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Hot Pressing of LaF_3-doped SrF_2 from Mixed and Hydrothermally Pre-reacted Powders

Kwang Jin Kim,* Masahiro Yoshimura

Research Laboratory of Engineering Materials and Department of Materials Science, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama-shi 227, Japan

&

Shigeyuki Sōmiya

The Nishi Tokyo University, 3-7-19, Seijo, Setagaya-ku, Tokyo 227, Japan

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Abstract

Sinterability and microstructure of fluorite-type fluoride solid solution ($Sr_{1-x}La_xF_{2+x}$) were studied for two ceramics: one by reaction hot-pressing of mixed fluoride powder and the other by hot-pressing of the solid solution powder synthesized hydrothermally. The latter ceramic was densified to 99% of relative density with pore-free and uniform grain size (40 μm) as the same of pure SrF_2. Fracture toughness, K_{IC} of this ceramics ($Sr_{1-x}La_xF_{2+x}$) ranged 0·2 to 0·7 MPa m$^{1/2}$.

Die Sinterfähigkeit und das Gefüge von ($Sr_{1-x}La_xF_{2+x}$)-Mischkristallzusammensetzungen des Fluorit-Typs wurden für zwei unterschiedliche Herstellungsweisen untersucht: einmal durch Reaktionsheißpressen der gemischten Fluoridpulver und zum anderen durch Heißpressen hydrothermisch hergestellter Mischkristallpulver. Die letztgenannte Verfahrensweise führte, wei bei reinem SrF_2, zu einem porenfreien Material mit 99% relativer Dichte und einheitlicher Korngröße (40 μm). Die Bruchzähigkeitswerte, K_{IC}, dieses ($Sr_{1-x}La_xF_{2+x}$)-Werkstoffs lagen zwischen 0·2 und 0·7 MPa m$^{1/2}$.

On a étudié l'aptitude au frittage et la microstructure de solutions solides de fluorures de type fluorite ($Sr_{1-x}La_xF_{2+x}$) dans le cas de deux céramiques, obtenues l'une par pressage réactif à chaud des mélanges des poudres de fluorures, l'autre par pressage à chaud de la poudre de solution solide synthétisée hydrothermiquement. Cette dernière atteint 99% de densité relative, sans porosité et avec une granulométrie uniforme (40 μm) comme le SrF_2 pur. La ténacité K_{IC} de ces céramiques ($Sr_{1-x}La_xF_{2+x}$) est comprise entre 0·2 et 0·7 MPa m$^{1/2}$.

1 Introduction

The fluorite(CaF_2)-type or tysonite(LaF_3)-type fluorides among inorganic fluorides are very stable in air at relatively low temperatures. The binary systems of these two types of fluoride have recently stimulated interest as fast ionic conductors at relatively low temperatures.[1,2] Polycrystalline pellets of these fluorides employed for measuring conductivity are almost sintered by solid state reaction in an inert atmosphere. The solid solutions are mostly synthesized by reaction sintering from mixed powder due to the low melting temperatures of the fluorides and in order to prevent their oxidation. The microstructure and strength or fracture toughness of pellets sintered by various process are scarcely reported.[3] The phase relation of the system SrF_2–LaF_3[4] and hydrothermal synthesis of SrF_2 solid solution ($Sr_{1-x}La_xF_{2+x}$)[5] have previously been reported. The hot-pressing of pure solid solutions of alkaline earth/fluorite-type and rare-earth/tysonite-type fluorides, has been carried out in order for the microstructure to be observed and then

* To whom all correspondence should be addressed at: R & D Center Gumi Plant, Samsung Corning Co. Ltd, 580 Simi-Dong, Gumi-City, Kyoung Sang Buk-do, Korea.

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the Vickers hardness (H_V) and fracture toughness (K_{IC}) were also measured. In this paper, the preliminary sinterability of two different powders by different processes is compared: reaction sintering by hot-pressing using the mixed powder and hot-pressing using the solid-solution powder synthesized hydrothermally.

