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Thermal and mechanical properties of BaWO₄ crystal

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A large single crystal of barium tungstate (BaWO₄) with dimensions of 22-mm diameter $\times$ 80-mm length was grown by the Czochralski method using an iridium crucible. The melting point, molar enthalpy of fusion, and molar entropy of fusion of the crystal were determined to be 1775.10 K, 96 913.80 J mol⁻¹, and 54.60 J K⁻¹ mol⁻¹, respectively. The average linear thermal-expansion coefficients are $\alpha_a = 10.9526 \times 10^{-6}/\text{K}$, $\alpha_b = 10.8069 \times 10^{-6}/\text{K}$, and $\alpha_c = 35.1063 \times 10^{-6}/\text{K}$ in the temperature range from 303.15 to 1423.15 K along the three respective crystallographic axes. The density of the crystal follows an almost linear decrease from 6.393×10^3 to 6.000×10^3 kg m⁻³ when the temperature is increased from 303.15 to 1423.15 K. The measured specific heat are 115.56–130.96 J K⁻¹ mol⁻¹ in the temperature range of 323.15–1173.15 K. The thermal diffusion coefficient of the crystal was measured in the temperature range of 297.15–563.15 K. The calculated thermal conductivity is 2.256 W m⁻¹ K⁻¹ along the [001] direction and 2.324 W m⁻¹ K⁻¹ along the [100] direction at 323.15 K. The microhardness of the BaWO₄ single crystal in the (001) and (100) planes is 1393 and 1814 MPa under a load of 0.050 kg. © 2005 American Institute of Physics. [DOI: 10.1063/1.1957125]

I. INTRODUCTION

In recent years, all-solid-state Raman lasers have attracted a great deal of attention^{1–10} because they can produce radiation over a wide range, including yellow and orange wavelengths with many important applications. These applications include optical remote sensing of the atmosphere, medical treatment, coastal bathymetry, laser guide stars, etc.^{11–13} A Raman-active material is a crucial part of the solid-state Raman laser. The most efficient and practical solid-state Raman lasers reported to date have been based on Ba(NO₃)₂, LiIO₃, and a variety of tungstate crystals including KGd(WO₄)₂, CaWO₄, and BaWO₄.^{1,12,14} Among the tungstate crystals, BaWO₄ is proposed to be a universal Raman-active crystal for its high gain in both the steady state and the transient state.^{8,14–17} However, the samples of BaWO₄ used in stimulated Raman-scattering (SRS) experiments are not longer than 40 mm,^{8,14,17,18} and since the intensity of Stokes radiation grows exponentially with the length of the crystal, it would be advantageous to increase this dimension.¹⁹ It is instructive to study the growth process of large dimension BaWO₄ crystals and try to process the longer SRS samples for Raman lasers. The growth of single-crystalline BaWO₄ has been reported in the literature,^{20–22} but the enthalpy and entropy of fusion, thermal diffusion coefficient, thermal conductivity, and microhardness of the crystal have not been reported. All of these factors have a

great influence on crystal growth and processing, and greatly affect the possible application of this material in all-solid-state Raman lasers.

The melting point and the enthalpy and entropy of fusion are important thermodynamic parameters in crystal-growth theory.^{23–25} Thermal expansion, specific heat, and thermal conductivity are the most important thermal properties of a crystal. If a crystal possesses a large anisotropic thermal expansion, it may be easily cracked during growth and processing if the temperature gradient is too large. During the operation of a Raman laser, the Raman-active crystal absorbs energy from the pump source and this energy is deposited as heat due to the inelastic nature of the SRS process, a phenomenon which is called thermal loading. Thermal loading must be taken into account in the design of Raman lasers, especially when scaling the devices to higher average power,¹ because thermal loading causes a temperature gradient in the crystal and leads to thermal expansion, which in turn causes thermal lensing and other thermo-optic effects. All of these effects that are related to thermal loading would lessen the quality of the laser beam and may even crack the Raman-active crystal. At the same time, if the Raman-active crystal possesses a large specific heat and a high thermal conductivity, the heat can be easily transferred to the environment, thereby decreasing the thermal loading effect. This allows for the possibility of pumping the crystal at high repetition rate (~ 10 kHz).¹⁷ There are, however, no reports on the thermal conductivity of single-crystal BaWO₄. A study of

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FIG. 1. The photograph of as-grown BaWO₄ crystal.

the thermal properties of this material, especially the thermal conductivity, could provide useful information for Raman laser designs.

