X-Ray Diffraction and Density Distribution Measurements on the Al₂O₃ Crystals Grown by Czochralski Method with Different Pull Rate

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Abstracts

The Al₂O₃ crystal has been done by Czochralki Method with different pull rate. The effect of pull rate on the Al₂O₃ single crystal was characterized using X-ray diffraction and density measurement. Based on the XRD result of Al₂O₃ crystal, which belongs to the hexagonal system, except for the difference in the relative intensity, present diffraction data which are found to be in good agreement with those of the powder diffraction file (PDF) 43-1484 provided by the JCPDS. It was observed the structure with symmetry group D₆₃d-R̅₃c and has lattice constants being a = 4.759 Å, c = 12.99 Å. The density of the crystals increased with the pull rate. This phenomenon is caused by the speed of the pull rate crystal that causes changes in the heat flow in the furnace and then changed homogeneities of species distribution of atoms along the crystal. © 2015 JNSMR UIN Walisongo. All rights reserved.

Key words: XRD; Density; Al₂O₃ Crystal; Czochralski Method; Pull Rate.

1. Introduction

Sapphire crystal is an important and widely used material in today’s technology. It was used for optical and electro-optical applications. As an optical material, sapphire has a broad transmission band spanning the ultraviolet, visible and infrared region. Sapphire has very good mechanical and physical properties, such as tensile strength, abrasion resistance, thermal conductivity and mechanical stability, which result in outstanding thermal shock resistance [1]. The crystal structure consists of octahedrons of AlO₆ placed in hexagonal layers [2].

Sapphire or corundum (Al₂O₃) has a trigonal Bravais lattice with belongs to the $R\overline{3}c$ space group where the anions are in an approximately hexagonal close-packed (hcp) arrangement and cations occupying two thirds of the octahedral interstitial sites [3]. It has a rhombohedral crystal structure, but is usually described in terms of hexagonal Miller-Bravais indices. The crystal structure consists of octahedrons of AlO₆ placed in
hexagonal layers. The layers are stacked in horizontal direction one above another. The structure has a trigonal symmetry and lattice constants being \( a = 4.7587 \text{ Å}, c = 12.99 \text{ Å} \) [2]. The Al\(^{3+}\) ion in corundum is surrounded by six octahedral coordinate O\(^2-\) ions. Only 2/3 octahedral interstitial sites are packed with Al\(^{3+}\) ions because the quantity ratio of Al\(^{3+}\) and O\(^2-\) ions is 2:3 [4].

The high quality sapphire was grown using the Cz method. The Cz method is also well-known as crystal pulling method, because the method is attractive crystals from melt by using the seed crystal. Cz method involves the relationship between seed crystal and melt [5]. The production single crystals by Cz method have better optical quality, much lower density of dislocations, higher purity and very small micro-twinning [6, 7]. To production of high quality of single crystal is necessary understanding of flow, heat and mass transfer in the Cz furnace and thermal stresses in the crystal. The quality of the crystal is closely related to its thermal history and the transport phenomena in the furnace [8]. Therefore, the crystal can be obtained with a high quality and homogeneous [9, 10].

This paper reports the influence of pull rate on the X-ray diffraction and Density measurement of Sapphire single crystal grown by Czochralski method.

2. Experiments Procedure

The sapphire crystal was grown by Cz method with different pull rate (0.50 mmh\(^{-1}\), 0.75 mmh\(^{-1}\) and 1.00 mmh\(^{-1}\)) and a constant rotation rate of at 15 rpm. The samples were transparent, free of pores and bubbles, and grains.

The all sample crystals have been cut in the discs form and after polishing placed on the sample holder to be characterized by using XRD and density measurement. The X-ray diffraction analysis has been used to determine the crystal structure and orientation, lattice spacing as well as the crystallite size of sapphire single crystal. The X-ray diffraction measurement by using machine made by a Bruker D8 Advance diffractometer. The machine was operated at 40 mA, 40 kV and the scanning was between 2\( \theta \) values of 10\(^{\circ} \) to 85\(^{\circ} \) with a step time of 1 seconds per step and a step resolution of 0.06\(^{\circ} \). The settings of these parameters were chosen using the DIFFRAC\(^{\text{plus}}\) and the DIFRACT.SUITE software provides a common look and feel for measurement and analysis software. Each run lasted for approximately 0.5 h and the data were saved as an EVA file.

The density of the samples Al\(_2\)O\(_3\) single crystals were measurements based on the Archimedes principle. The measurements of density of samples were made using a digital balance with a Precisa Model XT 220A.

