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F.Z. 법에 의한 Mg TiO_3 단결정 육성

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Growth of $MgTiO_3$ Single Crystals by the Floating Zone Method

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요 약

할로겐 램프를 熱源으로 하는 image furnace를 사용하여 소위 travelling solvent floating zone법에 의해 $MgTiO_3$ (가이킬라이트) 고용체 단결정을 육성했다. 육성된 결정은 직경 8mm, 길이 100mm이였으며 성장축은 [10$\bar{1}$0]이었다. $MgTiO_3$ 相은 고온에서 일정한 공용영역을 나타내고 있으며 완만한 속도로 냉각시키면 TiO_2 성분이 결정학적 방위의 콘트롤을 받아 (0001) 면에 평행하게 용출됨으로써 광채효과를 나타낸다. 육성된 boul은 검은색을 띠고 있으나 1100℃, 산소분위기에서 annealing시킬 경우 반투명한 다양한 색깔을 보여 준다. 따라서 가이킬라이트는 새로운 종류의 인공캣츠아이로 활용될 수 있다.

최적성장조건은 다음과 같다. 소성체 소결온도 ; 1300℃ / 3시간, 최대 성장속도 ; 2 - 2.5mm/hr, 소결체의 화학조성(몰비) ; MgO : TiO_2=1 : 1.05, 솔벤트의 화학조성(몰비) MgO : TiO_2=1 : 1.2.

Abstract

Single crystals of the peritectic compound $MgTiO_3$ up to 8 mm diameter and 100 mm long along the [10$\bar{1}$0] axis, were grown by the travelling solvent floating zone technique using a halogen lamp image furnace. The grown single crystal, which shows a solid solution range at high temperature, exsolves TiO_2 component if it is annealed very slowly to room termperature. Grown boules were black but become translucent with pinkish brown color after tempering at 1100℃ for 8-10 hours in oxygen atmosphere and showed distint chatoyancy along the (0001)-plane. The grown crystal can be used as a new modified cat's eye gemstone.

The optimum conditions were as follows;Sintering temperature of the charge rod, 1300℃ the growth rate, 2-2.5 mm/h and the composition of the charge rod in molar ratio, MgO : TiO_2 = 1:1.05.

INTRODUCTION

The phase equilibrium relations in the system Mg-Ti-O at the subsolidus temperature of 1000-1600℃ have been established by Coughanour and Depresse (1953). In a subsequent study, Woermann et al. (1969) suggests that $MgTiO_3$ is a incongruently melting compound. Shindo (1980) has proved its peritectic nature by application of the EPMA technique. $MgTiO_3$ is trigonal phase with a crystal structure of ilmenite type. $MgTiO_3$ is a very rare mineral, named geikielite, occurs exclusively in gemstone mine.

Although the Czochralski-and floating zone methods are, in general, the most useful growth techniques for large size crystals of industrial use, the compounds of peritectic character prevents the direct application of these techniques. Hydrothermal-and flux method are the possible alternatives but with finite limitation.

Crystal growth of refractory oxides by floating zone technique was first introduced by Poplawsky and Thomas (1960). A varity of techniques have been used with varying degrees of success. Recently, reported the successful single crystal growth of the peritectic compounds YFe_2O_4 (Shindo et al., 1979), $Y_3Fe_5O_{12}$ (Balbashov and Egorov, 1981) by so called travelling solvent float zone (TSFZ) method, the concept of which is essentially based on zone levelling reaction of Pfann (1966). The TSFZ method is fundamentally identical to the floating zone method, with the exception that the chemical composition of the grown crystal is appreciablly different from that of the melt zone.

A preliminary study on the crystal growth of geikielite was reported by NIRIM (1978) Japan, but without detailed description. The purpose of this study is to grow the large size single crystals of $MgTiO_3$, having good uniformity in composition, for the application of artificial cat's eye gemstone.

EXPERIMENTAL DETAILS

Instrumentation

The growth apparatus employed was a double-ellipsoidal image furnace with two 1.5 kw halogen lamps as the infrared radiation source. One of the foci is occupied by the halogen lamp and the another is located at the upper charge feeding and the lower seed holding shaft so that the charge is dissolved into the molter zone and precipitated from it onto the seed as it passes this position. Growth is carried out in the chamber isolated by a fused quartz tube for atmospheric control. The apparatus is designed in such a fashion that the external solid-liquid interface can be observed during the run (Fig. 1). This floating zone system may be preferred when it is necessary to grow peritectic compounds, to privide some gas pressure over melt, to prevent the contamination and to yield crystals of lower dislocations.

