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Growth and characterization of Fe:Ti:Al_2O_3 single crystal by floating zone method

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ABSTRACT

Fe:Ti:Al_2O_3 single crystals were successfully grown by the floating zone (FZ) method in different atmospheres. The grown crystals, typically about 7–8 mm in diameter and 50–70 mm in length, have been obtained from the materials of Al_2O_3 doped with $FeTiO_3$ and Fe_2O_3. The effect of the atmosphere on the growth was studied, and the obtained single crystals presented the best crystal quality when grown in argon. The optimum growth parameters by the FZ method for this single crystal were also studied in order to grow the highest quality single crystal. The crystal has been characterized by means of X-ray diffraction (XRD) and X-ray single crystal diffraction. Meanwhile, the Raman spectroscopy indicates that the single crystal grown in argon is similar to the natural blue sapphire. The transmittance was also measured by ultraviolet and visible spectrophotometry. Coloration mechanism in the single crystals of Fe:Ti:Al_2O_3 was analyzed by an electron probe X-ray microanalyser (EPMA). It is proved that iron is the main coloring element.

1. Introduction

Sapphire is a gemstone variety of α-Al_2O_3 (corundum) based crystal unlike ruby, with its hardness only second to diamond. It has high mechanical strength, high-temperature chemical stability, thermal conductivity, high insulation resistance and small friction coefficient, which are widely used in semiconductor devices, optoelectronic devices, lasers, vacuum devices and precision machinery. As a kind of gem, among all of sapphire's features, the color can be considered as one of the most important ones, which plays a key role in its beauty, value and popularity [1]. Trace amounts of other elements can give corundum different colors, among which, blue is the most well-known. Natural blue sapphire is a crystal that contains a small amount of titanium and iron in α-Al_2O_3 (corundum) [2–5], which requires very harsh growing conditions and therefore, it is extremely rare. Meanwhile, it is difficult to synthesize blue sapphire crystals similar to the natural ones. The growth of artificial blue sapphire crystals has been a focus for researchers.

As the melting point of Al_2O_3 is up to 2050 °C, in order to grow large-dimension and high-quality blue sapphire crystals, it seems that the floating zone (FZ) method is an optimized choice, because the in FZ method the growth of high melting point material has a unique advantage. In addition, another important advantage of the FZ method is that high temperature, high growth speed, high purity and doping uniformity can be obtained [6–11], which is very convenient for growing and doping research. Despite its great technological and industrial importance, the literature on the crystallization of gemstones is not yet sufficiently detailed, as companies dedicated to the production of blue sapphire maintain technically confidentiality. Moreover, few studies have been carried out using the FZ method for the growth of alumina-based crystals. To the best of our knowledge, none of these previous experiments have reported the growth of Fe:Ti:Al_2O_3 crystal by the floating zone method. We want to grow out a kind of blue sapphire crystal similar to the natural blue sapphire and meanwhile analyze the coloration mechanism in order to find out what is the main coloring element in the blue sapphire.

In this paper, we report our attempts to grow Fe:Ti:Al_2O_3 crystal with uniform composition by the FZ method using high-power halogen lamps as primary heat sources. We describe the crystal growth procedure of Fe:Ti:Al_2O_3 single crystal in different atmospheres, and the best growth conditions by the floating zone method for this single crystal are well studied. The crystal has been characterized by means of X-ray diffraction (XRD), X-ray single crystal diffraction and Raman spectroscopy. The coloration mechanism in single crystals of Fe:Ti:Al_2O_3 and transmittance were also measured.

2. Experimental procedure

The raw materials (powders purity of Al_2O_3 99.99%, $FeTiO_3$ 99.99%, Fe_2O_3 99.99%) were weighed in the stoichiometric amounts

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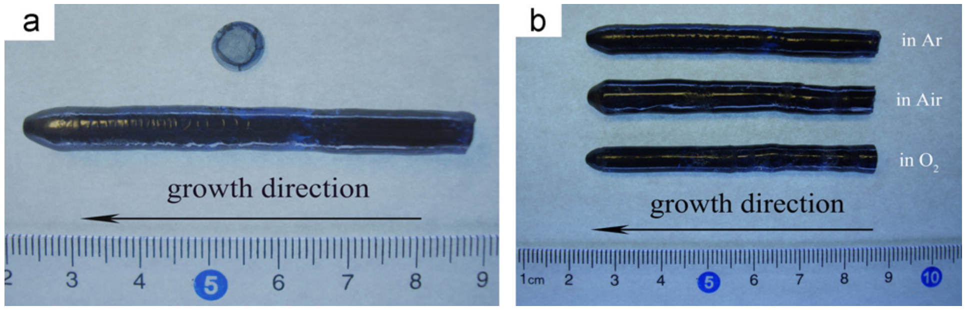

Fig. 1. Photograph of the as-grown Fe:Ti:Al_2O_3 single crystal by the FZ method: (a) the crystal grown in Ar and polished disk cut perpendicular to the growth direction and (b) the crystals grown in three different atmosphere.

