The density and compositional analysis of titanium doped sapphire single crystal grown by the Czochralski method

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Abstract. Titanium doped sapphire (Ti:Al₂O₃) crystal has attracted attention not only as beautiful gemstones, but also due to their applications as high power laser action. It is very important crystal for tunable solid state laser. Ti:Al₂O₃ crystals have been success grown using the Czochralski method with automatic diameter control (ADC) system. The crystals were grown with different pull rates. The structure of the crystal was characterized with X-Ray Diffraction (XRD). The density of the crystal was measurement based on the Archimedes principle and the chemical composition of the crystal was confirmed by the Energy Dispersive X-ray (EDX) Spectroscopy. The XRD patterns of crystals are showed single main peak with a high intensity. It shows that the samples are single crystal. The Ti:Al₂O₃ grown with different pull rate will affect the distribution of the concentration of dopant Ti³⁺ and densities on the sapphire crystals boules as well on the crystal growth process. The increment of the pull rate will increase the percentage distribution of Ti³⁺ and on the densities of the Ti:Al₂O₃ crystal boules. This may be attributed to the speed factor of the pull rate of the crystal that then caused changes in the heat flow in the furnace and then causes the homogeneities is changed of species distribution of atoms along crystal.

1. Introduction

Sapphire (Al₂O₃) single crystal is one of the most excellent and useful material for a number of high technology, optical and electro-optical applications [1]. 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 [2]. Doping sapphire with foreign ions can be used to modify the optical properties and makes the system useful for large variation application, such us tunable solid state laser [3-6] and optical waveguides [7-9].

Sapphire becomes a promising material for tunable lasers if doped with elements possessing wide absorption bands and wide emission regions [10]. The most interesting among such elements are Ti³⁺, Cu²⁺, V⁵⁺, Ni²⁺, Co³⁺, Cr³⁺ and Mn²⁺, where these elements are included in the transition metals. The transition-metal ions are also excellent alternatives and they are widely used in laser crystals [11]. Trivalent titanium (Ti³⁺) is a transition metal ion that has very desirable broad absorption and emission
spectra when doped into the correct host. It is therefore of great importance to find an appropriate host material for this impurity ion and thus increase the number of potential tunable solid state lasers. As a tunable laser medium, high quality titanium-doped sapphire crystals are required to have uniform trivalent dopant distribution [12]. High quality titanium-doped sapphire crystal can produce high-power tunable lasers for the wavelengths 670 nm –1100 nm, and also provide synthetic gemstone materials with pink color. However, the quality of the crystal is depend on the technique used to grow the crystal. The production single crystal by Czochralski (Cz) method has better optical quality, much lower density of dislocation, high purity and small micro-twinning [13,14]. To growth of high quality of single crystal is necessary understanding of the flows heat and mass transfer in the 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 [15]. Therefore, the crystal can be obtained with a high quality and homogeneous [16, 17].

In the present study, the stucture, density and the chemical composition of Ti:Al₂O₃ (Ti:Sapphire) crystal grown using the Cz method with different pull rates were investigated. The Ti:Sapphire crystal grown with different pull rate can be affect the distribution of the concentration of dopant Ti³⁺ and densities on the sapphire crystals boules are described in detail.

2. Methods

The polycrystalline trivalent titanium doped sapphire powders were used for growing Ti:Sapphire (TS) crystal. The crystals were grown using the Cz method with automatic diameter control (ADC) system. The melts were prepared in argon from polycrystalline powders of Al₂O₃ (aluminum Oxide) doped trivalent titanium (0.01 wt. % and 0.2 wt.%)) with purity 99.99% from the Shanghai Institute of Ceramics in iridium crucible. A seed of Ti:Sapphire single crystal oriented in the c-direction with a diameter of 5 mm and 60 mm long was used. After the Ti:Al₂O₃ polycrystalline materials have melted, the seed was dipped onto the melt surface and pulled. The Ti:Sapphire crystals were grown with different pull rates (0.50 mmh⁻¹, 0.75 mmh⁻¹, 1.00 mmh⁻¹ and 1.50 mmh⁻¹) and the rotation rate was kept constant at 15 rpm. The time it takes to grow a crystal was about 40 hours, depending on the speed of the pull and the length of the resulting crystal. The temperature was then lowered to room temperature for 60 hours so that the resulting crystal was crack free.

After the growth, the all samples were cut using a Linear Precision machine with a diamond cutter in form of a disc. The crystals were cut at particular orientation, [001]. Then, the samples crystals were grinded using a silicon carbide paper and alumina suspension on the surface of the crystal. The X-ray diffraction has been used to determine the crystal structure. The measurements of density of samples were made using a digital balance with a Precisa Model XT 220A. The EDXS (Energy Dispersive X-ray Spectroscopy) will show the chemical compositions of crystals, and also the density to describe distribution of different chemicals. EDXS is an analytical technique used for an element analysis or chemical characterization of a sample.

3. Result and Discussion

3.1. Growth of the Titanium Doped Sapphire Crystal

Ti:Sapphire (TS) crystals have been success grown using the Cz method with ADC system (see Figure 1). The all samples crystal were grown with different pull rates. Figure 1a, Figure 1b, and Figure 1c are shows of Ti (0.01 wt. %) doped sapphire crystals with pull rate at 0.50 mmh⁻¹, 0.75 mmh⁻¹ and 1.00 mmh⁻¹, respectively. As shown in the Figure 1a, the crystal is clear but there is same bubble and the main body of crystal is wavy (not straight). Meanwhile, in Figure 1b and Figure 1c, the crystals are clear, transparent, bubble-free and the main body is straight. The best result of Ti:Sapphire crystals (bubble-free, crack-free and transparent) was obtained with the pull rate at 0.75 mmh⁻¹ and 1.00 mmh⁻¹ and the rotation rate at 15 rpm.