2 Experimental

Starting materials of reagent grade of MF_2(M = Ca, Sr, Ba) and RF_3(R = La, Ce) were mixed with methanol for 2 h using an agate mortar, packed into a graphite mould (inner diameter 10 mm), and sintered by hot-pressing at about 900°C for 0·5–2·5 h under 22 MPa in dry Ar atmosphere. The equilibrium solid-solution powder ($Sr_{0\cdot7}La_{0\cdot3}F_{2\cdot3}$)[5] synthesized by hydrothermal reaction at 650°C for 1 day in 10 wt% LiCl solution were also employed. Linear shrinkage of the sample was monitored by a dial-gauge attached to the ram during hot-pressing. Microstructure and fracture toughness (K_{IC}) of the ceramics were examined by using a SEM and a micro-Vickers indenter under load of 100 g (0·98N), respectively. K_{IC} was calculated by Niihara's formula for median crack.[6]

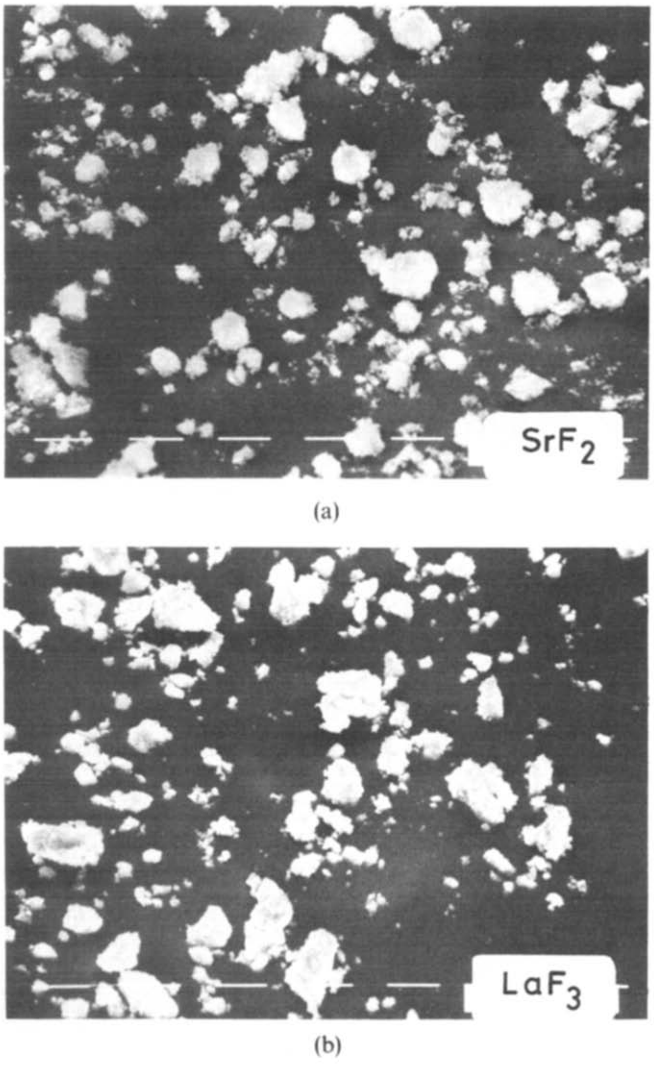

Fig. 1. SEM photographs of (a) the SrF_2 and (b) the LaF_3 starting materials (bar = 10 μm).

3 Results and Discussion

SEM photographs and typical shrinkage curves of the SrF_2 and LaF_3 starting materials are shown in Fig. 1 and Fig. 2, respectively; densities are not so very different from the initial green densities. Densification of fluorite-type of SrF_2 started at about 600°C and terminated at about 700°C, with linear shrinkage of about 80%. That of tysonite-type of LaF_3 started at about 700°C and terminated at about 800°C, with linear shrinkage of about 7%. This enormous difference in the linear shrinkage is considered to be due to the different structure types of cubic fluorite and hexagonal plate tysonite. Figure 3 (pure SrF_2) and Fig. 4 (pure LaF_3) show the SEM photographs of polished surfaces sintered by hot-pressing at 880°C and 910°C for 0·5 h under