Besides having excellent thermal properties, the Raman-active crystals should also have good mechanical stability to contribute to its robustness and to low processing costs. Hardness is the resistance offered by a material to a localized plastic deformation caused by scratching or by indentation. It can be regarded as a major indicator of what the mechanical properties of a material are like. Consequently, the hardness of single-crystal BaWO₄ is included as a part of this study.

II. EXPERIMENT

Polycrystalline BaWO₄ was synthesized through a solid-state reaction with high-purity (99.99%) BaCO₃ and WO₃ in a platinum crucible. A BaWO₄ single crystal up to 22-mm diameter $\times$ 80-mm length was grown by using the Czochralski method with an iridium crucible which was heated by a 2-kHz intermediate frequency furnace.²² Figure 1 shows a photograph of the BaWO₄ single crystal as-grown. When a 5-mW He–Ne laser is used to pump the as-grown crystal, no scattered light beam was observed, showing that it was of excellent optical quality.

X-ray powder diffraction shows that the as-grown BaWO₄ single crystal belongs to the tetragonal crystal system, I₄/a space group with unit-cell dimensions of $a=b=5.6041$ Å and $c=12.7080$ Å,²² in accordance with literature values.²⁶

A. Melting point and enthalpy of fusion measurements

A differential scanning calorimeter (DSC) made by NETZSCH Company (NETZSCH DSC 404C) was used to measure the melting point and enthalpy of fusion of the BaWO₄ crystal. A small piece of the crystal weighing 62.11 mg was used for the DSC measurement. The sample was kept in an Al₂O₃ crucible and another empty Al₂O₃ crucible was used as the reference crucible as they were heated together at a constant rate of 10 K/min from 300.15 to 1873.15 K.

B. Thermal-expansion measurements

The thermal expansion of the BaWO₄ crystal was measured in the temperature range from 303.15 to 1423.15 K by using a thermal dilatometer (NETZSCH DIL 402C). The crystal used for the thermal-expansion measurements was processed into a rectangular piece with dimensions of $7.80 \times 6.14 \times 4.32$ mm³ ($a \times b \times c$). The sample was annealed at 1273.15 K for 10 h in order to release any processing stress. During the thermal-expansion measurements, the sample was heated at a constant rate of 5 K/min from 303.15 to 1423.15 K and thermal-expansion ratio versus temperature curves along a , b , and c crystallographic directions were measured.

C. Specific-heat measurement

Specific heat was measured by the method of differential scanning calorimetry using a simultaneous thermal analyzer (NETZSCH STA 449C) using the following steps. First, two empty Pt–Rh crucibles were heated together to carry out the base line measurement; second, a sapphire calibration sample weighing 42.05 mg was kept in one of the two Pt–Rh crucibles and was heated together with the other empty Pt–Rh crucible; and third, the BaWO₄ sample weighing 46.55 mg was placed in the same Pt–Rh crucible and was heated together with the other empty Pt–Rh crucible. In all three operations, the temperature was raised from 323.15 to 1173.15 K at a constant rate of 10 K/min. Finally, the specific heat of BaWO₄ crystal was calculated by a comparison method using the CP software package provided by the NETZSCH Company.

D. Thermal diffusion coefficient measurements

The thermal diffusion coefficient of single-crystal BaWO₄ was measured by the laser flash method using a laser flash apparatus (NETZSCH LFA 447 Nanoflash) in the temperature range from 297.15 to 563.15 K. Two pieces of square ($8 \times 8 \times 1.820$ and $8 \times 8 \times 2.000$ mm³) wafers having polished faces perpendicular to the [100] and [001] crystallographic directions and coated with graphite on both sides were used to carry out the measurements.

During the experiment, a short light pulse heats the front surface of the plan-parallel BaWO₄ wafer and the temperature rise on the rear surface is measured versus time using an IR detector. The thermal diffusion coefficient of the crystal was calculated using analytical software provided by the NETZSCH Company.

E. Microhardness measurements

An HMV-2 microhardness tester made by Shimadzu Corporation for varying loads (0.010–0.050 kg) was used to measure the Vickers microhardness of BaWO₄ crystal at room temperature. For each load, the time of indentation was kept constant at 10 s, and several indentations were made. The average value of the diagonal indentation length was used to calculate the Vickers microhardness. The samples consisted of two polished BaWO₄ crystal wafers (20-mm diameter) having faces parallel to the (100) and (001) crystallographic planes.

FIG. 2. DSC curve of as-grown BaWO₄ crystal.

