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Growth and thermal properties of tetragonal double tungstate $KLa(WO_4)_2$ crystal

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ABSTRACT

An uncracked single crystal of double tungstate $KLa(WO_4)_2$ with the tetragonal scheelite structure has been successfully grown by the modified Czochralski method. For the first time, the thermal properties of this crystal, including the specific heat, thermal expansion, and thermal conductivity, were systematically investigated. The specific heat of the $KLa(WO_4)_2$ crystal changes slightly from 0.333 J g^{-1} K^{-1} to 0.394 J g^{-1} K^{-1} over the temperature range from 25 °C to 500 °C. The average linear expansion coefficients are $\alpha_1 = 14.3 \times 10^{-6}$ K^{-1} and $\alpha_3 = 29.3 \times 10^{-6}$ K^{-1}. The anisotropy of the thermal expansion is explained from the point of view of crystal structure. The calculated thermal conductivities are 1.056 W m^{-1} K^{-1} and 1.174 W m^{-1} K^{-1} along the *a*- and *c*-axes, respectively. Compared with other double tungstate crystals, the $KLa(WO_4)_2$ crystal has a relatively low anisotropy of thermal expansion, as well as good thermal characteristics, and is suitable as a promising disordered laser host.

1. Introduction

Disordered double tungstate crystals with tetragonal scheelite-type structure as host materials for solid state laser have attracted considerable attention because of their extended potential for broadly tunable laser operation and generation of ultra-short optical pulses [1–7]. Potassium lanthanum tungstate [$KLa(WO_4)_2$] is a novel member of the disordered double tungstate host family. Single crystals of $KLa(WO_4)_2$ were first synthesized by Han et al. using a cooling process from the flux melt [8]. They reported that $KLa(WO_4)_2$ crystallized in tetragonal with $I4_1/a$ space group, i.e. scheelite structure, and exhibited a disordered phase where K^+ and La^{3+} cations were randomly distributed over the same cationic sublattice. The random distribution of K^+ and La^{3+} cations in the crystal lattice may induce a local variable crystal field acting on the dopant ion that is expressed in the large bandwidths of the spectral lines of the electronic transitions for the rare-earth elements. A broad emission band has been confirmed from the fluorescence emission spectrum of Yb^{3+} doped $KLa(WO_4)_2$ crystal [9]. The spectroscopic properties of other active dopants, e.g. Tm^{3+}, Er^{3+}, have also been studied in the $KLa(WO_4)_2$ host crystal [10,11]. Laser emission at room temperature has been achieved for the Nd^{3+}:$KLa(WO_4)_2$ crystal pumped by a Xenon flash-lamp [12]. Up to now, however, the thermal characteristics of the $KLa(WO_4)_2$ crystal have not been reported.

As is well known, thermal properties such as the specific heat, thermal expansion and thermal conductivity of a crystal have a significant influence on crystal growth, wafer processing and other applications [13,14]. If a crystal possesses a large anisotropy in its thermal expansion, a low specific heat and low thermal conductivity, it can easily be cracked during growth and processing if the temperature gradient is too large. Therefore, the thermal properties should be regarded as important parameters for assessing possible practical applications of a particular crystal.

In the current study, the results on the crystal growth using the modified Czochralski method and the detailed thermal properties, including the specific heat, thermal expansion, and thermal conductivity, of the crystal are reported for the first time. In addition, the relation between the structure and thermal expansion has been discussed.

2. Experimental

2.1. Crystal growth and process

$KLa(WO_4)_2$ has a congruent melting composition, and there is no phase transition below its melt temperature [8]. Consequently, this crystal can be grown using the Czochralski method. The starting materials were prepared by mixing K_2CO_3 (4 N), La_2O_3 (4 N), and WO_3 (3 N) powders according to the nearly stoichiometric ratio. After complete mixing, the mixture was heated to 800 °C and kept for 24 h to decompose K_2CO_3 as well as form polycrystalline $KLa(WO_4)_2$. The polycrystalline was placed in a platinum crucible (Φ50 mm × 30 mm) heated from the outside by a Pt cylinder which was heated inductively using intermediate-frequency. An active after-heater with a size of Φ75 mm × 50 mm made of platinum cylinder was placed just above the crucible to

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reduce the thermal gradient above the melt. After the material melted, several hours were necessary to homogenize the melt. A *c*-oriented seed was used for pulling. The pulling rate was ~0.5 mm/h and the rotation rate was 25 rpm during the crystal growth. The crystal was slowly cooled to room temperature after growth completion.

In order to eliminate the remanent thermal stress, the as-grown $KLa(WO_4)_2$ crystal was annealed according to the following procedure. First, the crystal was placed in a constant-temperature field in an annealing furnace and was slowly heated to 1050 °C in atmosphere. It was maintained at that temperature for 24 h, and then was cooled to room temperature at a low rate of about 20 °C h^{-1}.

2.2. X-ray powder diffraction

The phase and the lattice parameters of the as-grown crystal were investigated by means of X-ray powder diffraction (XRPD). The diffraction data were collected on a DX-2700 (Dandong Fangyuan, China) diffractometer with a graphite monochromatized Cu *Kα* radiation in the 2θ ranges from 10° to 70° at a step size of 0.02°.

