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RESEARCH ARTICLE

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Synthesis of polycrystalline materials of $SrWO_4$ and growth of its single crystal

Abstract The polycrystalline materials of $SrWO_4$ were synthesized by means of a solid phase reaction with analytical purity $SrCO_3$ and WO_3 at high temperature. The transparent $SrWO_4$ single crystal with dimension of Φ 22 mm×40 mm has been successfully grown along *a*-axis by Czochralski method. X-ray powder diffraction results show that the as-grown $SrWO_4$ single crystal belongs to tetragonal system and $I4_1/a$ space group. The measured density of $SrWO_4$ is 6.439 $g \cdot cm^{-3}$ by buoyancy method. The effective segregation coefficients of W and Sr elements in $SrWO_4$ single crystal are close to 1 by the X-ray fluorescence method.

Keywords $SrWO_4$, solid phase reaction, czochralski method, X-ray powder diffraction, effective segregation coefficient

1 Introduction

In the past decades there has been tremendous surge of interest in tungstate crystal in fields such as electron paramagnetic resonance, dielectric properties, microstructure, Raman spectra characteristics and stimulated Raman scattering (SRS) [1–5]. The studies of all-solid-state Raman lasers based on SRS in crystals are becoming wide-spread, which can availably transfer the wavelength of laser. These all-solid-state Raman lasers can give out a wide laser emission range from ultraviolet to near infrared depending on pump lasers and Raman active crystals. Thus, the research and development of all-solid-state Raman lasers become a new trend in the field of laser technology.

As well known the Raman active crystals are the key to transfer the frequency of laser in all-solid-state Raman lasers. As a Raman active crystal for all-solid-state Raman lasers, strontium tungstate ($SrWO_4$) crystal is a potential for Raman converters, lasers and amplifiers [6]. $SrWO_4$ belongs to the scheelite family and the uniaxial crystal, the unit cell parameters are: $a=b=5.4168\times10^{-10}$ m; $c=11.951\times10^{-10}$ m, $V=350.66\times10^{-30}$ m^3; $z=4$, $D_c=6.356$ $g \cdot cm^{-3}$, and the space group is $I4_1/a$ [7].

$SrWO_4$ crystal can be grown by different methods, such as: Czochralski method, co-precipitation technique, solid state reaction method, film technique [8] and so on. The $SrWO_4$ crystal with large dimension and high optical quality is the foundation for the study of all-solid-state Raman lasers. Therefore, it is necessary to further study and to discuss its crystal growth. The transparent $SrWO_4$ single crystal with dimension of Φ 22 mm × 40 mm was successfully grown along *a*-axis by Czochralski method, and the orientation procedure is presented in this paper. The theory density of $SrWO_4$ crystal was calculated and compared to its experimental density that was measured by buoyancy method. The measurements of X-ray powder diffraction of crystal and effective segregation coefficients of elements in $SrWO_4$ crystal were recorded.

2 Crystal growth

2.1 Polycrystalline materials synthesis

The polycrystalline materials with high purity are the precondition to grow the crystal with high optical quality. The polycrystalline materials for growing $SrWO_4$ single crystal were prepared by the solid-phase reaction. Strontium carbonate ($SrCO_3$) and tungsten oxide (WO_3) compounds with

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a purity of 99.99% were weighted according to stoichiometric ratio of $SrWO_4$. The chemical reaction equation is as follows:

$$SrCO_3 + WO_3 = SrWO_4 + CO_2\uparrow \quad (1)$$

In addition, 1–2 wt% WO_3 was added into the polycrystalline materials to compensate the volatilization of WO_3 so as to maintain the stoichiometric ratio of $SrWO_4$ in the processes of synthesizing the polycrystalline materials and crystal growth. After the compounds were adequately ground and mixed, they were put into a platinum crucible and were heated to 1273 K for 10 h to decompose the carbonate and form $SrWO_4$ polycrystalline materials. Then the polycrystalline materials were ground and mixed again, pressed into cylindroid substance with the dimension of Φ 50 mm × 40 mm and sintered with the same procedure as the first step. Through the solid-state reaction, the $SrWO_4$ polycrystalline materials were obtained for single crystal growth.

