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# Textured lithium lanthanum titanate polycrystals prepared by a reactive-templated grain growth method

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ABSTRACT

Textured polycrystals of lithium lanthanum titanate ($La_{(2/3)-x}Li_{3x}TiO_3$, $3x = 0.16$ and 0.33) were topochemically designed and fabricated by the heat treatment of stacked tape-cast sheets including aligned elongated $La_2Ti_2O_7$ platelets as reactive templates. The crystallographic orientation relationship between the reactive template and the resultant sintered bodies was examined by X-ray diffraction analysis. A small amount of the plate-like template effectively controlled the crystallographic orientation of the sintered bodies and the Lotgering factor for the pseudocubic {1 1 0} with a $3x = 0.16$ composition reached as high as 0.65 for the polished surface parallel to the original sheet. A secondary preferred orientation of the pseudocubic {1 0 0} was also detected in the polycrystals with $3x = 0.16$ for sections perpendicular to the sheet forming direction as a result of the elongated shape of the template. The formation of biaxially oriented polycrystals can be explained by the inheritance of octahedral $TiO_6$ blocks from the layered to regular perovskites.



## 1. Introduction

Oxides with high lithium-ion conductivities, such as perovskite-type lithium lanthanum titanate ($La_{(2/3)-x}Li_{3x}TiO_3$, abbreviated as LLTO) [1], garnet-type lithium lanthanum niobate ($Li_5La_3Nb_2O_{12}$) [2] and lithium lanthanum zirconate ($Li_7La_3Zr_2O_{12}$) [3] have attracted increasing attention as candidate electrolyte materials for all-solid-state secondary batteries. In polycrystalline materials, the total ionic conduction is often considered to be a sum of contributions from the crystal and the boundary. Although the latter could include contributions from grain boundaries, domain boundaries, or both, it is sometimes regarded as a negative factor in the total ionic conduction. Possible approaches for improving the total performance would be to minimize the total boundary area and to reduce the effects of the boundary. Garnet-type structured electrolytes with a cubic system are isotropic in their ionic conductivity. Although perovskite-type structured electrolytes have a pseudocubic system, both orthorhombic and tetragonal LLTO have La-rich and La-poor planes alternating along the <001> (pseudocubic <100>) direction [4,5]. Thus, LLTO can have orientation-dependent performance despite its pseudocubic crystal structure. Furthermore, recent investigations revealed that Li-poor LLTO has 90° domain boundaries that influence the migration of lithium [6,7]. The bulk conductivity was considerably lower than the in-grain value for Li-poor LLTO ceramics because of the effects of grain boundaries and domain boundaries. Attaining the intrinsic conductivity in LLTO polycrystals requires the optimum orientations of both the crystal lattice and domains with optimum boundaries for the ionic transport. In this work, we designed an in-situ reaction on an anisometric template and fabricated textured LLTO ceramics.

The study of textured ceramics formed by the addition of an anisometric template powder began in the 1990s [8–10]. Plate-like particles, as templates, were mixed with equiaxed small particles with the same composition and a thin sheet was formed by a doctor blade technique to align the platelets parallel to the sheet surface. Through a process called TGG (templated grain growth), the template became a seed crystal for grain growth during sintering, and highly textured ceramics were obtained. The TGG process was extended to reactive-templated grain growth (RTGG) for the fabrication of textured ceramics with a pseudocubic crystal structure [11]. For textured ceramics with a regular perovskite-type structure, anisometric particles with a layered perovskite-type structure have been used as reactive templates. The template particles react with the complementary reactants topochemically and grow into a textured ceramic with the target composition while maintain-

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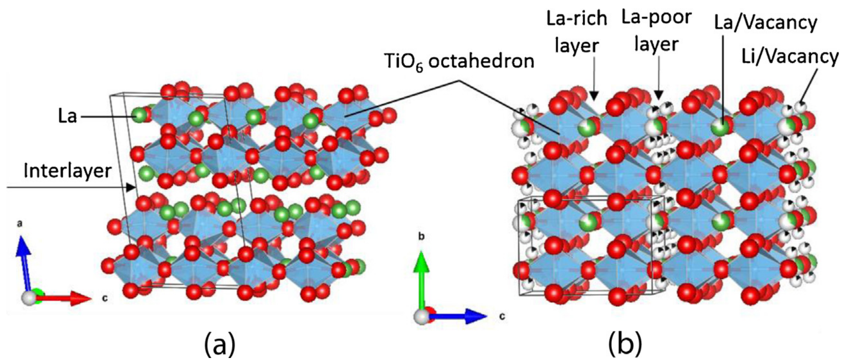


**Fig. 1.** Crystal structures of (a) monoclinic $La_2Ti_2O_7$ and (b) tetragonal $La_{(2/3)-x}Li_{3x}TiO_3$.

ing the orientation of corner-sharing oxygen octahedron networks [12]. Bismuth layer-structured-type [13], Ruddlesden–Popper-type [14,15] and layered titanate materials [16] are known to be effective reactive templates for $\{1\,0\,0\}_{pc}$-textured regular perovskite-type polycrystals ("*pc*" indicates a pseudocubic notation of the Miller indices). Improved piezoelectric properties were reported for RTGG-processed $\{1\,0\,0\}_{pc}$-textured ceramics, compared with randomly oriented specimens of the same compositions. On the other hand, strontium pyroniobate-type $Sr_2Nb_2O_7$ and $Nd_2Ti_2O_7$ platelets were used as reactive templates for $\{1\,1\,0\}_{pc}$-textured ceramics [15,17].