3. Result and Discussion

The XRD patterns of pure sapphire crystals were grown at different pull rate and the results are as shown in Figure 1. It can be observed that the XRD patterns of the samples are basically similar. The difference is apparent on the intensity and the number of peaks of the sample.

The XRD patterns for samples (Figure 1) showed single main peak with a high intensity. It shows that the samples are single crystal. The crystal structure of sapphire single crystals can be analytically indentified by noting the systematic presence or absence of reflections in the diffraction pattern based on the selection rule of the indexing crystal [11]. Furthermore, indexing of the diffraction pattern can also be done by comparing the XRD pattern with the Joint Committee on Powder Diffraction Standards (JCPDS) data. From indentifying and indexing the XRD pattern using the first technique, it can be said that the diffraction pattern of the samples has a hexagonal structure. The result is supported and confirmed by the JCPDS data base of sapphire material.

The sapphire single crystal, which belongs to the hexagonal system, except for the difference in the relative intensity, present diffraction data which are found to be in good
agreement with those of the powder diffraction file (PDF) 43-1484 provided by the JCPDS. It was observed the structure with symmetry group $D_{3d}^h - R3C$ and has lattice constants being $a = 4.759\, \text{Å}$, $c = 12.99\, \text{Å}$.

The crystalline grain size for all of samples studied was calculated using Equation: \[
\text{Crystallite size}, t = \frac{0.9\lambda}{\beta_{hkl} \cos \theta_{hkl}}
\]
based on the XRD peak boarding. By using the main peak position ($2\theta$ angle) with high intensity and measurement of full width at half maximum (FWHM) of the main peak, the crystalline grain size can then be calculated. The calculated crystalline grain size is shown in Table 1. The crystalline grain size for samples was between 24.6 nm to 46.7 nm. It can be observed that the crystalline grain sizes of all samples are basically similar. This suggests that the all samples are good single crystals.

The density of the Al$_2$O$_3$ single crystals with different pull rate were measurements based on the Archimedes principle. The densities results of sapphire single crystals with different pull rate are shown in Table 2, with each crystal cut in the middle. The aim was investigate the influence of pull rate on the density of sapphire crystals.

### Table 1: Calculation of crystalline grain size based on XRD data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$</th>
<th>$d_{(hkl)}$ (Å)</th>
<th>FWHM</th>
<th>$t$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>41.919</td>
<td>2.15342</td>
<td>0.346</td>
<td>24.599</td>
</tr>
<tr>
<td>S-2</td>
<td>41.751</td>
<td>2.16169</td>
<td>0.339</td>
<td>25.093</td>
</tr>
<tr>
<td>S-3</td>
<td>41.785</td>
<td>2.16082</td>
<td>0.182</td>
<td>46.742</td>
</tr>
</tbody>
</table>

### Table 2: EDX and density of Al$_2$O$_3$ crystals grown with different pull rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pull Rate (mmh$^{-1}$)</th>
<th>Density (g/cm$^3$)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0.50</td>
<td>3.9934±0.0004</td>
<td>Middle</td>
</tr>
<tr>
<td>S-2</td>
<td>0.75</td>
<td>3.9936±0.0007</td>
<td>Middle</td>
</tr>
<tr>
<td>S-3</td>
<td>1.00</td>
<td>3.9941±0.0004</td>
<td>Middle</td>
</tr>
</tbody>
</table>

### Figure 1. XRD patterns of Al$_2$O$_3$ single crystals grown at different pull rate.

### Figure 2. Density in the Al$_2$O$_3$ single crystal grown with different pull rate.

The influence of different pull rate on density is shown in Figure 2. The density of the crystals increased with the pull rate. This phenomenon is caused by the speed of the pull rate crystal that causes changes in the heat flow in the furnace and then changed...
homogeneities of species distribution of atoms along the crystal [12]. When the crystal pull rate is fast, then the solid-liquid surface advance is faster than the mass transport and enveloped by the solid phase.

4. Conclusion

The single crystal of Sapphire have been successfully grown using the Czochralski method. The best sapphire crystal (free bubble, free crack and transparent) was obtained with a pull rate of 0.75 mmh\(^{-1}\). In the density results of the sapphire crystal increase with pull rate increased. The X-ray diffraction measurement, the sapphire single crystals have prominent single main peak and the crystalline grain size found between 19.16 nm to 46.74 nm. This suggests that, the all crystals are good single crystals.

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References