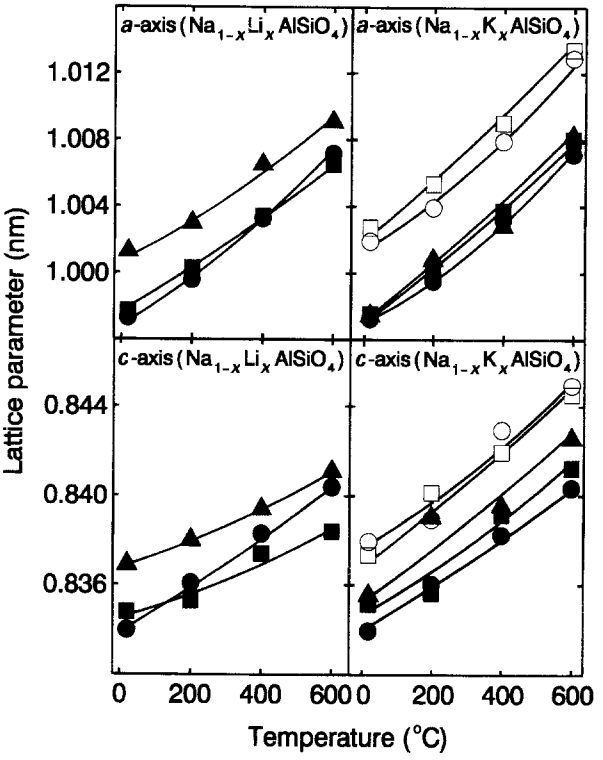

Figure 2 Lattice parameters of nepheline homogeneous solid solutions plotted against temperature (● $x = 0$, ■ $x = 0.07$, ▲ $x = 0.15$ in $Na_{1-x}Li_xAlSiO_4$; ● $x = 0$, ■ $x = 0.11$, ▲ $x = 0.22$, ○ $x = 0.32$, □ $x = 0.43$ in $Na_{1-x}K_xAlSiO_4$).

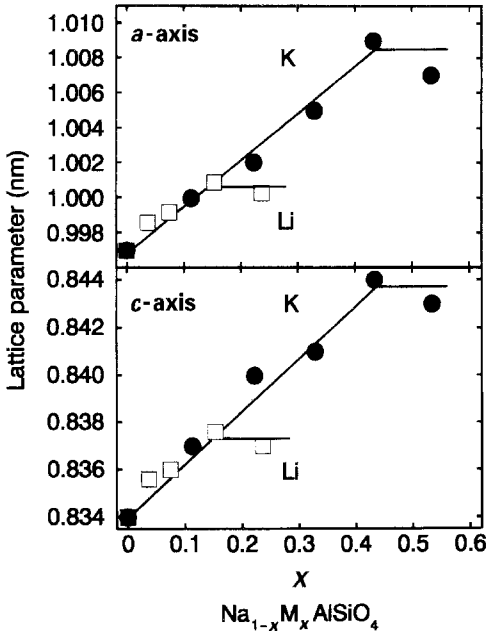

Figure 1 Variation of lattice parameters with composition x in $Na_{1-x}M_xAlSiO_4$ (M = Li and K).

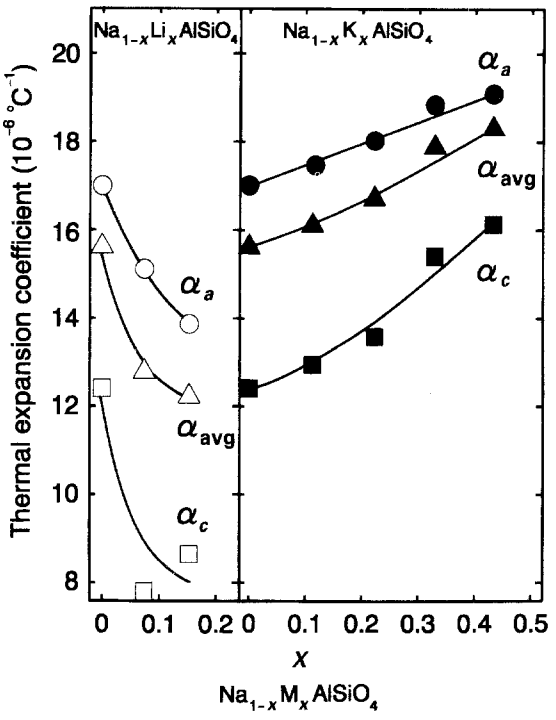

Figure 3 Variation of thermal expansion coefficients with composition x in $Na_{1-x}M_xAlSiO_4$ (M = Li and K).

