Decarbonization and Decolorization of Large Sapphire Crystals Grown by the Temperature Gradient Technique *

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Abstract: A crystalline sapphire (Al_2O_3) boule (Φ110 ×80mm^3) grown by the temperature gradient technique (TGT) is a bit colored due to carbon volatilization from the graphite heater at high temperatures and the absorption of transitional metal inclusions in the raw material. The sapphire becomes colorless and transparent after decolorization and decarbonization in successive annealings in air and hydrogen at high temperatures. The quality, optical transmissivity, and homogeneity of the sapphire are remarkably improved.

Key words: sapphire; decolorization; decarbonization; annealing
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1 Introduction

The temperature gradient technique (TGT) has been used to grow a variety of crystals such as YAG, Nd:YAG, Al_2O_3, Ti:Al_2O_3, $LiAlO_2$ for three decades[1~4]. The TGT is a directional solidification technique which has been adapted for the growth of large sapphire crystal boules of Φ110 × 80mm^3. The TGT-growth furnace is a vacuum graphite resistance furnace with a specially-designed heater to establish a suitable temperature gradient for sapphire. Unfortunately, carbon has such strong volatilization at 2050 ℃ as to make the growth atmosphere reductive. Under these growth conditions, some transitional metals such as Cr and Ti in the raw material enter the as-grown sapphire in the form of Cr^{3+} and Ti^{3+} ions, which absorb strongly in the visible spectrum, resulting in the colorization of the as-grown sapphire. These sapphire boules are light red at the shoulder and light yellow at the end.

The effect of annealing in an oxidizing atmosphere at 1200 ℃ for 48h on decolorization has been studied for sapphire grown with the Bridgman-Stockbarger method[5], but the size of the sapphire studied was merely 25mm ×25mm × 3mm.

We attempt to decolorize and decarbonize TGT-sapphire in an oxidizing atmosphere at 1600 ℃ for 96h. After annealing, the sapphire becomes black. The sapphire becomes red after direct annealing in a strongly reductive atmosphere (H_2) at 1600 ℃ for 96h, due to the light absorption of Cr^{3+} and Ti^{3+} ions.

The purpose of this work is to develop a practicable method for TGT-sapphire annealing which will make the sapphire colorless.

2 Annealing procedure

The TGT-grown Φ110 ×80mm^3 sapphire (Fig. 1) was annealed first in an oxidizing atmosphere in a resistance-heated furnace at 1600 ℃ for 120h. The heating rate must be lower than 60 ℃/h to keep the sapphire integrated. The sapphire surface became darker after it was cooled to room tem-

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perature at the rate of 40 ℃/h and removed from the furnace. After the above annealing, the sapphire was then annealed in a reductive atmosphere in a vacuum furnace similar to the TGT growth furnace but with no temperature gradient. Figure 2 shows the internal structure of the vacuum annealing furnace. The W bar is used to frame the heater for this furnace. After the vacuum pressure reached below 2×10^{-5} Pa, high purity H_2 was pumped into the furnace to a pressure of 0.03MPa. The heating and cooling rates for the reductive annealing were 60 ℃ and 20 ℃/h, respectively. The sapphire boule turned out colorless and transparent after reductive annealing for 120h.

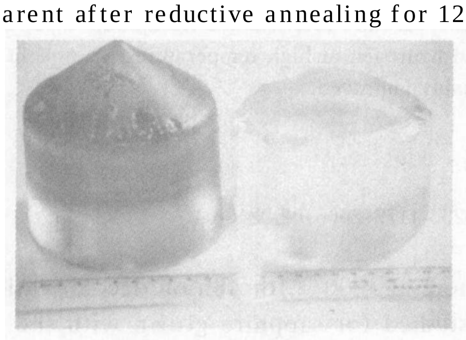

Fig. 1 As-grown (left) and annealed (right) sapphire boules ($\Phi 110 \times 80 mm^3$)