Meanwhile, in Figure 2a, Figure 2b, and Figure 2c are shows Ti (0.2 wt. %) doped sapphire crystals with different pull rates at 0.75 mmh⁻¹, 1.00 mmh⁻¹ and 1.50 mmh⁻¹, respectively. The crystals formed are of different quality and the main body is wavy. In Figure 1a and Figure 1b, the crystals are clear,
transparent and bubble-free, while in Figure 1c, the crystal is not clear and bubbles are present. The best result of Ti:Sapphire crystal (bubble-free, crack-free and transparent) was obtained with a pull rate of 0.75 mmh\(^{-1}\) and 1.00 mmh\(^{-1}\) and the rotation rate was at 15 rpm.

![Figure 1](image1.png)

**Figure 1.** Ti (0.01 wt. %): Sapphire crystals with pull rates: (a) 0.50 mmh\(^{-1}\), (b) 0.75 mmh\(^{-1}\) and (c) 1.00 mmh\(^{-1}\).

![Figure 2](image2.png)

**Figure 2.** Ti (0.2 wt. %): Sapphire crystals with pull rates: (a) 0.75 mmh\(^{-1}\), (b) 1.00 mmh\(^{-1}\) and (c) 1.50 mmh\(^{-1}\).

### 3.2. The XRD, Density and Compositional Analysis

The XRD patterns of Ti:Sapphire crystals were grown at different pull rate and the results are as shown in Figure 3. 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 EDX and density results of Ti:Al\(_2\)O\(_3\) crystals with 0.01 wt. % doped Ti grown at different pull rate is shown in Table 1, with each crystal was cut at the top part of the crystal boules. The EDX and density results of Ti:Sapphire crystals with 0.2 wt. % doped Ti grown at different pull rate is shown in Table 2, with the crystals were cut in the middle part of the crystal boules. The effect of pull rate on the distribution of Ti and density of Ti:Sapphire crystals are shown in Figure 4.

### Table 1. EDX and density of Ti (0.01 wt. %): Sapphire crystals grown with different pull rates

| Sample Name | Pull Rate (mmh\(^{-1}\)) | Average Percentage of Atomic (%) | Density (g/cm\(^3\)) | Remark |
|-------------|---------------------------|----------------------------------|----------------------|--------|
| TS1-1       | 0.50                      | 0.04 51.00 48.24 0.72 (Pt)       | 3.9943±0.0018        | Top    |
| TS1-2       | 0.75                      | 0.05 54.75 43.20 2.00 (Au)       | 3.9950±0.0006        | Top    |
| TS1-3       | 1.00                      | 0.07 54.26 44.41 1.26 (Pt)       | 3.9971±0.0008        | Top    |
### Table 2: EDX and density of Ti (0.2 wt. %): Sapphire crystals grown with different pull rates

| Sample Name | Pull Rate (mm/h) | Average Percentage of Atomic (%) | Density (g/cm$^3$) | Remark |
|-------------|-----------------|----------------------------------|-------------------|--------|
| TS4-1       | 0.75            | Ti 0.07, Al 57.39, O 40.54, Au Pt 2.00 (Au) | 3.9976±0.0005    | Middle |
| TS4-2       | 1.00            | Ti 0.08, Al 49.73, O 47.93, Au Pt 2.26 (Au) | 3.9978±0.0007    | Middle |
| TS4-3       | 1.50            | Ti 0.10, Al 55.75, O 42.53, Au Pt 1.61 (Pt) | 3.9980±0.0005    | Middle |

![XRD patterns](image)

**Figure 3.** XRD patterns of Ti:Al$_2$O$_3$ single crystals grown at different pull rates (a) Ti (0.01 wt. %) doped Al$_2$O$_3$ (b) Ti (0.2 wt. %) doped Al$_2$O$_3$. 
In Figure 4, it can be observed that Ti:Al₂O₃ grown with different pull rates will affect the distribution of the concentration of dopant Ti³⁺ and densities on the sapphire crystals boules as well on the crystal growth process. The increment of the pull rate will increase the percentage distribution of Ti³⁺ and on the densities of the Ti:Al₂O₃ crystal boules. This may be attributed to the speed factor of the pull rate of the crystal that then caused changes in the heat flow in the furnace [18, 19] and then causes the homogeneities is changed of species distribution of atoms along crystal. When solid–liquid surface advance slower than the mass transport, the foreign impurity may easily be trapped in the melt and enveloped by the solid phase [20]. The dopant is added in the beginning of the process and its concentration changed continuously with the growth. During the crystal growth, the pull rate crystal has a tendency to entrap the dopant or foreign impurity from the melt due to segregation. Dopant distribution thus cannot be treated as quasi-static like flow and temperature fields. During solidification, the solute concentration piled up in front of the solidification interface due to segregation.

![Graph](image_url)

**Figure 4.** Density and percentages doped Ti atom (in at. %) on Al₂O₃ single crystal grown with different pull rate, (a) growth on raw material with 0.01 wt. % Ti, (b) growth on raw material with 0.2 wt. % Ti.
4. Conclusion
The single crystals of Ti:Sapphire have been successful grown using the Czochralski method. The best Ti:Sapphire crystal (free bubble, free crack and transparent) was obtained with a pull rates of 0.75 mmh^{-1} and 1.00 mmh^{-1} with Ti doped 0.01 wt.%. The XRD patterns, the all samples are single crystal. In the EDX and density results, the Ti:Al2O3 crystal boules the increment of the pull rate will increase the percentage of Ti^{3+} and the density. The density and percentage of Ti^{3+} increased from the top part to the bottom part of the crystal.

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