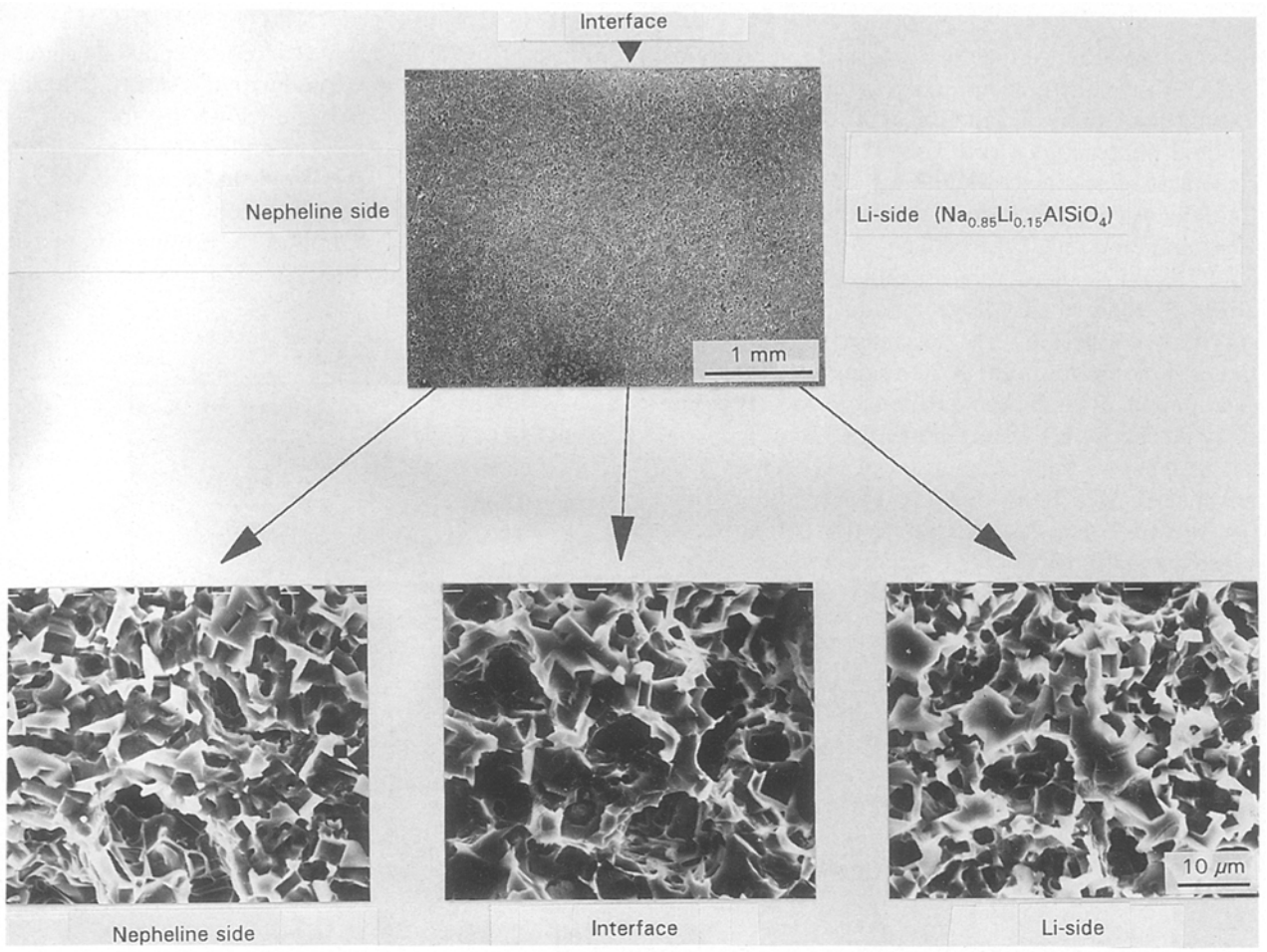

Figure 4 SEM micrographs of cross-section of $Na_{1-x}Li_xAlSiO_4$ gradient solid-solution ceramic sintered at 1200 °C for 10 min.