III. RESULTS AND DISCUSSION

A. Melting point and enthalpy and entropy of fusion

Since the melt growth of crystals takes place through the motion of the liquid-solid interface, $\Delta_{\text{fus}}H_m$ (the molar enthalpy of fusion) and $\Delta_{\text{fus}}S_m$ (the molar entropy of fusion) are important thermodynamic parameters, both for computer simulation and actual crystal-growth experiments. The roughness of the interface will determine the growth kinetics of the crystal.²³ Jackson showed that the roughness of the interface can be predicted by the Jackson factor,²⁴ which is given as follows:

$$\alpha = \frac{L}{kT_E}f, \quad (1)$$

where L is the latent heat of crystallization, k is the Boltzmann constant, T_E is the melting point, and f is the fraction of the binding energy associated with the layer, which depends on the crystal face. If $\alpha \leq 2$, the interface is considered a rough surface; otherwise, it is considered a smooth surface. For a smooth interface, the crystal exhibits faceted morphology, and growth rates are slower.²⁵

Figure 2 shows the DSC curve of the BaWO₄ crystal. From Fig. 2, a single sharp endothermic peak was observed in the temperature range from 1745.65 to 1792.50 K. This peak exhibits the characteristics of a first-order phase transition with a peak temperature at 1775.10 K. Evidence of the fusion of the BaWO₄ crystal was found in the sample cell after the DSC measurement. The transition can be ascribed to a solid-to-liquid phase change. The sharp peak temperature of 1775.10 K was identified as the melting point of the crystal, a value that is 27 K higher than that reported in the literature.²⁷ The difference can be understood as follows: a BaWO₄ single-crystal was used to measure the melting temperature, and the purity of the single-crystal material is higher than that of polycrystalline BaWO₄.

The molar enthalpy of fusion $\Delta_{\text{fus}}H_m$ of single-crystal BaWO₄ was derived from the DSC curve using the area integration method included in the DSC analytical software

TABLE I. Thermodynamic parameters of BaWO₄ crystal gained from DSC measurement.

Thermodynamic parameters	Values
T_E (K)	1775.10
$\Delta_{\text{fus}}H_m$ (J mol ⁻¹)	96 913.80
$\Delta_{\text{fus}}S_m$ (J K ⁻¹ mol ⁻¹)	54.60

provided by the NETZSCH Company. The molar entropy of fusion $\Delta_{\text{fus}}S_m$ was calculated using the following thermodynamic equation:

$$\Delta_{\text{fus}}S_m = \frac{\Delta_{\text{fus}}H_m}{T_E}, \quad (2)$$

where T_E is the melting point of the BaWO₄ crystal. The calculated results are listed in Table I.

For single-crystal BaWO₄, the Jackson factor is

$$\alpha = \frac{L}{kT_E}f = \frac{\Delta_{\text{fus}}H_m}{RT_E}f = \frac{\Delta_{\text{fus}}S_m}{R}f = \frac{54.60}{8.314}f = 6.57f.$$

Since $\Delta_{\text{fus}}S_m/R=6.57$ is a large number, the liquid-solid interface most probably is a smooth surface when the crystal grows from the melt, and the growth rate should be relatively slow. In our experiment, the pulling rate is less than 2 mm/h and a high-quality BaWO₄ crystal was obtained.

B. Thermal expansion

The thermal-expansion coefficient $[\alpha_{ij}]$ of a crystal is a symmetrical second-rank tensor.²⁸ The quadric representation equation for $[\alpha_{ij}]$ referred to the principal axes is

$$\alpha_{11}x_1^2 + \alpha_{22}x_2^2 + \alpha_{33}x_3^2 = 1. \quad (3)$$

Correspondingly, in the principal coordinate system the $[\alpha_{ij}]$ is diagonal,

$$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix} \text{ or } \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{bmatrix}.$$

The quantities α_1 , α_2 , and α_3 are the principal components of the thermal-expansion coefficient tensor.

BaWO₄ belongs to the tetragonal system and 4/ m point group. The unique symmetry axis is a fourfold axis along the crystallographic c axis; the axes of the crystallographic and crystallophysical coordinate systems in BaWO₄ have the same direction, that is,

$$a//X_1, \quad b//X_2, \quad c//X_3.$$

In compliance with Neumann's principle, the representation quadric for $[\alpha_{ij}]$ is a surface of a fourfold revolution about X_3 and there are only two independent principal components of the thermal-expansion coefficient tensor. These components are $\alpha_1 = \alpha_2$ and α_3 . The values of α_1 , α_2 , and α_3 can be obtained by measuring the thermal expansion of the a -, b -, and c -oriented crystal samples because $a//X_1$, $b//X_2$, and $c//X_3$.

