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Note

Growth of $MgTa_2O_6$ Single Crystals by Floating Zone Method and Their Optical Properties

Mikio HIGUCHI, Kazuto ANDO, Junichi TAKAHASHI and Kohei KODAIRA

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo-shi 060

FZ法による$MgTa_2O_6$単結晶の育成とその光学的性質

樋口幹雄・安藤和人・高橋順一・小平紘平

北海道大学工学部応用化学科，060 札幌市北区北13条西8丁目

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$MgTa_2O_6$ single crystals, which adopt trirutile structure, were successfully grown by a floating zone method, and their optical properties were investigated. The as-grown crystals were black and opaque, but subsequent annealing in air from 1200° to 800°C rendered the crystals pale-yellow and transparent. The refractive indices for ordinary and extraordinary rays were 2.07 and 2.18 under white light, respectively, and the birefringence was 0.11. The interference figure observed with a polarizing microscope was typical one for an optically uniaxial crystal, which indicates that the crystal was optically uniform. Transmittance in the wavelength range of 500 to 2000 nm was about 75%, which approximately corresponded to the theoretical value calculated from the refractive index. The absorption edge of $MgTa_2O_6$ was at 290 nm.

Key-words : *$MgTa_2O_6$ single crystal, Floating zone method, Refractive index, Birefringence, Transmittance*

1. Introduction

In recent years, the demand for optically uniaxial crystals with large birefringence has been increasing to serve for polarizers in optical communications and other optical devices. Rutile (TiO_2) single crystals are one of the most promising materials because of large refractive indices and large birefringence, i.e. for ordinary ray $n_0=2.616$, for extraordinary ray $n_e=2.903$ and birefringence $\Delta n=0.287$, which contribute to fabricate smaller optical devices.[1),2)]

Cassiterite (SnO_2), which adopts the rutile structure, also has appreciably large refractive indices and birefringence, i.e. $n_0=1.997$, $n_e=2.093$ and $\Delta n=0.096$.[3)] Tapiolite ($FeTa_2O_6$) is known to adopt the trirutile structure,[4)] which is superstructure of rutile. Also, tapiolite has large refractive indices and birefringence, i.e. $n_0=2.27$, $n_e=2.42$ and $\Delta n=0.15$.[5)] From these facts, the oxides which adopt the rutile or trirutile structure are expected to have large refractive indices and birefringence on the basis of their structures.

$MgTa_2O_6$ is one of the double oxides adopting the trirutile structure,[6)] but the optical properties of $MgTa_2O_6$ has not been clarified. In this study, we have successfully grown $MgTa_2O_6$ single crystals by a floating zone (FZ) method. This paper deals with some important optical properties, such as refractive indices and transmittance, of the $MgTa_2O_6$ single crystal.

2. Experimental procedure

MgO (99.9%) and Ta_2O_5 (99.9%) powders were used as starting materials. The powders were mixed stoichiometrically and calcined at 1000°C for 10h. After grinding, the powder was molded by cipping under 100 MPa to be a rod 10 mm in diameter and 60 mm long. The molded specimen was sintered at 1400°C for 3h in a vertical tube furnace.

The used growth apparatus was of infrared convergence type with double ellipsoidal mirrors (Nichiden Kikai; SC-4B), in which two halogen lamps of 1.5 kW were placed as heat source. Crystal growth was performed with the same manner as described elsewhere.[2),7)] Growth conditions were as follows; growth rate was 5 mm/h, rotation rate was 30 rpm for both a feed rod and a seed crystal (counter-rotation), and atmosphere was an Ar stream of 2 dm^3/min.

After annealing in air from 1200° to 800°C at a cooling rate of 8°C/h, grown crystals were cut at various angles with the *c*-axis, which is optical axis of trirutile structure, and polished to be mirror finish. For the determination of refractive indices, a parallel plate which was cut parallel to the *c*-axis was used. The refractive indices for both ordinary and extraordinary rays were determined distinctively by the direct focalizing method using a polarizing microscope with a tungsten-filament lamp as light source. An interference (conoscopic) figure of the crystal which was cut perpendicularly to the *c*-axis was also observed with the polarizing microscope. Transmittance in a range of wavelength from 200 to 2000 nm was measured with a spectrophotometer (Hitachi-330).