(Al_2O_3 99.4 wt%, $FeTiO_3$ 0.3 wt%, Fe_2O_3 0.3 wt%) and well mixed in alcohol for 12 h. Then the mixed powders were dried in the air oven. The powder was placed in a rubber tube under 70 MPa by hydrostatically pressing it to form a rod with 8–10 mm diameter and 70–90 mm length. The rods were sintered in air at 1400 °C for 6 h. The diameter of the sintered rods was about 7–9 mm. The sintered rods were used as both feed and seed rods. In the process of crystal growth, the sintered polycrystalline ceramic rods were used as seeds; consequently, crystal growth was achieved through spontaneous nucleation.

A four ellipsoidal mirrors type optical floating zone furnace (Crystal Systems Co., 10000H-HR-I-VPO-PC) was used for the FZ method [12–14]. Four halogen lamps of 1.5 kW were used as an infrared heating source. The highest growing temperature is up to 2200 °C.

Some of the grown crystals were ground into powder and crystal structure studies were performed by X-ray diffraction (XRD) measurements in a Bruker-D8 with a step size of 0.02° in a range of 20–80° (2θ). X-ray single crystal diffraction data was gathered on a CCD diffractometer (Bruker Smart APEX II) with graphite monochromatic MoKα radiation (λ=0.71073 Å) at room temperature. The grown crystals were cut into wafers perpendicular to the growth direction, and both surfaces were polished. Rocking curves were recorded to study the structural perfection. Raman measurements were carried out using a JY-T64000 of 532-nm excitation wavelength in the range of 200–900 cm^{-1} to investigate the microstructure of the polished sections and the differences of lattice vibrations. The transmittance analyzed was measured by UV 3600 ultraviolet and visible spectrophotometry. To determine the composition of different elements and the coloration mechanism of the as-grown crystal, a JXA-8100 electron probe X-ray microanalyser with 5 μm beam diameter was employed.

3. Results and discussion

3.1. Floating zone crystal growth

Since the melting point of Al_2O_3 is up to 2050 °C, in order to optimize both the stability of the molten zone and the eventual crystal quality, certain experimental parameters need to be controlled when the crystals are growing. After several experiments, we have found that a steady molten zone, a proper crystal growth process and the fabrication technology of the feed rod are the key to the growth of high-quality single crystals. The feed rods were melted slowly and then the molten zone was formed under three different atmospheres. The crystal growing conditions were upper shaft lifting at 3–10 mm/h with 20–40 rpm rotation, and lower shaft at 3–10 mm/h with 20–40 rpm rotation. The crystals obtained were approximately 7–8 mm in diameter and 50–70 mm in length. In the initial stages of crystal growth, many nuclei were formed and grew along the axis by competition [8]. After growing for tens of millimeters from the seed touch, the seed will transform into a single crystalline slowly. During this stage, a stable melt zone can be easily maintained, and only minor adjustments to the growth conditions were needed. Furthermore, we also consider the effect of other parameters, e.g. the growth rate changing from 3 mm/h to 6 mm/h and the rotation rate changing from 10 rpm to 30 rpm. However, there is no significant effect on the molten zone and crystal quality when these preparation conditions are changed. Moreover, the growth rate is inversely proportional to the crystal quality. When the growth rate is lower than 6 mm/h, a high quality crystal without visible defects such as gas bubbles and cracks can be obtained.

The crystal growth was carried out in an enclosed quartz tube, where a controlled Ar gas with a pressure of 0.7 MPa and a flowing rate of 1 L/min is applied to reduce the evaporation rate during growth. The photos of the Fe:Ti:Al_2O_3 single crystals grown under 0.7 MPa ambient argon gas and polished cross section cut perpendicular to the growth direction are shown in Fig. 1a. And three samples grown in three different atmospheres are shown in Fig. 1b. The grown crystals were cut into wafers perpendicular to the growth direction, and the surfaces of wafers were polished. It is known that alumina-based crystals are very hard to cut into wafers and polish, so the production processes including cutting, roughening and fine grinding are very complex and time-consuming. The as-grown Fe:Ti:Al_2O_3 single crystals were grown at a traveling rate of 3 mm/h and rotation rate of 30 rpm under different atmospheres. The as-grown sample grown in argon was blue, with 8 mm in diameter and about 70 mm in length without visible defects such as gas bubbles, cracks. Moreover, the color of the crystal is uniform. The as-grown sample grown in air and O_2 was also blue, but not uniform compared with the sample grown under argon atmosphere. It seems that increased cracking and more bubbles in growing crystals may occur at higher O_2 pressures. The occurrence of bubbles in the molten zone during FZ crystal growth of $LuFe_2O_4$ [15] and increased cracking in crystals of $(La_{1-x}Ca_x)_2CaCu_2O_{6+\delta}$ [16] has been reported when the oxygen pressures were increased during growth. However, there are fewer cracks and defects at high Ar pressures, and iron and Ti^{3+} are easier for doping into the α-Al_2O_3. That is, the Fe:Ti:Al_2O_3 single crystals grown in argon have a higher crystal quality than that grown in air and O_2. The growth of Fe:Ti:Al_2O_3 single crystals is more suitable at the argon atmosphere.

3.2. X-ray diffraction

X-ray powder diffraction pattern of the as-grown crystal grown in Ar is shown in Fig. 2. The crystal symmetry at room temperature was found to be rhombohedral with R-3c space group and lattice constants: $a=b=0.4759$ nm and $c=1.2993$ nm. The domain peaks corresponded to the pure Al_2O_3 phase which is shown in the PDF