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Optical floating zone growth and dielectric constants of near-3:2 mullite crystals

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ABSTRACT

Near-3:2 mullite crystals have been grown successfully with the optical floating zone technique. The growth direction of mullite crystals is along the c axis and growth rate can be reached 10 mm/h. The effect of growth rates on the crystal quality has been studied. The crystalline phase, crystal quality, microstructure, composition distribution of the grown crystals were characterized by powder X-ray diffraction, single crystal X-ray diffraction, scanning electron microscope, electron probe micro-analyzer and Raman spectra, respectively. The grown mullite crystal is formed by peritectic structure with near 3:2 mullite crystal as main face and lamellar or needle-like SiO_2-rich aluminosilicate as secondary phase that parallel to the crystal growth direction. The measured dielectric properties show large dielectric anisotropy and good temperature stability in near-3:2 mullite crystals.

1. Introduction

Mullite compound occurred rarely in nature due to its formation conditions with high temperature and low pressure [1,2]. Mullite compound is always recognized one of the most important materials due to its many excellent properties, such as high mechanical strength [3–5], low thermal expansion coefficient [6–8], high creep resistance [9], and high elastic modulus [10]. Mullite compound is an ideal refractory material widely used as traditional and advanced ceramics [11–14]. In recent years, mullite is becoming more and more important in electronic, optical, and high-temperature structural applications [15,16]. Because of its low dielectric constant, mullite has now emerges as a substrate material in high-performance packaging applications [15]. Moreover the optical applications mainly focus on window material at elevated temperatures because of its good transmission within the mid-infrared range [17–19].

Mullite is the only crystalline compound of $\alpha Al_2O_3 \cdot \beta SiO_2$. The composition of mullite depends on the kind of the production process. Mullite has a composition of $3Al_2O_3 \cdot 2SiO_2$ by sintered process. Grown from the melt, mullite has the composition $2Al_2O_3 \cdot SiO_2$ [20]. With different value of α:β, its crystalline structure and physical property are different. In 1950, Bauer et al. grew out mullite crystal with 2 cm long and 1 cm at its thickest prepared by flame fusion method [21]. In 1974, Guse and Mateika grew 2:1 mullite crystal by the Czochralski method [22]. In 1999, Kriven et al. grew out single-crystalline mullite fibers of composition $2.5Al_2O_3 \cdot SiO_2$ with using the Laser Heated Pedestal Growth (LHPG) technique [23]. Also in 2010, Carvalho et al. grew out $2Al_2O_3 \cdot SiO_2$ mullite fibers up to 1.6 mm in diameter and 40 mm in length by the LHPG technique [24]. However, there is no report so far on the growth of 3:2 mullite crystals.

The optical floating zone technique is of several unique features which are important for growing 3:2 mullite crystals. These advantages include rapid growth rate, high temperature gradient, visual floating zone and precise and real-time parameter adjusting, etc. [25–28].

In this paper, the 3:2 mullite crystals were grown by the optical floating zone technique. The effect of growth rate on the crystal quality will be discussed. The crystalline phase, growth direction, microstructure, composition profile, as well as the dielectric constants of the as grown crystals are characterized. The aim of this research is to determine the dielectric constants of 3:2 mullite crystals, and to verify the feasibility of optical floating zone crystal growth for 3:2 mullite crystal with peritectic structure.

2. Experimental procedure

The raw materials Al_2O_3 powder (purity 99.99%, Alfa Aesar) and SiO_2 powder (purity 99.999%, Alfa Aesar) were weighed at a molar ratio of 3:2 and ball-milled for 20 h in nylon bottle with

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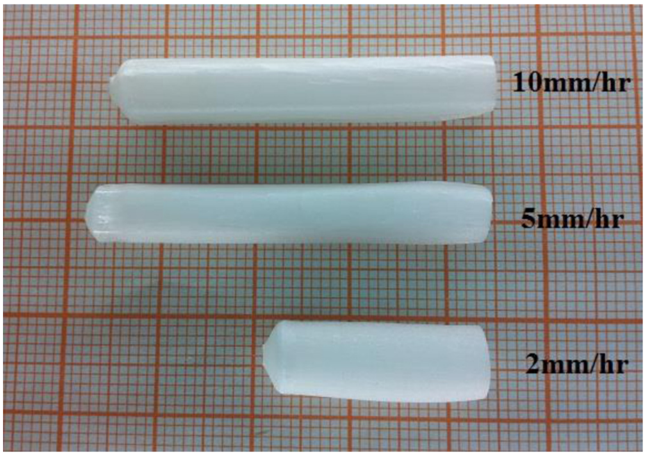

Fig. 1. The picture of mullite crystals grown at different rates by the optical floating zone method.

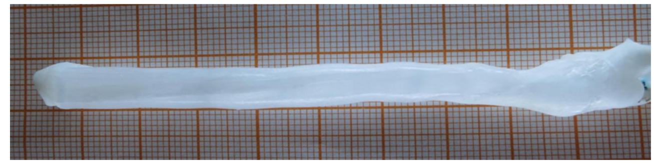

Fig. 2. The picture of the longest mullite crystal grown at a rate of 10 mm/h.

