Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 5772–5776
www.elsevier.com/locate/tsf

Growth of $12CaO{\cdot}7Al_2O_3$ single crystal with tetragonal symmetry by Czochralski method

Kazuhisa Kurashige [a,b,*], Shunsuke Ueda [a], Masashi Miyakawa [b], Yoshitake Toda [b], Satoru Matsuishi [b], Sungwng Kim [b], Masahiro Hirano [b], Hideo Hosono [b]

[a] *High Performance Materials R&D Center, Hitachi Chemical Co., Ltd., Japan*
[b] *Frontier Collaborative Research Center, Tokyo Institute of Technology, Japan*

Available online 16 October 2007

Abstract

Single crystals of $12CaO{\cdot}7Al_2O_3$ (C12A7) have been grown by the Czochralski method with three different growth directions of <100>, <110>, and <111>. Employment of a 2.0% oxygen-containing nitrogen atmosphere and use of an iridium crucible were the critical factors for obtaining the single crystal. The crystal exhibited orange color resulting from the incorporation of Ir^{4+} ions of $\sim 5\times10^{17}$ cm^{-3}, presumably occupying at Ca^{2+} sites. High resolution X-ray diffraction analyses indicated that the C12A7 single crystal shows the tetragonal symmetry belonging to the space group $I\bar{4}2m$.
© 2007 Elsevier B.V. All rights reserved.

Keywords: $12CaO{\cdot}7Al_2O_3$; Czochralski method; Single crystal

1. Introduction

The unit cell of $12CaO{\cdot}7Al_2O_3$ consists of two molecules, and its chemical formula is represented as $[Ca_{24}Al_{28}O_{64}]^{4+}+2O^{2-}$. The first part constitutes a positively charged lattice framework containing twelve cages with a free space of ~0.4 nm in inner diameter [1,2]. Two oxygen ions in the second part occupy two cages out of the twelve, compensating for the positive charges of the framework, and the rest of the cages are empty. If the oxygen ions randomly distribute over the cages, the C12A7 crystal will approximately exhibit a cubic symmetry, belonging to the space group $I\bar{4}3d$ [1]. On the other hand, when the oxygen ions distribute periodically occupying specific cage sites or are ordered, the crystal symmetry becomes tetragonal, represented by the space group of $I\bar{4}2m$. Regardless of the space group, the oxygen ions, called "free oxygen ions" or "extra framework oxygen ions", can be replaced by monovalent anions such as OH^-, F^-, and Cl^- [2,3]. Recently, we have found that the free oxygen ions are replaced by active anion species such as O^-, O_2^-, H^-, and electron [4–9]. In particular, the electron doping will vary electrical transport nature from insulator to metallic conductor [10,11] and further to superconductor [12]. Because of its exceptional features such as involvement of oxygen radicals with high concentration, extremely low work functions [13,14], control of the electrical conductivity [9,10], the C12A7 derivatives are expected to have various applications including transparent electrodes, electrical wirings, solid sources of anion beams [6], cold electron emitters [11], and chemical oxidation as well as reduction reagents [5]. To realize some of these applications single crystals are indispensable. Further, C12A7 single crystal substrates make it possible to grow C12A7 homo-epitaxial thin films, which are favorable for various electronic device applications. More importantly, the single crystal is essential in clarifying the intrinsic material properties of C12A7 and its derivatives.

So far, single crystals of C12A7 have been grown by two kinds of techniques, the Czochralski (CZ) and floating zone (FZ) methods. Single crystals of ~20 mm in diameter grown by the CZ method exhibited a strong Tyndal scattering due to the inclusion of small Ir particles [15]. On the other hand, a transparent C12A7

* Corresponding author. High Performance Materials R&D Center, Hitachi Chemical Co., Ltd. 1380-1, Tarazaki, Hitachinaka-city, Ibaraki, 312-0003 Japan. Tel.: +81 029 285 1153; fax: +81 029 285 7101.
E-mail address: k-kurashige@hitachi-chem.co.jp (K. Kurashige).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.10.027

single crystal of ~10 mm diameter was grown by an FZ method [16].

However, it is extremely difficult to eliminate micropores from the grown crystal, especially in the FZ process. Because C12A7 melt is a very good solvent for O_2 gas, whose solubility significantly decreases in the super cooled liquid or glass state [17], O_2 molecules dissolved in the melt will precipitate upon cooling. This is the primary origin of micropores remaining in the grown crystal. Although iridium crucibles are commonly used in the CZ method to grow crystals having high melting points, it is difficult to use them in an oxidative atmosphere due to the strong reactivity of iridium with oxygen at high temperatures. Since platinum crucibles are less reactive with oxygen, they are commonly used instead of iridium crucibles in the O_2 bearing atmosphere for the growth of crystals with the melting point of <1600 °C.