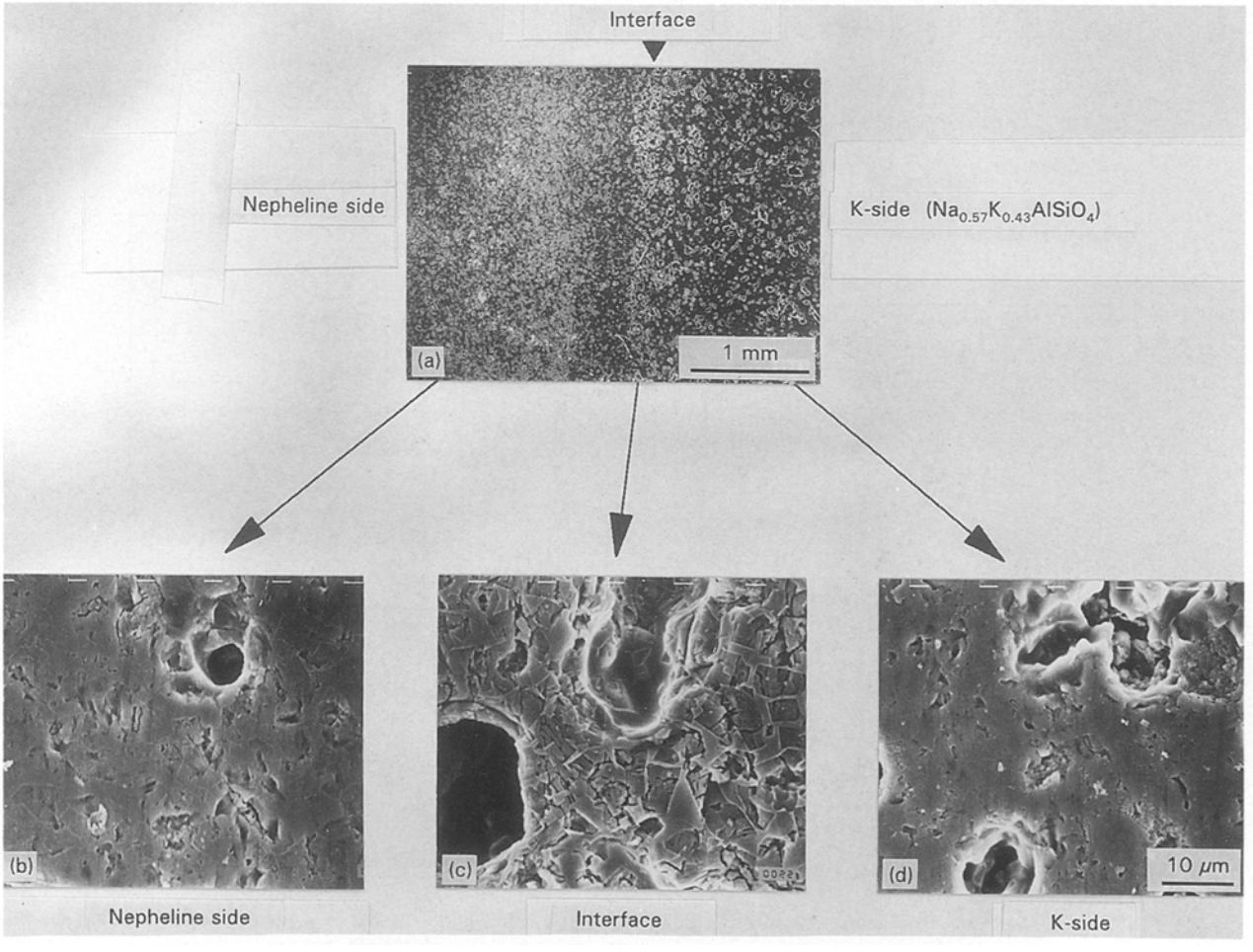

Figure 5 SEM micrographs of cross-section of $Na_{1-x}K_xAlSiO_4$ gradient solid-solution ceramic sintered at 1250 °C for 10 min.

the specimen bonded together to form a single ceramic body. Above these temperatures, the specimen deformed due to the formation of a large amount of a liquid phase. Figs 4 and 5 show the typical microstructures of products, where Figs 4(b) to (d) and 5(b) to (d) show magnification of each region indicated in Figs 4(a) and 5(a), respectively. In both cases of M = Li and K there were no splits at the interfaces, although there was a large amount of pore in the specimens. Especially, the specimen of M = K contained larger pores in the K-rich side. The grains were surrounded by a molten substance, which was partially etched by HF solution in Figs 4 and 5.