Starting material

Powders of MgO(99.9%, High Purity Co.) and TiO_2(99.5%, Fluka Co.) were mechanically mixed in the alumina mortar in the required molar ratios for the preparation of the $MgTiO_3$ charge and the solvent zone materials, respectively. Each of the mixed batches was placed in a sealed rubber tube

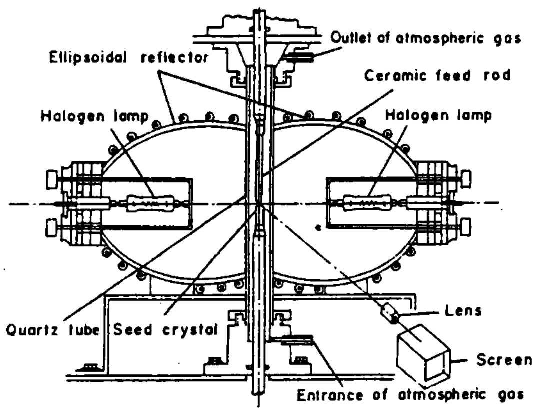


Fig. 1. Schematic diagram of the floating zone apparatus.

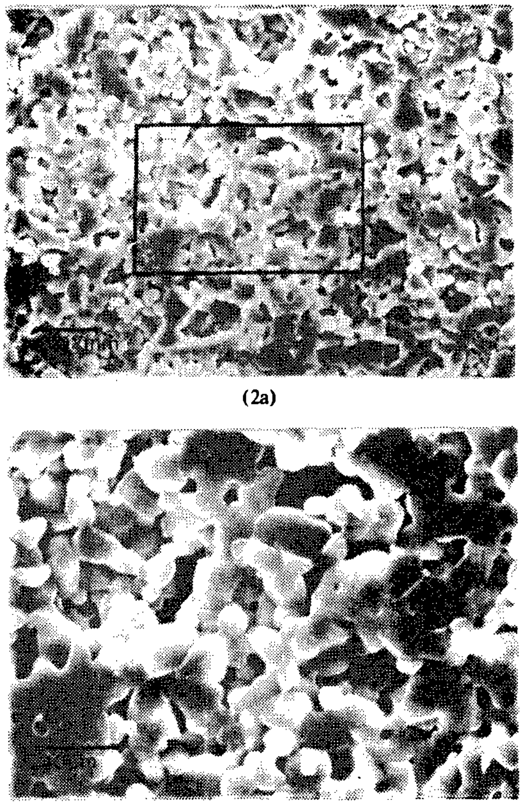
and pressed to a pressure of approximately 1000 kg/cm^2 hydrostatically.

The pressed rod was then heated at an elevated temperature(1300–1350 ℃) in air to give a sintered material with an apparent density of 80–85% of the theoretical value. In order to grow high quality crystals, it was prerequisite that charge rod must be homogeneous, straight and uniform.

Formation of a TSFZ system

At first sintered $MgTiO_3$ rod was suspended at the bottom of the upper shaft and the seed crystal was fixed at the top of the lower shaft. The disk-shaped pressed solvent zone material, which is separately sintered at different conditions, was simply put onto the seed crystal. An atmosphere of pure oxygen was introduced to the growth chamber and the solvent zone was heated. After the solvent material was melted, feed part was connected with seed crystal via solvent zone. The width and the length of the molten zone were easily controlled because its image can be measured indirectly through the screen. The molten zone is sustained by surface tension between the melt and configuous solids.

The charge and the seed shafts were synchronously driven downward at a rate of 2-2.5 mm/h, after 10-30 minutes after the zone become stationary. The two shaft were counter-rotated both at 30 rpm in order to secure complete mixing of the melt. The run was terminated when the zone had traversed from the bottom nearly to the top of the feed rod, leaving behind a boul.



(2a)

(2b)

Fig. 2. Scanning electron micrographs of the sintered rod of $MgTiO_3$ at 1350℃ (1 hr), relative density; 86%, (2a)× 710, (2b)× 1600.

RESULT AND DISCUSSION

The formation of a stable TSFZ for successful single crystal growth depended on several growth parameters ; the ratio of the zone length to the zone diameter, the composition of the solvent zone and its amount, the composition of the feeding part, the degree of sintering, the growth rate etc. The charge rod was satisfactorily prepared at temperature 1300℃ for 2 hours in air. The grain growth and coherence of the grains was more important than a degree of relative density (Fig. 2). Those factors can be the reason why the solvent material and feed rod should be prepared in different conditions separately (The sintering at the higher temperature result in the higher relative density but the in-crease of the residual pore space simultaneo-usly).