2.2 Single crystal growth

$SrWO_4$ is a congruent melting composition and there is no phase transition under its melt temperature (1813 K) [9]. Therefore, $SrWO_4$ crystal can be grown by the Czochralski method. In this experiment, the apparatus used for crystal growth was a JTL-400 growth furnace with the crystal pulling rate: 0.3−10 mm/h and crystal rotation rate: 0−50 rad /min. $SrWO_4$ crystal was grown from an iridium (Ir) crucible, which was 66 mm in diameter, 40 mm in height and contained about 350 g $SrWO_4$ polycrystalline materials. The Ir crucible was heated by using a 2 kHz intermediate frequency furnace. The temperature-control apparatus was EUROTHERM 818 Controller/Programmer with a precision of ±0.5 K. The crawling distance of pulling apparatus was less than 1 μm, and the growth atmosphere was N_2.

In this experiment, the high quality seed was obtained by the method eliminating inferior seed through selection. Initially, a randomly oriented crystal was obtained from a polycrystalline material nucleation at the end of a platinum-rhodium (Pt-Rh) rod by restricting the diameter of the crystalline material so that only one crystal should be grown. Then an *a*-axis rectangular $SrWO_4$ single crystal bar with the dimensions of 3mm×3mm×20mm, cut from the as-grown crystal boule, was used as the seed. In order to avoid the formation of poly-crystal in the crystal growth process, a temperature of 100 K higher than the melting point of $SrWO_4$ polycrystalline materials was required initially, to melt the micro-crystal particles in the Ir crucible and maintain the temperature for 1 h. The temperature was then lowered to the melting point of $SrWO_4$. The Pt-Rh rod was slowly dropped down and maintained 5 mm distance over the melt for 15 min so as to equally heat the Pt-Rh rod. The seed was necked down before it was tapered off to a diameter of about 1 mm. Then the crystal growth processes such as the contract neck, release shoulder, maintain diameter, pull out, cool down were carried out. The technical parameters of crystal growth are listed in Table 1.

2.3 Crystal anneal

The as-grown $SrWO_4$ crystal probably have thermal stress because the crystal was grown in the furnace with high temperature gradient, and also the color centre because the growth atmosphere used was N_2. In order to eliminate the remnant thermal stress and the color centre caused by the process of crystal growth due to oxygen deficiency, the as-grown $SrWO_4$ crystal boule was annealed according to the following procedure: the crystal was put into a constant temperature field of annealing furnace and slowly heated to 1273 K in air and maintained at that temperature for 10 h, then was cooled down to room temperature at a low speed of 30 ℃/h.

3 Characterization and measurements

3.1 Crystal characterization

Figure 1 shows the as-grown $SrWO_4$ crystal boule using *a*-axis seed. The dimensions of $SrWO_4$ crystal boule are about Φ 22 mm×40 mm. There are no low angle boundaries, no inclusions as well as no other macroscopic defects in $SrWO_4$ crystal, and also no light-scattering pellets were observed when the crystal was illuminated under 10 mW He-Ne laser. All of these results mean that the as-grown $SrWO_4$ crystal has good optical quality and is suitable for Raman laser applications.

Table 1 The parameters of $SrWO_4$ single crystal growth

Processes	Parameters		
	Pulling rate (mm/h)	Rotation rate (r/min)	Temperature change (℃/h)
Contract neck	6.0–8.0	15	0
Release shoulder	1.0–3.0	15	–10
Maintain diameter	0.5–2.0	15	0.5–1.5
Pull out	10.0	15	30
Cool down	0	5	–30

Fig. 1 The $SrWO_4$ single crystal grown along *a*-axis

3.2 X-ray powder diffraction

X-ray powder diffraction (XRPD) method was used to determine the lattice structure and parameters of $SrWO_4$ crystal. A little part of $SrWO_4$ crystal was ground into thin powder as sample to be measured by the X-ray powder diffraction apparatus (Rigaku D/Max-rA) using the Cu Kα lines (λ=1.54184 $\times 10^{-10}$ m).

Figure 2 show the XRPD patterns of $SrWO_4$ crystal and the standard XRPD card of $SrWO_4$ [10], respectively. It can be seen that the XRPD patterns of $SrWO_4$ crystal was in good accordance with the standard XRPD card of $SrWO_4$. This suggests that $SrWO_4$ crystal possesses the scheelite structure and belongs to the tetragonal system, $I4_1/a$ space group. The unit-cell parameters were calculated according to the XRPD data, and they are $a=b=5.133\times10^{-10}$ m, $c=12.3902\times10^{-10}$ m. These results are similar with the standard parameters of $SrWO_4$.