Fig. 6 shows the line analyses of Na and K of the products of M = K by an X-ray microanalyser, where the noises arose from the detection of pores. In Figs 6(a) to (c), Na and K concentration curves gave certain gradients. This suggested that K and Na inter-

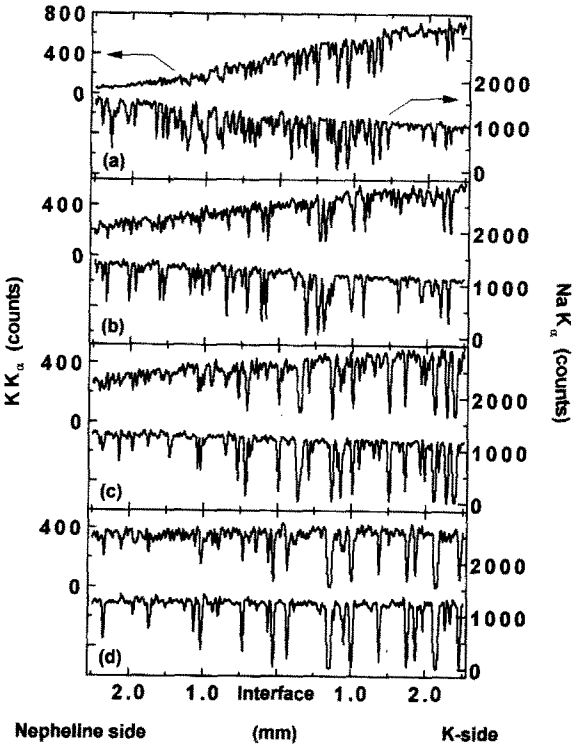

Figure 6 X-ray micro-analysis of $Na_{1-x}K_xAlSiO_4$ gradient solid-solution ceramics sintered at 1250 °C for (a) 10 min, (b) 4 h, (c) 8 h and (d) 16 h.

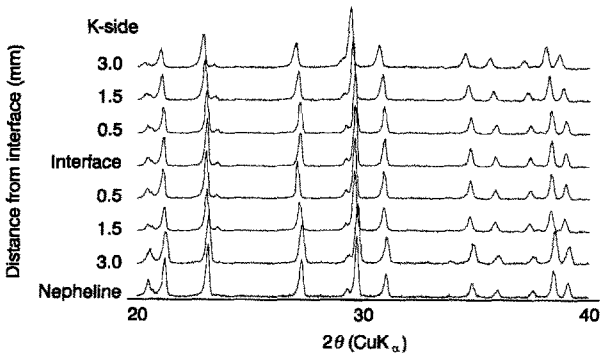

Figure 7 Variation of X-ray pattern of cross-section with position in $Na_{1-x}K_xAlSiO_4$ gradient solid-solution ceramic sintered at 1250 °C for 10 min.

diffused. The slope of these curves depended on sintering time. The slope decreased with increasing sintering time, and became zero after sintering for 16 h as shown in Fig. 6(d), which indicated the formation of homogeneous solid solution in the ceramic body.

Fig. 7 shows X-ray diffraction patterns of 0.5-mm × 0.5-mm cross-sections of the product sintered at 1250 °C for 10 min in the case of M = K shaved from