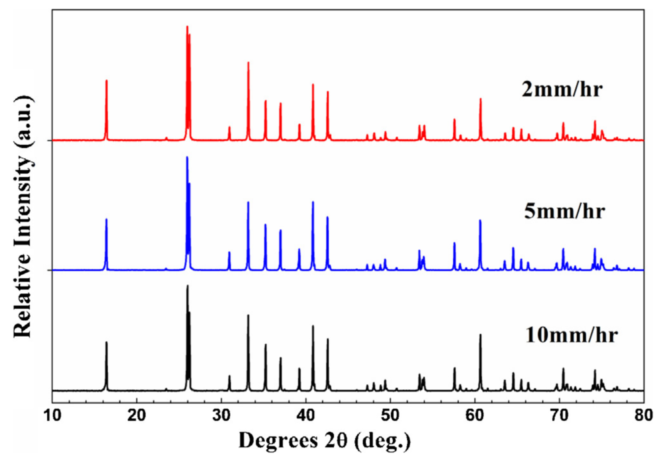

Fig. 3. XRD patterns of mullite crystals grown at different rates.

ethyl–alcohol and ZrO_2 small balls as medium. Then the prepared powder was dried in the air oven and then pre-sintered at 1450–1500 °C for 15–20 h, ground powder was placed into a long balloon and isostatic-pressed to be a rod with size of approximately 8 mm in diameter and 80–100 mm in length under about 70 M Pa. Then the rod were sintered at 1550–1650 °C for 15–30 h in the air to be a high quality ceramic rod.

The crystal growth equipment is optical floating zone furnace (Crystal Systems Co., FZ-T-12000-S-BU-PC) with four xenon lamps as heating source. The highest growing temperature is up to 3000 °C [27,28].

The seed rod was optimized by spontaneous nucleation technique of floating zone method. The feed rod and seed rod rotated reversely at rate of 30–20 rpm. The growth rate was selected to 2 mm/h.

The crystalline phase and accurate lattice parameter were measured by the X-ray diffraction (XRD) method with Ni-filtered Cu Kα radiation (Bruker-D8 discover) analysis with a step size of 0.02° in the range of 20–80°. The crystal growth direction was identified by measuring XRD patterns of polished cross-section wafer. X-ray single crystal diffraction data was collected on a CCD diffractometer (Bruker Smart APEX II) with graphite monochromatic MoKα radiation (λ = 0.071073 nm) at room temperature, Then the data processing software can show the projection maps of reciprocal lattice along any orientation. The composition profile was analyzed by using a JXA-8100 Electron Probe Micro Analyser (EPMA) with 5 μm beam diameter. Micro-Raman spectra of different area of grown mullite crystal were measured by JY T64000 Raman Spectrometer with 532 nm wavelength excitation laser.

Microstructure characteristics of polished surface parallel and perpendicular to growth direction were analyzed by a scanning electron microscope (SEM, FEI Quanta 200). The microscope imagines of cross-section wafer cut from crystal rods (see Fig. 1) grown at different rates were characterized by confocal laser scanning microscope (CLSM, Olympus OLS 3000).

The (0 0 1), (0 1 0), (1 0 0) cut-type specimens were polished and spurted with gold electrode on both faces. The capacitance and loss tangent at room temperature were measureed by using HP4284A LCR Meter. As a result, the relative permittivity was calculate by formula of ϵ:

$$\epsilon = \frac{C \times d}{\epsilon_0 \times S}$$

Also the dielectric temperature spectrums (25–280 °C, rate: 1 °C/min) under four frequencies (1, 10, 100, 1000 kHz) were measured by a computer-controlled system combined with a heating equipments and an HP4284A Precision LCR meter.

3. Results and discussion

3.1. Optical floating zone crystal growth

As shown in Figs. 1 and 2, the 3:2 mullite crystals with 6–8 mm in diameter and 20–80 mm in length were grown out at rate of 2, 5 and 10 mm/h by optical floating zone method. Their surface shows milky white and glossy. They are opaque due to the composition 3:2 located at the peritectic structure position, which is the only stable phase under atmospheric condition [15].It is important to prepare a pure, dense and uniform mullite ceramic rod for crystal growing. We optimized the pre-sintering and sintering conditions to be 1450–1500 °C for 15–20 h and 1550–1650 °C for 15–30 h, respectively. The light absorption rate increased largely when mullite started melt at the initial growth stage. So we have to decrease the out power to around one half rapidly to stabilize the molten zone.

During the early growth experiments that use the ceramic rod as seed for spontaneous nucleation, as a result, the crystal can grow along preferred orientation and its crystalline quality become better and better.

When the growth rate exceeded 10 mm/h, it was difficult to keep the molten zone stable. So we optimized the growth rate to 2 mm/h and the feed rod and seed rod rotating reversely at rate of 30 and 20 rpm respectively.

3.2. X-ray diffraction

The grown crystal rods were cut into slices with 1–1.5 mm thickness and some of them were ground into powder and then analyzed by XRD. Fig. 3 shows the powder XRD patterns of the mullite crystals grown at different rates. That the height of the second highest peak (2 1 0) around 26° decrease with increasing growth rate, indicate the microstructure of this plane changed significantly with different rates. Mullite crystals were determined to be orthorhombic with