3. Results and discussion

The sintered $MgTa_2O_6$ feed rods were not so densified that bubbles were easily introduced into the melt zone. The amount of the bubbles was sensitive to the atmosphere, and Ar was effective to suppress the formation of the bubbles. Nevertheless, the bubbles were gradually accumulated with proceeding growth run, and the melt zone occasionally became unstable when the bubbles burst. By using a feed rod which was once passed through the melt zone at a relatively high rate of 27 mm/h, a stable growth run was effected without introducing the bubbles into the melt zone.

Growth direction was an important factor to prevent the grown crystals from cracking on cooling to room temperature after the growth run. If the growth direction was perpendicular to (110) plane, many cracks were formed parallel to the (110) plane, which is cleavage plane of the trirutile structure. The growth along the *c*-axis was effective to obtain crack-free crystals. The crystals grown along the *c*-axis had nearly square-prism morphology covered with four {110} planes, which was the same as that of a rutile single crystal grown along the *c*-axis.

The as-grown $MgTa_2O_6$ single crystal obtained by the FZ method was black and opaque as shown in Fig. 1(a). The reduction of Ta^{5+} to Ta^{4+} would occur to form oxygen vacancies at high temperatures. Subsequent annealing in air rendered the crystal pale-yellow and transparent as shown in Fig. 1(b).

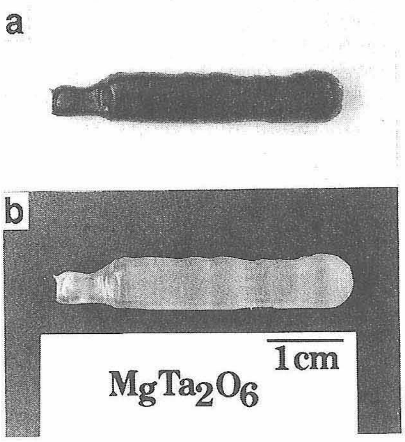

Fig. 1. $MgTa_2O_6$ single crystals grown by the FZ method.
a: as-grown, b: annealed in air from 1200° to 800°C at a cooling rate of 8°C/h.

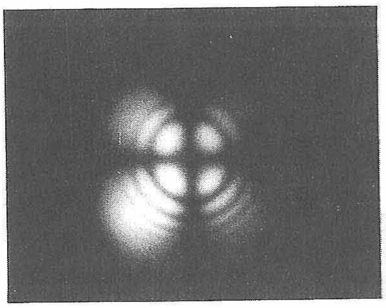

Fig. 2. Interference figure of a $MgTa_2O_6$ single crystal grown by the FZ method.

The crystal did not have cracks and other macroscopic defects such as inclusions.

Figure 2 shows an interference figure of the FZ-grown $MgTa_2O_6$ single crystal observed by the polarizing microscope. The isogyers cross perpendicularly at approximately one point, and all the isochromatic curves are concentric circles. This figure is typical for an optically uniaxial crystal, and accordingly the $MgTa_2O_6$ single crystal obtained in this study would be optically uniform and would have little stress birefringence.

Refractive indices for ordinary ray (n_0) and extraordinary ray (n_e) of $MgTa_2O_6$ were 2.07 and 2.18, respectively, and thus birefringence was 0.11. Since the light source was a tungsten-filament lamp which emmit approximately white light, the refractive indices measured would be average over the range of visible light. The optic character was positive as well as rutile. The refractive indices and the birefringence were not so large as compared with those of the rutile, but as shown in Fig. 3 they are considerably larger than those of the other optically uniaxial crystals, e.g. quartz (SiO_2), which has been conventionally used for polarizing devices.