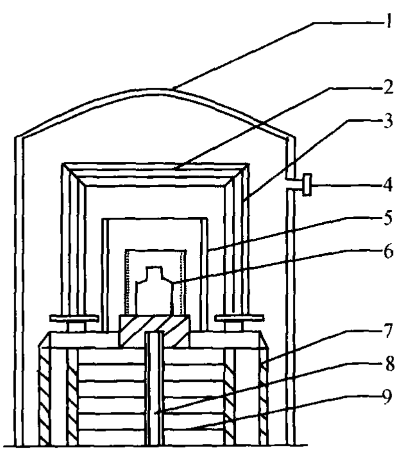

Fig. 2 Schematic structure of vacuum annealing furnace 1: Stainless steel cover; 2, 3: Molybdenum and tungsten shield; 4: Gas valve; 5: Tungsten bar heater; 6: Crystal sample; 7: Supporter; 8: Water-cooling tube; 9: Molybdenum plate shield

3 Analysis and results

3.1 Colorization mechanism in the TGT-sapphire

The direction of the temperature gradient in melt for the TGT crystal growth method is opposite to the gravitational field. The crystallization begins from the seed crystal buried at the bottom of the molybdenum crucible, and a planar solid-liquid surface emerges slowly. The primary transition metal inclusions, such as Cr and Ti, mostly accumulate near the seed due to its larger density. They enter the top of as-grown sapphire in the form of Cr^{3+} and Ti^{3+}, and their strong absorptions in the visible spectrum make the as-grown sapphire light red at the top. The impurity of the Al_2O_3 powder and a typical crystal (from top to bottom in a boule) were analyzed by Shiva Technologies West Inc. using glow discharge mass spectroscopy (GDMS). The results are shown in Table 1.

Table 1 GDMS analysis of Al_2O_3 powder and a typical sapphire crystal grown by TGT

Elements	Powder	Concentration/ppm	
		Bottom of crystal	Top of crystal
Mo	< 5	120	< 5
Sn	0.8	0.3	0.4
Zr	1.1	0.2	0.8
Co	0.5	< 0.1	< 0.1
Cr	10	< 10	< 10
S	1.2	< 0.5	< 0.5
Si	2.9	< 8	< 1
Mg	7.6	2	4
Na	16	< 1	< 1
Ti	0.5	< 0.5	< 0.5
Ba	0.09	0.09	0.09
B	1	2.5	17
Cu	0.9	0.5	1.5
Ni	7.5	< 5	30
Ca	1.5	1	17
Cl	0.8	2.5	3

Besides the effects of Cr^{3+} and Ti^{3+}, carbon volatilization from the graphite heater during the growth process is another factor affecting the sapphire color. Borodin et al.[6] believed that C reacts with Al melt at 2100 ℃ according to the following reactions:

$$2Al_2O_3 + 3C \rightarrow Al_4O_4C + 2CO$$

$$3Al_2O_3 + C \rightarrow 2Al_3O_4 + CO$$

$$Al_2O_3 + 2C \rightarrow Al_2O + 2CO$$

With the TGT method, the highest temperature reached in the growth furnace is 2200 ℃. Carbon is diffused in the melt and becomes most concentrated at the end of the as-grown sapphire. This assumption is consistent with the GDMS results[7]. Therefore, the light red at the top of the as-grown sapphire is mainly caused by the strong absorption of Cr^{3+} and Ti^{3+} ions in the visible spectrum; the faint yellow at the bottom is mainly caused by the carbon.

3.2 Mechanism of decolorization and decarbonization

The as-grown sapphire must first be annealed at 1600 ℃ for 120h in oxidizing atmosphere in order to be decolorized and decarbonized. In oxidizing atmosphere at high temperatures, Cr^{3+} and Ti^{3+} ions in the sapphire crystal were easily oxidized into Cr^{4+} and Ti^{4+} ions by the following reactions:

$$2Cr^{3+} + O_2 \rightarrow 2Cr^{4+} + O^{2-}$$

$$2Ti^{3+} + O_2 \rightarrow 2Ti^{4+} + O^{2-}$$

Because Cr^{4+} and Ti^{4+} have no absorption in the visible spectrum, the optical absorption of Cr^{3+} and Ti^{3+} in the sapphire was mostly eliminated. The carbon in the interior of the as-grown sapphire penetrates towards the edge of the boule and volatilizes in the form of CO or CO_2 after combining with oxygen. The corresponding reactions are

$$C + O_2 \rightarrow CO_2$$

$$2C + O_2 \rightarrow 2CO$$

$$Al_4O_4C + 2O_2 \rightarrow 2Al_2O_3 + CO_2$$

However, the above decarbonization reactions are not completed because of the large diameter of the sapphire boule. Most of the carbon is still accumulated on the surface or near the edge of the boule. Thus the sapphire crystal surface is darker after this annealing.

After the first annealing, the sapphire must be annealed a second time at 1900 ℃ for 120h in hydrogen. Hydrogen has strong a decarbonizing effect at 2000 ℃ as shown in Table 2[8].

Table 2 Dependence of carbon loss rate on temperature in hydrogen atmosphere

Temperature/ ℃	1800	2000	2200	2400	2600
Carbon loss rate / (10^{-5}g · cm^{-2} · s)	0.0367	0.133	0.3	0.8	1.83

The Cr^{4+} and Ti^{4+} are not converted back into Cr^{3+} and Ti^{3+} because the former are much more stable than the latter in the sapphire structure. The purpose of annealing in hydrogen at such a high temperature is to eliminate any remaining carbon.

After this "two-step" annealing, the sapphire turns out colorless and transparent as Figure 1 (right) shows.

3.3 Comparison of sapphire quality before and after annealing

The dislocation density, rocking curve FWHM, optical transmissivity, and homogeneity of the sapphire were measured at different stages during the annealing process. The results show (Table 3) that the sapphire quality and the exterior color have been improved remarkably after the whole process.

Table 3 Comparison of dislocation density, FWHM, transmissivity, and homogeneity in the as-grown crystal annealed in the two steps (first in air and then in hydrogen)

	As-grown sapphire	Annealed in air	Annealed in hydrogen
Dislocation density/ cm^{-2}	(3～6) ×10^4	(5～8) ×10^3	(2～3) ×10^3
FWHM/ (″)	15～40	15～20	10
Transmissivity/ % (300～3000nm)	80	85	88
Homogeneity	bad	(2～3) ×10^{-5}	< (2～3) ×10^{-5}

The dislocation density decreases to just one tenth that of the as-grown sapphire, as determined by X-ray diffraction topography.

The above annealing procedure is suitable for any sapphire boule grown with a graphite heater, especially for improving the optical quality of large boules.

4 Conclusion

(1) The as-grown TGT-sapphire has some color because of the absorption of various metal inclusions such as Cr^{3+} and Ti^{3+} ions and carbon. The boules are light red at the top and light yellow at the bottom.

(2) The sapphire turns out transparent and colorless after being annealed by our "two-step" method (first in air and then in hydrogen) for at least 120h at high temperatures. To our knowledge, this is the first report of a two-step annealing method for sapphire crystal. It is available for sapphire crystals grown by resistance-heated Verneuil, Czochraski, HEM[9] and EFG.

(3) The sapphire quality is significantly improved after annealing.

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温梯法生长大尺寸蓝宝石晶体的脱碳去色退火研究*

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提要: 温度梯度法(temperature gradient technique, TGT)生长的 Al_2O_3 晶体因石墨发热体在高温时的挥发和原料中过渡性金属离子的存在, 在不同部位呈现不同颜色, 一般上部为浅红色, 尾部为浅黄绿色. 将 TGT 法生长的 Al_2O_3 晶体(φ110 ×80mm^3)依次经过高温氧化气氛、高温还原气氛脱碳、去色退火实验, 即"两步法"退火实验, 晶体变成无色、透明. 经测试, Al_2O_3 晶体的完整性、光学透过率和光学均匀性均有显著提高.

关键词: Al_2O_3 晶体; 去色; 脱碳; 退火

PACC: 6170; 8140

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