2.3. Density measurement

The density of $KLa(WO_4)_2$ crystal at room temperature (25 °C) had been measured by using the buoyancy method. A bulk crystal was weighted (m) in the air firstly. The crystal was then hung by a bit of filament and immersed into the water without touching the bottom of the beaker, and the weight of the crystal in the water (m') was obtained. The measured density can be calculated by the following equation:

$$\rho = \frac{m}{m - m'}\rho_{\text{water}}, \quad (1)$$

where ρ_{water} is the density of water at the measured temperature.

2.4. Measurements of the thermal properties

The specific heat was analyzed by differential scanning calorimetry (DSC) using a DSC 200 F3 Maia® made by NETZSCH in the range between 25 °C and 500 °C at a heating rate of 10 °C/min. The thermal expansion was investigated using a thermal dilatometer (DIL 402PC) made by NETZSCH from room temperature up to 500 °C. The two crystal samples used for the thermal expansion measurement were processed into rectangular pieces with similar dimensions [6 mm × 6 mm × 6 mm ($a \times b \times c$)] and then the *a* crystal faces of one sample and the *c* faces of the other were polished, respectively. The thermal diffusion coefficient was measured by the laser flash method using a laser flash apparatus (NETZSCH LFA 447 Nanoflash) in the temperature range from 25 °C to 300 °C at approximate intervals of 50 °C. Two pieces of square wafers [2 mm × 10 mm × 10 mm and 8 mm × 8 mm × 3 mm ($a \times b \times c$)] were used to perform the measurements. These wafers with faces perpendicular to the *a* and *c* crystallographic directions were polished and coated with graphite on both sides.

3. Results and discussion

3.1. Crystal growth

The as-grown $KLa(WO_4)_2$ crystal using a *c*-axis seed is shown in Fig. 1(a). The crystal does not crack, and there are no inclusions and other macroscopic defects in it, which indicates that the $KLa(WO_4)_2$ crystal possesses good optical quality. Four growth ridges are revealed symmetrically around the as-grown crystal, and they represent the degenerating {1 0 1} facet groups. The normal directions of the four growth ridges correspond to ⟨1 0 0⟩ and ⟨0 1 0⟩, so this is very convenient to orient the crystal.

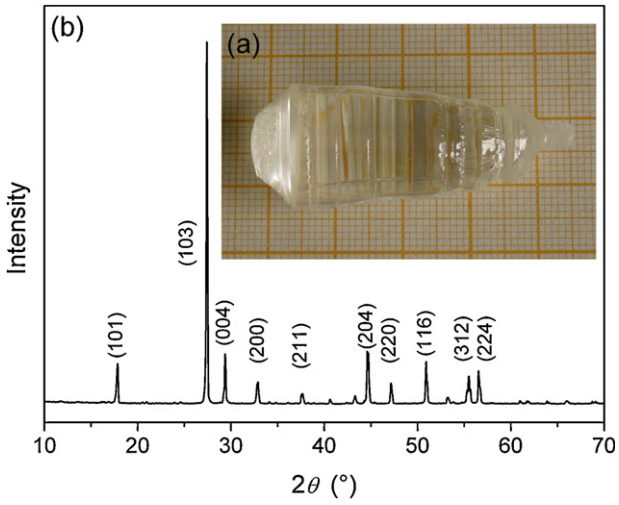

Fig. 1. (a) Photograph and (b) XPRD pattern of the as-grown $KLa(WO_4)_2$ crystal.

The XRPD pattern of the as-grown crystal [Fig. 1(b)] is identical with the standard pattern of $KLa(WO_4)_2$ (JCPDS Card no. 01-070-9242), demonstrating that the as-grown $KLa(WO_4)_2$ crystal has a tetragonal scheelite structure (space group $I4_1/a$). The calculated unit-cell parameters are $a = b = 5.445$ Å and $c = 12.121$ Å, similar to the values in Ref. [8] (5.447 and 12.080 Å, respectively).

After crystal growth, some WO_3 powdered layers were always observed on the pulling rod and on the top parts of the furnace thermal insulation. This indicates that some decomposition of the melt took place. The volatilization of WO_3 could probably result in the nonstoichiometry of the material remaining in the crucible. Thereby, based on the experience of several experiments, we added an additional 2 wt% WO_3 on the basis of the stoichiometry to compensate for its volatilization in the processes of single crystal growth and even synthesizing the polycrystalline materials.

Though some measures, such as the growth of crystal with smaller diameter and the slower annealing rate, had been taken to reduce the thermal stress, a few cracks still existed in the crystal grown by Tang and Wang [15]. This is attributed to the strong thermal expansion of $KLa(WO_4)_2$ crystal along the growth direction, i.e. the *c*-axis, according to our results (discussed in Section 3.4). Since it was able to efficiently ameliorate the sharp thermal gradient above the melt, an active after-heater above the crucible was adopted in our experiments. So the thermal stress was less accumulated and the as-grown crystal did not crack any more.

3.2. Density

The experimental density of the $KLa(WO_4)_2$ crystal is 6.25 g/cm^3 at 25 °C, which agrees very well with the calculated value of 6.23 g/cm^3 from the crystallographic data using the formula

$$\rho = \frac{MZ}{NV}, \quad (2)$$

where M is the molecular weight, Z is the number of molecules per unit cell, N is Avogadro's number and V is the volume of the unit cell. The densities at different temperatures can be deduced from the thermal expansion coefficients for the calculation of thermal conductivity. The curve of density *vs* temperature is shown in Fig. 2, and we can see that the density of $KLa(WO_4)_2$ crystal decreases linearly with the increasing temperature.