We have already reported the growth of C12A7 crystals by the CZ method and their evaluations briefly [18]. In this paper, we will report the crystal growth process and crystallographic analyses in detail. Large-sized crystals have been obtained using iridium crucibles in a dry nitrogen atmosphere containing 2% oxygen. The crystallographic evaluation clarified that the crystal has the tetragonal symmetry, providing an experimental evidence that the extra framework oxygen ions are ordered, distributing regularly over the cage sites.

2. Experimental

$CaCO_3$ and Al_2O_3 powders of a commercial grade of 4 N (99.99%) were used as the starting materials. We used both α- and γ-alumina, which did not make any significant difference in the crystal quality.

First, in order to clarify the effect of synthesizing atmosphere in preparing the C12A7 phase, C12A7 powder was prepared by sintering the stoichiometric mixture of $CaCO_3$ and Al_2O_3 powders at 1300 °C in air. After confirming the sinter of C12A7 phase by X-ray diffraction (XRD) analysis, it was put in an Ir crucible and induction-heated above the melting point in dry nitrogen atmospheres containing oxygen gas in several concentrations. The phases of resultant polycrystal (slug) were identified by powder XRD.

For the single crystal growth, the stoichiometric mixture of the $CaCO_3$ and Al_2O_3 powders was melted in an Ir crucible in an induction heating furnace at a controlled temperature above the melting point of 1450 °C in a 2% oxygen-containing nitrogen atmosphere. An Ir rod was employed as the seed for the first trial and a small piece of the grown single crystal with a specific crystal orientation was used as the seed for subsequent crystal growth trials. The crystal was slowly pulled up from the melt at a rate of 0.8–1.0 mm/h with the seed rotation rate of 1.0–5.0 min^{-1}. After completion of the growth, the crystal ingot was separated from the melt and was gradually cooled to room temperature in 20–50 h to avoid cracking due to thermal stress.

Quality of the grown crystal was analyzed by powder XRD, X-ray Laue diffraction, and high-resolution XRD rocking curve. Optical transmission spectra were measured with a conventional UV–visible spectrophotometer. The concentration of Ir ions in the crystal was evaluated by an inductively coupled plasma (ICP) emission method.

3. Results and discussion

To clarify the minimum oxygen concentration in dry nitrogen atmosphere for obtaining the C12A7 phase, slugs were prepared in dry nitrogen atmospheres with various oxygen concentrations. The oxygen content should be minimized when the Ir crucible is employed, because Ir would react heavily with oxygen gas. Fig. 1 shows the photos of the slugs in the Ir crucible after heated above the melting point in 0%, 0.1%, 0.5%, 1.0%, 1.5%, and 2.0% oxygen-containing atmospheres. Only the slug with 2.0% oxygen-containing atmosphere was

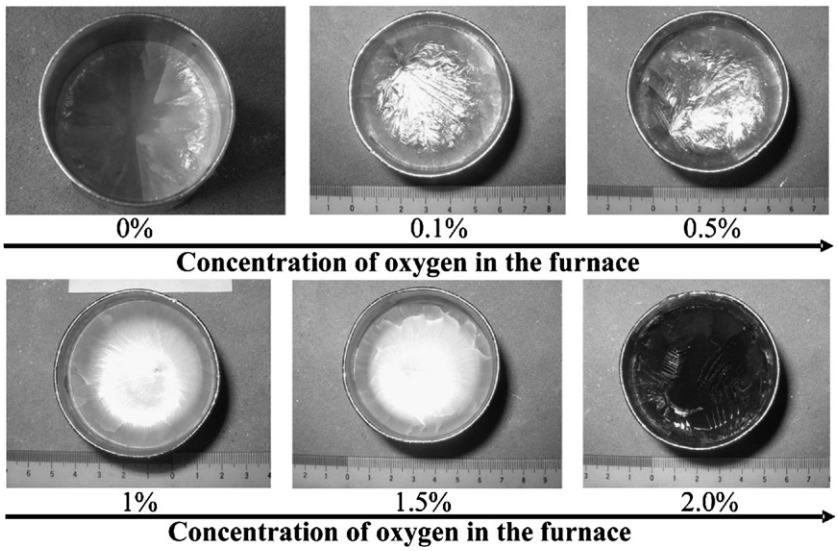

Fig. 1.

Download English Version:

https://daneshyari.com/en/article/1674586

Download Persian Version:

https://daneshyari.com/article/1674586

Daneshyari.com