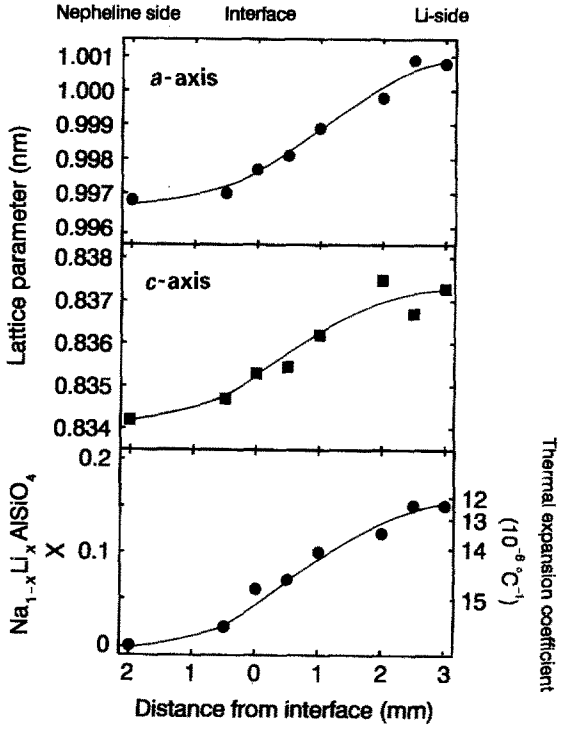

Figure 8 Variations of lattice parameters and composition with position in $Na_{1-x}Li_xAlSiO_4$ gradient solid-solution ceramic sintered at 1200 °C for 10 min.

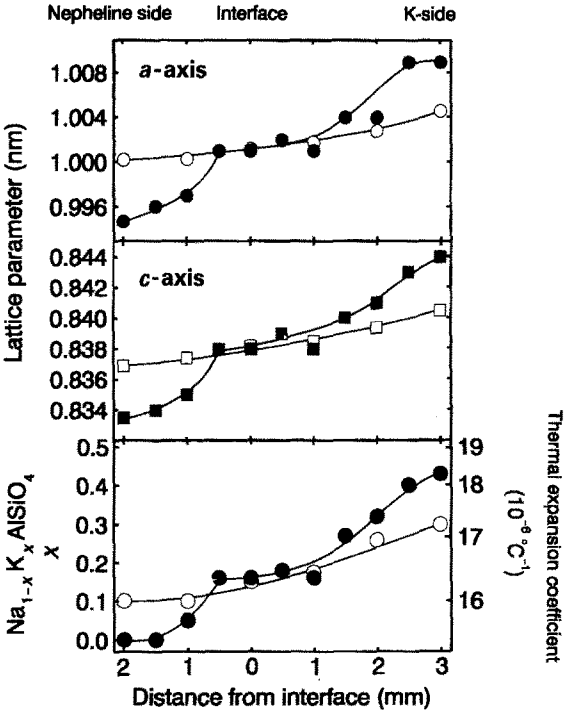

Figure 9 Variations of lattice parameters and composition with position in $Na_{1-x}K_xAlSiO_4$ gradient solid-solution ceramics sintered at 1250 °C for (●) 10 min and (○) 4 h.

the interface. It illustrates that each cross-section was not the mixture, but a single phase of nepheline solid solution. The peaks shifted with the distance from the interface. From these data the lattice parameters at each cross-section were calculated, and then the composition x at each cross-section was determined by referring the lattice parameters to the results of homogeneous solid solutions shown in Fig. 1. Figs 8 and 9 show the results in the cases of M = Li and K, respectively. The composition gradually varied with the distance from the interface. That is to say, gradient solid solutions were just formed. Needless to say these nepheline gradient solid-solution ceramics are functionally gradient materials having continuously varying thermal expansions.

4. Conclusion

A new FGM with respect to thermal expansion was prepared by forming a series of nepheline solid solutions ($Na_{1-x}M_xAlSiO_4$: M = K and Li) in a single ceramic body. By sintering green-compact layers composed of $NaAlSiO_4$ powder and $\{(1-x)NaAlSiO_4 + xMAlSiO_4$ (M = Li and K)$\}$ mixed powder, they bonded together to form a gradient solid solution, whose composition continuously varied with the distance from the interface. Nepheline solid solutions had high thermal expansion coefficients equal to those of metals. The thermal expansion coefficient decreased from $1.6 \times 10^{-5}\,°C^{-1}$ for $x = 0$ to $1.2 \times 10^{-5}\,°C^{-1}$ for $x = 0.15$ in $Na_{1-x}Li_xAlSiO_4$, and increased to $1.8 \times 10^{-5}\,°C^{-1}$ for $x = 0.43$ in $Na_{1-x}K_xAlSiO_4$ with increasing x. Consequently, the thermal expansion coefficient of the gradient solid solutions should gradually vary with position according to the composition of solid solution. This nepheline gradient solid solution could be applied to metal–ceramic joining, although presently there are problems such as porosity, densification or sintering.

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