Otherwise the cooperation of vapor phase in melt zone prevent the steady state crystallization and result in collapse of the melt zone or precipitation of foreign phase. The latter case cause, in turn, in the abrupt change of the composition of floating molten zone, and thus drive the composition of the zone to the binary or ternary eutectic point, because the floating zone seems to have a finite compositional "endurance range" for the precipitation of $MgTiO_3$ solid solution on to the growing crystal. X-ray diffraction analysis reveals that such a disturbance of steady precipitation cause the poly-phase crystalization of $MgTiO_3 - MgTi_2O_5 - Mg_2TiO_4$ (or $MgTi_2O_4$) $- TiO_2$

The penetration of liquid phase into the charge rod and the disintegration of the dissolving interface, as discussed by Shindo et al. (1979) and Hosaya and Takei (1982), was not observed during the experiments. In the present study, the charge rods were sintered under the conditions described earlier and liquid–solid interface could be kept even and steady. Fig. 3 is a photograph of the molten zone under the conditions mentioned above.

The growth experiment were carried out using both polycrystalline and single crystal seeds. When a sintered rod was used as the seed, polycrystalline boul with a rough surface, which can be observed easily through the screen during the run, was obtained at the initial stage of the growth procedure, but a single crystal was eventually

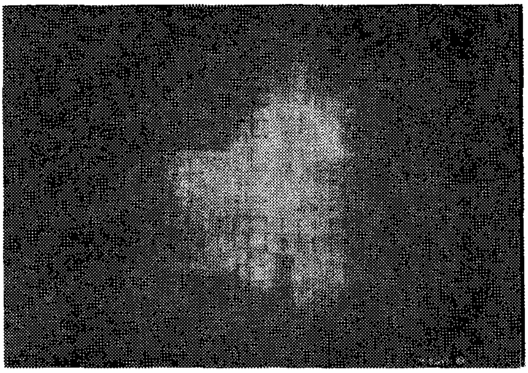


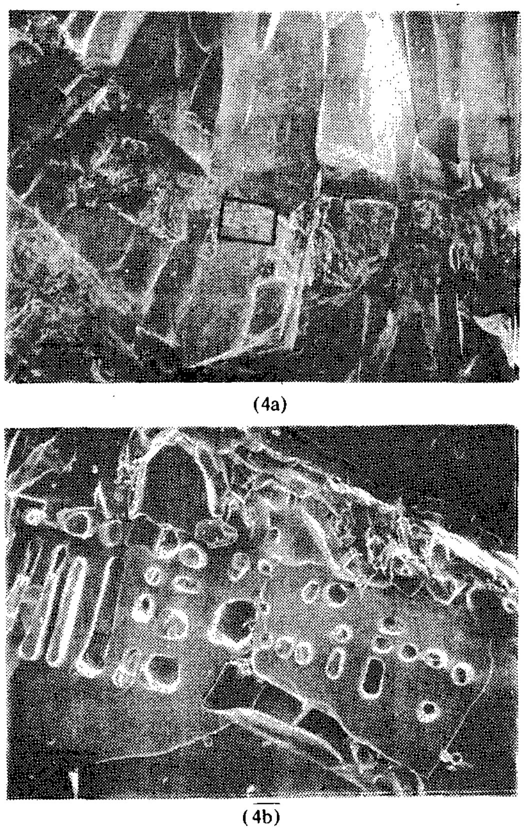
Fig. 3. Direct observation of the melting zone. The dissolving interface is kept steady without disintergration which can be caused by the penetration of the liquid phase.

obtained, after the growth of, on average, 10–20mm in length.

In order to improve the yield of a single crystal, the seeded growth was carried out using a single crystal seed obtained in a non–seeded run. The orientation of the seed crystal was conveyed to the grown crystal. The grown single crystals in optimal condition are smooth and black with glassy luster. The maximum growth rate of $MgTiO_3$ solid soultion single crystals of high quality was between 2–2.5 mm/h. A higher growth rate cause the possible precipitation of other phase and incoorporation of voids, fluid inclusion etc., (Fig. 4) and therefore degrade the quality of the grown crystal. Moreover with a zone speed of more than 2.5 mm/h, the vaporization of the material, which is accelerated in the container–free condition, could not be effectively suppessed.