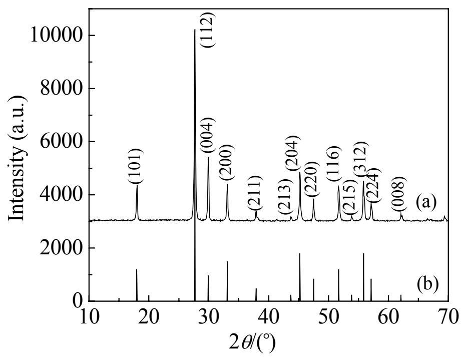

Fig. 2 X-ray powder diffraction patterns: (a) as-grown $SrWO_4$ crystal; (b) JCPDS diffraction file: 85–0490

3.3 Density measurement

The theoretical density of $SrWO_4$ crystal was calculated by using the ratio of the cell mass to cell volume, the equation to calculate the density is:

$$\rho_{theor} = \frac{MZ}{N_A abc} \tag{2}$$

where M=335.456 is chemical formula weight of $SrWO_4$; Z=4 is the number of formula units in the unit cell; N_A is Avogadro´s Number and *a, b, c* are the cell parameters of $SrWO_4$ crystal.

The experimental density of $SrWO_4$ crystal is measured by buoyancy method at room temperature (22℃), and the measured density can be obtained by the following equation:

$$\rho = \frac{m\rho_{water}}{m - m'} \tag{3}$$

where m is the mass of $SrWO_4$ crystal sample in the air, m' is the mass when the $SrWO_4$ crystal sample is immersed in distilled water, and ρ_{water} is the density of water at measured temperature (ρ_{water} is 0.998 2 g·cm^{-3} at 22℃).

The theoretical density of $SrWO_4$ crystal was calculated according to the cell parameters with Eq.(2) and the result is 6.356 g·cm^{-3}. The experimental density of $SrWO_4$ crystal was measured by buoyancy method at room temperature (22℃) and the results are listed in Table 2. It can be seen that the experimental density is approximately equal to the theoretical density.

Table 2 Data of the measured density of $SrWO_4$ crystal (22℃, ρ_{water}=0.998 2 g·cm^{-3})

	First crystal	Second crystal	Third crystal
m/g	2.519	5.192	7.712
$(m-m')$/g	0.383	0.809	1.213
ρ_{exp} (g·cm^{-3})	6.565	6.406	6.346
$\overline{\rho_{exp}}$(g·cm^{-3})	6.439		

3.4 Effective segregation coefficients measurements

The X-ray fluorescence analysis method was used to measure the concentrations of Sr and W elements in $SrWO_4$ single crystal, and based on the measured results the effective segregation coefficients of Sr and W elements in the $SrWO_4$ crystal growth process could be calculated. The measured samples were cut from the top and bottom of the $SrWO_4$ crystal, and were ground into powder to be measured by the X-ray fluorescence analysis apparatus (S/max3080E2), and the poly-crystalline materials for growing $SrWO_4$ crystal was used as compared sample. The experimental results are listed in Table 3.

Table 3 The effective segregation coefficient (K_{eff}) of elements in $SrWO_4$

	Top	Bottom
K_{eff} (Sr)	0.988 7	1.028 3
K_{eff} (W)	0.965 4	1.015 0

Table 3 shows the effective segregation coefficients of Sr and W elements in $SrWO_4$ crystal growth. It can be seen from Table 3 that the effective segregation coefficients of Sr and W elements in $SrWO_4$ crystal are very close to 1. Since the density of W ion is larger than that of Sr ion, the effective segregation coefficient of Sr is larger than that of W in the top and bottom part of the as-grown $SrWO_4$ crystal. The volatilization of WO_3 during the process of crystal growth could also account for the phenomenon that the effective segregation coefficient of Sr is larger than that of W. Therefore, the compensation of 1–2 wt% WO_3 is important to obtain uniform $SrWO_4$ single crystal.

4 Conclusions

The transparent $SrWO_4$ single crystal with dimensions of Φ 22 mm × 40 mm can be grown by Czochralski method. The X-ray powder diffraction results show that the as-grown $SrWO_4$ single crystal belongs to the tetragonal system and $I4_1/a$ space group. The unit-cell parameters were calculated and they consist of the standard parameters of $SrWO_4$. The measured density of $SrWO_4$ is 6.439 $g\cdot cm^{-3}$ by buoyancy method and closes to its theoretical density. The effective segregation coefficients of Sr and W elements in $SrWO_4$ crystal were measured and the values were close to 1, which means that the components of $SrWO_4$ crystal are uniform.

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