The solid lines in Fig. 3 are the thermal-expansion ratio curves along the three crystallographic axes. The thermal-

FIG. 3. Solid lines: Thermal-expansion ratio curves of BaWO₄ crystal. Dotted lines: Average linear thermal-expansion coefficients of BaWO₄.

expansion ratio is almost linear over the entire measured temperature range from 303.15 to 1423.15 K. The average linear thermal-expansion coefficient for all three crystallographic directions can be calculated according to the following formula:

$$\bar{\alpha}(T_0 \rightarrow T) = \frac{\Delta L}{L_0} \frac{1}{\Delta T}, \quad (4)$$

where $\bar{\alpha}(T_0 \rightarrow T)$ is the average linear thermal-expansion coefficient in the temperature range from T_0 to T , L_0 is the sample length at T_0 , ΔL is the length change when the temperature changes from T_0 to T , and the temperature change $\Delta T = T - T_0$. In our experiment, $T_0 = 303.15$ K, $L_0(a) = 7.80$ mm, $L_0(b) = 6.14$ mm, and $L_0(c) = 4.32$ mm.

From Fig. 3, it can be seen that the crystal exhibits only expansion when it is heated, which means that all the thermal-expansion coefficients are positive. The average positive linear thermal-expansion coefficients in the temperature range from 303.15 to 1423.15 K, which were calculated with the formula (4) according to the thermal-expansion ratio curves, are shown as dotted lines in Fig. 3. From these dotted lines, it can be seen that the average linear thermal-expansion coefficients $\alpha_c > \alpha_a \approx \alpha_b$ increase with rising temperature. When the temperature is varied from 303.15 to 1423.15 K, the average linear thermal-expansion coefficients are $\alpha_a = 10.9526 \times 10^{-6}/\text{K}$, $\alpha_b = 10.8069 \times 10^{-6}/\text{K}$, and $\alpha_c = 35.1063 \times 10^{-6}/\text{K}$. These results indicate that $\alpha_a \approx \alpha_b > 0$ and $\alpha_c/\alpha_a \approx 3.25$ and suggest that the crystal possesses a large anisotropic thermal expansion. The representation quadric for $[\alpha_{ij}]$ is thus an ellipsoid with the semiaxis lengths of $x_1 = x_2 > x_3$ according to Eq. (3).

The large anisotropic thermal expansion suggests that crystalline BaWO₄ should be cooled to room temperature at a low rate after growth; otherwise, the crystal will more than likely crack. In our crystal-growth experiment, the cooling rate is less than 50 K/h and a large dimension high-quality BaWO₄ crystal was obtained, as shown in Fig. 1.

C. Density versus temperature curve of BaWO₄ crystal

The density of the BaWO₄ crystal can be calculated with the following equation when it is processed into a rectangular sample:

$$\rho = \frac{m}{V} = \frac{m}{abc}, \quad (5)$$

where m is the mass of the crystal (the mass does not change with temperature because the crystal has good thermal stability below the melting point), V is the volume of the crystal, and a , b , and c are the dimensions of the rectangular sample.

When the temperature is varied from T_0 to T , the dimension of the rectangular sample will also change. The length changes can be determined from the thermal-expansion ratio,

$$a = a_0 \times \left(1 + \frac{\Delta a}{a_0}\right), \quad (6)$$

$$b = b_0 \times \left(1 + \frac{\Delta b}{b_0}\right), \quad (7)$$

$$c = c_0 \times \left(1 + \frac{\Delta c}{c_0}\right), \quad (8)$$

where $\Delta a/a_0$, $\Delta b/b_0$ and $\Delta c/c_0$ are the thermal-expansion ratios when temperature is varied from T_0 to T . Correspondingly, the density of the BaWO₄ crystal is

$$\begin{aligned} \rho &= \frac{m}{abc} \\ &= \frac{m}{a_0 b_0 c_0 [1 + (\Delta a/a_0)][1 + (\Delta b/b_0)][1 + (\Delta c/c_0)]} \\ &= \frac{\rho_0}{[1 + (\Delta a/a_0)] \left[1 + \frac{\Delta b}{b_0}\right] [1 + (\Delta c/c_0)]}, \end{aligned} \quad (9)$$