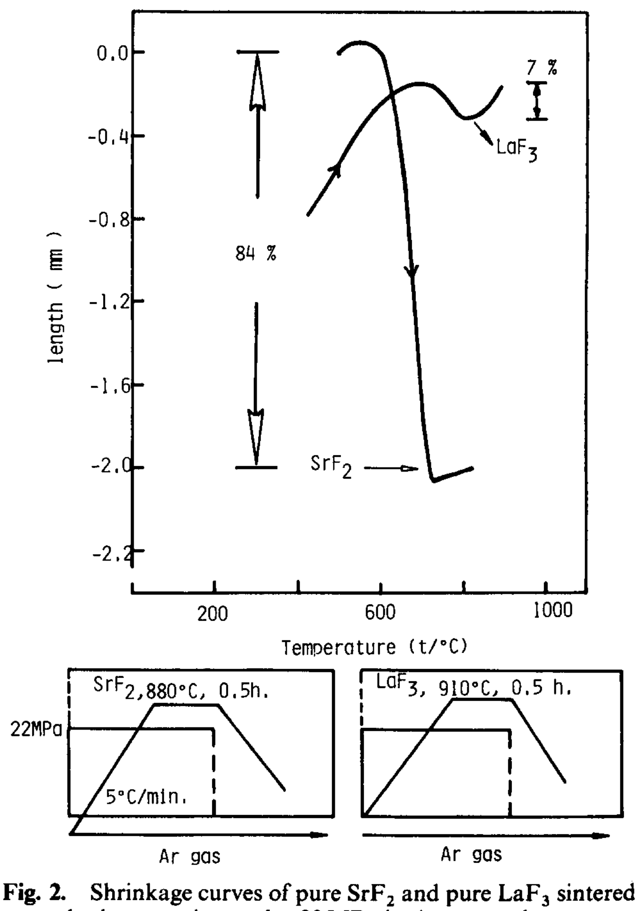

Fig. 2. Shrinkage curves of pure SrF_2 and pure LaF_3 sintered by hot-pressing under 22 MPa in Ar atmosphere.

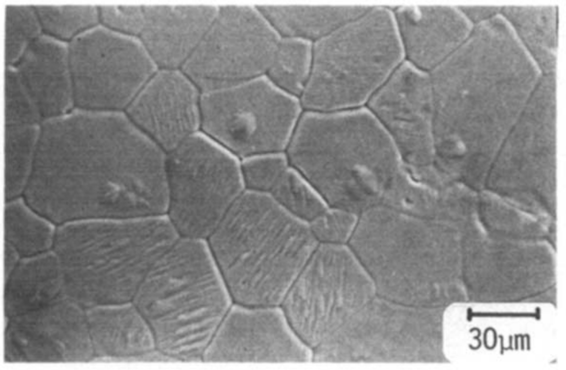

Fig. 3. SEM photograph of the polished surface of SrF_2 sintered by hot-pressing at 880°C for 30 min under 22 MPa in Ar atmosphere (thermal etching at 1300°C for 2 min in Ar).

22 MPa in an Ar atmosphere, respectively. Both SrF_2 and LaF_3 were well compacted with 99% relative density. Thus, hot-pressing using a graphite mould is verified to be a suitable method for fluorides. SrF_2 ceramics consist of homogeneous grains of about 40 μm in size with pores free. This grain size in SrF_2 ceramics is similar to that of hot-pressed CaF_2 under 550 MPa.[3] On the other hand, a grain size for LaF_3 of only about 4 μm was achieved by the present hot-pressing method. This indicates that mass transfer diffusion or some other mechanism is considered to be slower in LaF_3 than that in SrF_2.

In the $Sr_{1-x}La_xF_{2+x}$ ceramics made by reaction hot-pressing the mixed powder with the composition of $Sr_{0\cdot78}La_{0\cdot22}F_{2\cdot22}$, heterogeneous microstructures with varied composition (La/Sr = 0·2 to 0·6) could be found as shown in Fig. 5(a). The LaF_3-rich portion yielded a porous structure, probably due to inhomogeneous mixing. This ceramic showed a relative density lower than 90%, and fractured along grain boundaries (Fig. 5(b)). The $Sr_{0\cdot7}La_{0\cdot3}F_{2\cdot3}$ ceramics hot-pressed using the powder pre-reacted hydrothermally[5] reached a density

