Ionic conductivity enhancement of grain-oriented ceramics fabricated by reactive diffusion technique

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Sintered polycrystals synthesized by normal sintering methods generally possess a randomly oriented grain structure, and isotropic mechanical (e.g. bending strength and fracture toughness) and physical (e.g. thermoelectric, piezoelectric, pyroelectric, and magnetic) properties. However, their manufacturing methods normally require complicated processes of such as templated grain growth and high-temperature pressing. In recent years, a novel technique utilizing *reactive diffusion* has made it possible to readily produce the well-aligned polycrystalline materials [1]. We will review the recent progress and future perspective on the fabrication of grain-oriented ion-conductive ceramics using the reactive diffusion technique.

The lanthanum silicate oxyapatite (LSO, space group $P6_3/m$) shows much higher oxide-ion conductivity parallel to the *c*-axis than perpendicular to this direction [2,3]. We have isothermally heated the sandwich-type diffusion couple of $La_2SiO_5/La_2Si_2O_7/La_2SiO_5$ (φ13 mm) at 1873 K for 100 h, and mechanically extracted the *c*-axis-oriented polycrystal of $La_{9.50}Si_{5.87}O_{26}$ from the inner part of the annealed couple [4]. The thin-plate polycrystalline electrolyte as obtained (ca. 290 μm in thickness) showed the relatively high oxide-ion conductivity along the grain-alignment direction, which steadily increased from 3.04×10^{-2} S/cm at 823 K to 1.26×10^{-1} S/cm at 1073 K. The present reactive diffusion for the preparation of polycrystalline LSO occurs in the *binary* system La_2SiO_5–$La_2Si_2O_7$.

In the *ternary* system Na_2O–Ga_2O_3–TiO_2, we have successfully prepared the *b*-axis-oriented polycrystalline $Na_{0.85}Ti_{0.51}Ga_{4.37}O_8$ (NTGO, space group $C2/m$), in the presence of a liquid phase, by heating the sandwich-type $Ga_2TiO_5/NaGaO_2/Ga_2TiO_5$ diffusion couple at 1323 K for 24 h [5]. This reaction is characterized by the intersecting tie-lines between the reactants and the products. The crystal structure of NTGO showed the positional disordering of one of the two Ga sites and the deficiency of Na site, the latter of which would contribute to the relatively high ionic conductivity along the *b*-axis. The thin-plate polycrystalline NTGO electrolyte (ca. 230 μm in thickness) showed the Na^+-ion conductivity ranging from 1.3×10^{-4} S/cm at 573 K to 7.3×10^{-3} S/cm at 1073 K. The similar reactive diffusion technique could be widely applicable to the preparation of other grain-aligned ceramics of multi-component systems.

The end members of diffusion couples were necessarily solids for the above mentioned reactions. We have also succeeded in the fabrication of highly grain-aligned polycrystals of LSO and lanthanum germanate oxyapatite by the reactive diffusion between *solid and gases* [6,7]. The textured LSO polycrystal was readily formed according to the reaction expressed by $(14 + 3x)La_2SiO_5\ (s) + (4 - 7.5x)[SiO\ (g) + 1/2O_2\ (g)] \rightarrow 3La_{9.33+2x}(Si_{6-1.5x}\square_{1.5x})O_{26}\ (s)$, where the amount of Si-deficiency in the resulting LSO was 1.5*x*.

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