Typical examples of grown $MgTiO_3$ crystal with brilliant chatoyancy are shown in Fig. 5a and Fig. 5b. The grown bouls were always colored black which can be interpreted by the patial reduction of Ti^{+4} to Ti^{+3}. The geikielite crystal has a strong prefered orientation. The growth direction is always [$10\bar{1}0$] without exception, even if the polycrystalline rod was used for seeds, and the chatoyant effect can be observed in the plane (0001) perpendicular to the growth direction. The orientational continuity was confirmed by this chatoyancy.

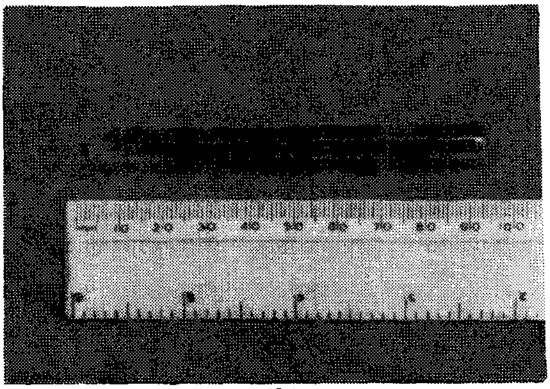
The amount of solvent for the molten zone to be introduced was determined on try–and–error basis. In order to reach a dynamical equilibrium the quantity of crystallizing molten material and of



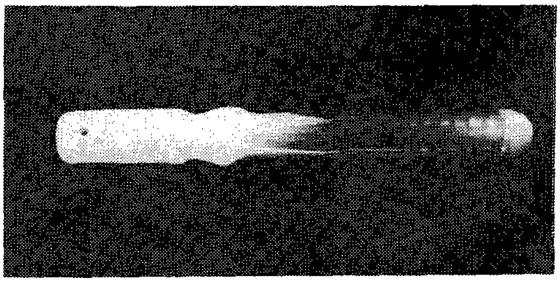
(4a)

(4b)

Fig. 4. Scanning electron micrograph of one of polypart of the grown crystal. The produced voids were apparantly related with the polyphase precipitation. (4a)× 25, (4b)× 220



(5a)



(5b)

Fig. 5. The grown bouls of $MgTiO_3$ crystals (5a) with seed crystal and (5b) with a polycrystalline seed.

resolving feeding material must be appropriatly balanced. As pointed out by Abernethy et al. (1961), the solvent zone has a self-control power to attain a suitable composition regardless of the initial composition, as the compositional variation of the molten zone is possible with some limited range, as mentioned above. Such a compositional variation within the range of $MgTiO_3$ primary crystallization field did not raise, however, any serious problems in the grown crystals.

Another characteristic feature of the TSFZ system is the development of vapour phase in the molten zone by complex mechanism as discussed by Kimura & Shindo (1977). They ascribed the bubble to the liberation of oxygen by the partial reduction of Ti^{+4} to Ti^{+3} at the dissolving interface and oxidation at the crystallization interface to the original valence state, patially. Tne bubble phase could not be observed, when the TSFZ system seems to attained to the dynamic equilibrium. Therefore the growth rate must be controlled suitably in order to allow the diffusion of oxygen, which may otherwise destroyed the steady-state zone.

The rapid cooling after completion of growth procedure must be avoided, because of the development of cracks on a large scale, especially at the end part of the bouls. The reasonable cooling rate for the growth of $MgTiO_3$ was about 400 ℃/hr. Two facets along the growth direction $[10\bar{1}0]$ which were not conspicuous but observable, were developed, but only in the crystal grown under optimal conditions.

CONCLUSION

The successful growth of $MgTiO_3$ solid solution crystals was carried out by the travelling solvent floating zone method. The optimal growth parameters determined are as follows:

1) The growth speed, which is actually the speed of zone travelling, was 2–2.5mm/h.
2) The composition of feeding material was $MgO:TiO_2$ = 1 : 1.05 and of the solvent zone 1:1.20–1.25 in molar ratio.
3) The charge rods at 1300 ℃ (2–3 hr long) had the sintering density of 82–85%.
4) The grown bouls were black with glassy luster and became brown easily by annealling procedure at 1100 ℃ (8–10 hr long).
5) $MgTiO_3$ single crystals shows chatoyancy developed parallel to the growth direction $[10\bar{1}0]$ and can be used as a modified cat's eye gemstone.

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