Title: Orientation mechanism during crystallization of apatite-type lanthanum silicate thin films from an amorphous precursor

Authors: Shigeo Hori, Teruhisa Akashi, Hirofumi Funabashi, Hiroko Iguchi, Hidehito Matsuo, Toshihiko Tani

PII: S0955-2219(17)30457-0
DOI: http://dx.doi.org/doi:10.1016/j.jeurceramsoc.2017.06.034
Reference: JECS 11338

To appear in: *Journal of the European Ceramic Society*

Received date: 25-5-2017
Revised date: 20-6-2017
Accepted date: 21-6-2017

Please cite this article as: Hori Shigeo, Akashi Teruhisa, Funabashi Hirofumi, Iguchi Hiroko, Matsuo Hidehito, Tani Toshihiko.Orientation mechanism during crystallization of apatite-type lanthanum silicate thin films from an amorphous precursor.*Journal of The European Ceramic Society* http://dx.doi.org/10.1016/j.jeurceramsoc.2017.06.034

Orientation mechanism during crystallization of apatite-type lanthanum silicate thin films from an amorphous precursor

Shigeo Hori[a], Teruhisa Akashi[a], Hirofumi Funabashi[a], Hiroko Iguchi[a], Hidehito Matsuo[a], Toshihiko Tani[a,b,*]

[a]Toyota Central Research and Development Labs. Inc., 41-1 Yokomichi, Nagakute, Aichi, 480-1192, Japan
[b]Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya, 468-8511, Japan

[*]Corresponding author, E-mail: toshit@mosk.tytlabs.co.jp (T.T.)

Abstract

Control of the crystallization and orientation of apatite-type lanthanum silicate (LSO) plays an important role in designing and improving the LSO synthesis process. The mechanisms that determine the *c*-axis preferential orientation of LSO thin films synthesized by chemical solution deposition and their correlation with preparation conditions were investigated. Crystallization was found to be initiated preferentially at the surface of the precursor thin films. It was also found that the orientation of LSO thin films was largely governed by the orientations of the LSO nuclei that formed at the surface of the precursor thin films. In addition, the *c*-axis orientation was influenced by the atmosphere used during crystallization and the Si/La ratio in the precursor thin films. An oxygen atmosphere during annealing and lower Si/La ratios reduced the degree of *c*-axis orientation.

Keywords: lanthanum silicate; oxyapatite; spin-coating; texturing; crystallization

1. Introduction

Apatite-type lanthanum silicate, $La_{9.33+2x}(SiO_4)_6O_{2+3x}$ (LSO), is a promising electrolyte material for solid oxide fuel cells operating at lower temperature [1-9]. LSO has an anisotropic oxide ion conductivity that is the highest parallel to the *c*-axis [10,11], and texturing of LSO is one of the factors to be controlled. Two types of texturing methods have been reported, one employing LSO crystalline powders and the other utilizing precursor materials [12-15]. The latter-type methods have achieved orientation control through the crystallization process and thus they can be applied to various configurations such as pellets and thin films [14-17]. In addition, the reduction of grain boundaries which impede oxide ion conductivity is also possible by some of these methods [14,17,18]. Therefore, precursor crystallization methods are expected to yield high oxide ion conductivity in practice.

We have previously reported a chemical solution deposition (CSD) method for preparing highly *c*-axis-oriented LSO thin films through self-orientation [19]. However, the orientation mechanism was unclear and it must be clarified for further improvement of the texture in the LSO thin films. In this paper, the *c*-axis orientation mechanism of LSO thin films is identified and correlated to the preparation conditions.

2. Experimental

LSO thin films were prepared by a spin-coating method. 10 mL of a ~0.3166 M aqueous solution of lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$; 99.9%, Wako) and 10 mL of ethanol (99.5%, Wako) were mixed and stirred by using a magnetic stirrer. Then, 0.8–2 mmol of tetraethoxy silane (TEOS; 99.9999%, Kojundo) was added. The mixed solution was stirred for 30–90 min at room temperature to obtain a coating solution.

Si (100) wafers and Pt plates were employed as substrates. The Si wafers were soaked in water at 80°C for 60 min before coating. The Pt plates were polished sequentially with diamond (10, 1 μm) and alumina (50 nm)