Figure 4 shows typical double refraction images

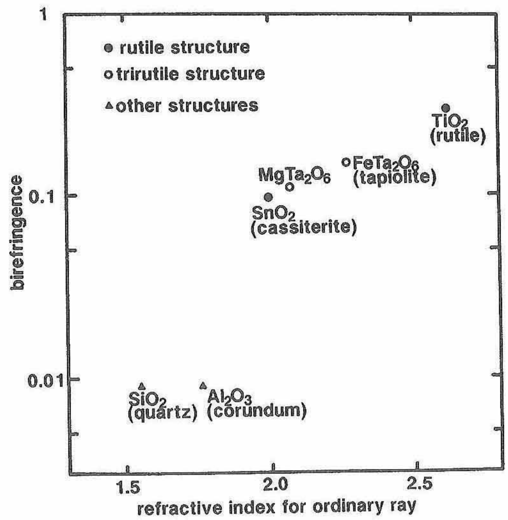

Fig. 3. The relation between refractive index for ordinary ray and birefringence in various optically uniaxial crystals.

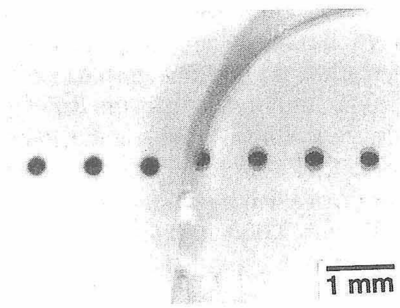

Fig. 4. Double refraction images through a $MgTa_2O_6$ single crystal. The crystal was cut at an angle of 45 degrees with the *c*-axis and polished to be 1.6 mm thick.

through the $MgTa_2O_6$ single crystal which was cut at an angle of 45 degrees with the *c*-axis. An appreciable split of light-beam can be observed between ordinary and extraordinary rays. The ratio of the split to crystal thickness is 1 : 20, which is close to theoretical value calculated from the refractive indices. The magnitude of the split is about a half of that of rutile but about eight times larger than that of quartz. Accordingly, the $MgTa_2O_6$ single crystal has the possibility to serve in practical polarizing devices.

The $MgTa_2O_6$ single crystal did not have remarkable absorption spectra in a range of wavelength from 500 to 2000 nm as shown in Fig. 5. The transmittance through the crystal perpendicular to the *c*-axis was about 75%, which approximately corresponded to the theoretical value calculated from the refractive index of 2.07. The transmittance gradually decreased below 500 nm, which would be responsible for the color of pale-yellow. The absorption edge of $MgTa_2O_6$ was at 290 nm, which was appreciably extended to ultraviolet region as compared with that of the rutile (420 nm).

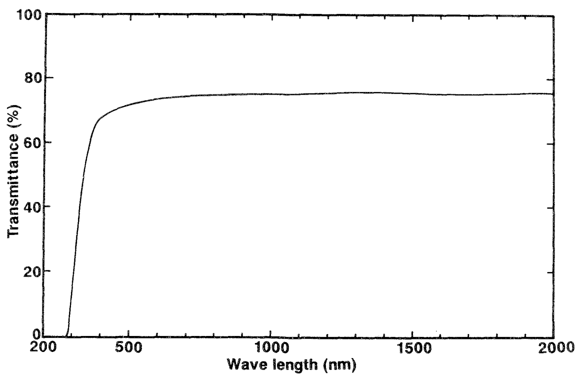

Fig. 5. Transmittance of the FZ-grown $MgTa_2O_6$ single crystal in a range of wavelength from 200 to 2000 nm.

4. Conclusion

$MgTa_2O_6$ single crystals were successfully grown by the floating zone method and their optical properties revealed in this study are as follows;

(1) From the conoscopic observation with the polarizing microscope, the $MgTa_2O_6$ single crystal grown by the FZ method was found to have good optical uniformity.

(2) The refractive indices for ordinary and extraordinary rays of $MgTa_2O_6$ were 2.07 and 2.18 under white light, respectively, and birefringence was 0.11.

(3) $MgTa_2O_6$ did not have marked absorption spectra in the wavelength range of 500–2000 nm, and the transmittance was about 75%. The absorption edge was at 290 nm.

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