We examined the crystallographic and compositional similarities between pyroniobate-type $La_2Ti_2O_7$ and LLTO, and considered the former to be a reactive template material for texturing the latter using the RTGG method. Fig. 1(a) shows a crystal structure of $La_2Ti_2O_7$, in which four layers of $TiO_6$ octahedra are stacked along the monoclinic <100> direction and terminated with the edges of the octahedra at its "interlayer" parallel to the $\{1\,1\,0\}_{pc}$ plane in the perovskite unit cell [18]. The topochemical relationship between $La_2Ti_2O_7$ and tetragonal LLTO [5] is schematically shown in Fig. 1. Molten salt synthesized (MSS) $La_2Ti_2O_7$ particles were reported to have an elongated rectangular plate-like morphology with a developed *b*–*c* plane [19,20]. Thus if we align plate-like $La_2Ti_2O_7$ particles with their developed planes parallel to each other in the presence of complementary reactants for desired LLTO compositions, we can design and fabricate LLTO ceramics with a preferred $\{1\,1\,0\}_{pc}$ plane. Furthermore, if we can also align the elongated *c*-axis in the tape-casting direction, biaxially textured LLTO ceramics could be fabricated. The three-dimensional alignment of plate-like $La_2Ti_2O_7$ particles by a combination of magnetic field alignment and TGG has been reported [21]. However, biaxially textured ceramics can be prepared without magnetic field by using elongated plate-like template particles and gated doctor blade [22]. In this study, we tape-cast a slurry containing different amounts of rectangular $La_2Ti_2O_7$ platelets with complementary reactants using a doctor blade technique with a comb-like gate and investigated the texture of targeted LLTO ceramics with Li-rich ($x = 0.33$) and Li-poor ($x = 0.16$) compositions.

## 2. Experimental procedures

### 2.1. Preparation of ceramics

The experimental procedure used in this study is schematically shown in Fig. 2.

In the MSS process, lanthanum carbonate ($La_2(CO_3)_3$, LAH13XB, Kojundo Chemical Laboratory, 99.9%) and titanium dioxide ($TiO_2$, Tipaque A-100, anatase, Ishihara Sangyo Kaisha, 99.2%) were mixed in a 1:2 molar ratio and placed in a platinum crucible with the same weight of potassium chloride (KCl, Wako Pure Chemical Industries, ≥99.9%). The platinum crucible was placed in a large alumina crucible with a lid, which was placed in a furnace and heated to 1473 K for 8 h. The product was washed repeatedly by hot deionized water to rinse away solidified KCl and obtain dispersed $La_2Ti_2O_7$ platelets.

The in-house $La_2Ti_2O_7$ platelets, commercial lanthanum titanate ($La_2Ti_2O_7$, Mitsuwa chemicals, >99%), lithium titanate ($Li_4Ti_5O_{12}$, Ishihara Sangyo Kaisha, 99.5%), and titanium dioxide (Tipaque A-100) were mixed with an organic solvent premix solution in a polyethylene bottle containing zirconia balls to form a slurry for sheet forming. The specimen names and the corresponding inorganic compositions are listed in Table 1. To examine the effect of the La/Li ratio on the crystallographic texture, two compositions ($La_{0.62}Li_{0.16}TiO_3$ and $La_{0.56}Li_{0.33}TiO_3$) were chosen as representative orthorhombic and tetragonal crystal structures, respectively. The reaction schemes are shown below:

$$0.31La_2Ti_2O_7 + 0.04Li_4Ti_5O_{12} + 0.18TiO_2 \rightarrow La_{0.62}Li_{0.16}TiO_3 \quad (1)$$

$$0.28La_2Ti_2O_7 + 0.0825Li_4Ti_5O_{12} + 0.0275TiO_2 \rightarrow La_{0.56}Li_{0.33}TiO_3 \quad (2)$$

A series of four specimens was prepared for each composition so that the in-house $La_2Ti_2O_7$ platelet content of the overall $La_2Ti_2O_7$ powder was 0, 5, 20, or 100%. Specimens Li16LT and Li16LT-100T contain only commercial equiaxed $La_2Ti_2O_7$ powder and only in-house $La_2Ti_2O_7$ platelets, respectively, as the La source. The organic

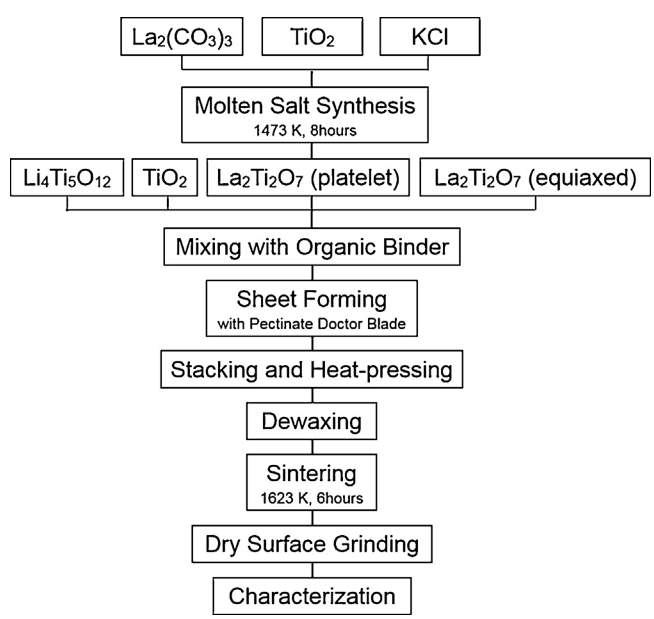


**Fig. 2.** Experimental procedure of the present study.