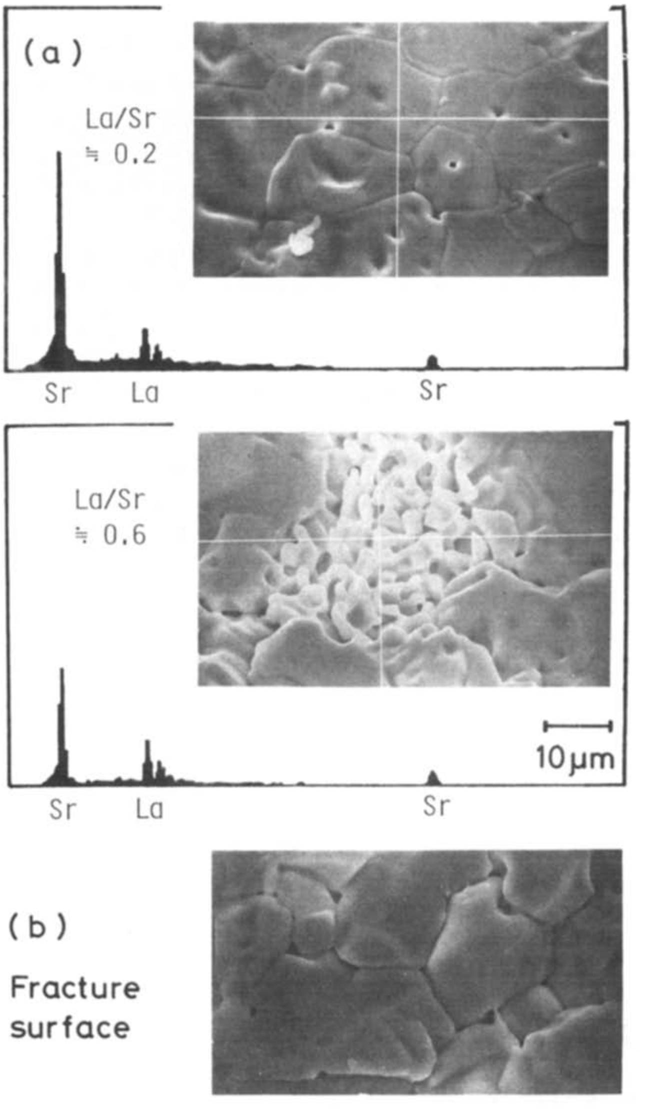

Fig. 5. (a) EDS analysis of the $Sr_{1-x}La_xF_{2+x}$ solid solution sintered by reaction hot-pressing (at 870°C for 150 min under 22 MPa in Ar) using the mixed powder (78 mol% SrF_2 + 22 mol% LaF_3), and (b) SEM photograph of fracture surface.

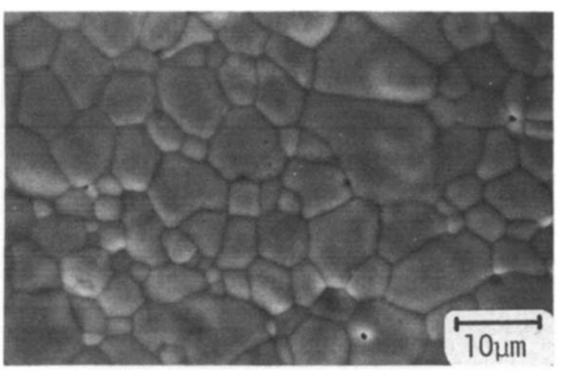

Fig. 4. SEM photograph of the polished surface of LaF_3 sintered by hot-pressing at 910°C for 30 min under 22 MPa in Ar atmosphere (thermal etching at 1300°C for 2·5 min in Ar).

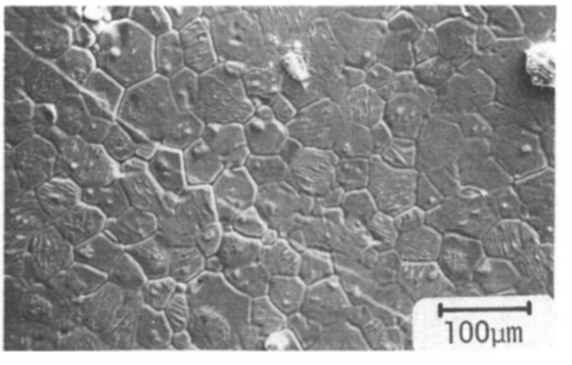

Fig. 6. SEM photograph of the polished surface of $Sr_{0\cdot7}La_{0\cdot3}F_{2\cdot3}$ sintered by hot-pressing at 880°C for 30 min under 22 MPa in Ar using the solid-solution powder synthesized hydrothermally (at 750°C for 1 day under 100 MPa in 10 wt% LiCl solution; thermal etching at 1300°C for 2 min in Ar).

of 99%. This ceramic, as well as pure SrF_2 (Fig. 3), consists of homogeneous grains of about 40 μm with pores free (Fig. 5). This result reveals that hydrothermally synthesized powders which are homogeneous, non-aggregated and well-crystallized fine powders, are preferable to obtain well-sintered homogeneous ceramics of dominantly ionic fluorides.

Fracture toughness, K_{IC}, of SrF_2, LaF_3 and $Sr_{0\cdot7}La_{0\cdot3}F_{2\cdot3}$ was in the range 0·5–1·4 MPa $m^{1/2}$, 0·1–0·5 MPa $m^{1/2}$ and 0·2–0·7 MPa $m^{1/2}$, respectively, about the same as that of generally monolithic glass (SiO_2, $K_{IC} = 0{\cdot}7$ MPa $m^{1/2}$).[7] Vickers hardness of each of the compounds was about 1·5, 2·5 and 2·5 GPa with a deviation of 0·5 GPa, respectively. Since these values are not as high as for dense ceramics, the fluorides are thus shown to be soft materials. For the application to devices, where mechanical strengths are required, the fluorite-type (solid solution) fluorides appear to be more appropriate than tysonite-type (solid solution) fluorides.

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