where ρ_0 is the density of the crystal at T_0 . The values of $\Delta a/a_0$, $\Delta b/b_0$, and $\Delta c/c_0$ can be obtained from the solid lines in Fig. 3, and T_0 is 303.15 K. The density of the crystal had been measured at 295.15 K by using the buoyancy method with a resulting value of $6.393 \times 10^3 \text{ kg m}^{-3}$.²² There should be little difference between the densities at 295.15 and 303.15 K. So we assume that the density of the crystal at 303.15 K is also equal to $6.393 \times 10^3 \text{ kg m}^{-3}$, that is, $\rho_0 = 6.393 \times 10^3 \text{ kg m}^{-3}$. The density versus temperature curve of the crystal in the temperature range from 303.15 to 1423.15 K is shown in Fig. 4. It can be seen that the density of the crystal almost linearly decreases as the temperature increases and that the density is $6.000 \times 10^3 \text{ kg m}^{-3}$ at 1423.15 K.

D. Specific heat

Figure 5 shows the specific heat versus temperature curve of BaWO₄ crystal, measured by the method of differential scanning calorimetry. It can be seen that the specific heat of the crystal is almost constant with a value of

FIG. 4. Density vs temperature curve of BaWO₄ crystal.

300–340 J kg⁻¹ K⁻¹ in the temperature range of 323.15–1173.15 K. The molar mass of BaWO₄ is 385.19 g mol⁻¹, and the molar specific heat of the crystal ranges from 115.56 to 130.96 J K⁻¹ mol⁻¹ in the temperature range of 323.15–1173.15 K.

The specific heat of one substance can also be calculated according to the Dulong-Petit law when the temperature of this substance is higher than its Debye temperature θ_D .²⁹ According to the Dulong-Petit law, the specific heat of 1 mol at.

$$C_v \approx 3NK = 3R = 3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ \approx 25 \text{ J K}^{-1} \text{ mol}^{-1}.$$

But the specific heat of lighter element, such as oxygen, is 16.7 J K⁻¹ mol⁻¹.³⁰ According to Kopp's law, the specific heat of 1-mol substance is the sum over all the atoms, so the specific heat of the BaWO₄ crystal can be calculated as follows:

$$C_v = 25 \times 1 + 25 \times 1 + 16.7 \times 4 = 116.8 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Because there is little difference between C_p and C_v for solid substance, we can take the measured specific heat C_p to be equal to C_v , the specific heat at constant volume. It can be seen that the calculated value of C_v is in accordance with the measured value. These results show that the BaWO₄ crystal is in compliance with Dulong-Petit law and the Debye tem-

FIG. 5. Specific heat vs temperature curve of BaWO₄ crystal. FIG. 6. Solid lines: Thermal diffusion coefficient of BaWO₄ crystal. Dotted lines: The calculated thermal conductivity of BaWO₄ crystal.

perature of the crystal is apparently not higher than 323.15 K.

E. Thermal diffusion coefficient and thermal conductivity

The thermal conductivity $[k_{ij}]$ of a crystal is also a symmetrical second-rank tensor.²⁸ In the principal coordinate system, the $[k_{ij}]$ tensor is diagonal like the thermal-expansion coefficient tensor and has only two independent principal components for a tetragonal crystal system. These components can be obtained by making measurements on *a*- and *c*-oriented crystal samples.

In our experiment, the thermal diffusion coefficients of the BaWO₄ crystal were measured directly and the thermal-conductivity tensor components were calculated using the following equation:

$$k = \lambda \rho C_p, \quad (10)$$

where k , λ , ρ , and C_p denote the principal thermal conductivity, thermal diffusion coefficient, density, and specific heat of the crystal, respectively.

The solid lines in Fig. 6 show the thermal diffusion coefficients of single-crystal BaWO₄ in the temperature range from 297.15 to 563.15 K at 20-K interval between measured temperature points. The dotted lines in Fig. 6 show the thermal-conductivity components of the crystal in the temperature range of 323.15–563.15 K, as calculated according to Figs. 4 and 5 and the solid lines in Fig. 6. From Fig. 6, it can be seen that the thermal diffusion components and thermal-conductivity components are anisotropic and that the anisotropy decreases with increasing temperature. The thermal diffusion coefficients of the crystal along the [100] direction are 1.307 mm² s⁻¹ at 300.15 K and 1.214 mm² s⁻¹ at 323.15 K; along the [001] direction, they are 1.260 mm² s⁻¹ at 300.15 K and 1.178 mm² s⁻¹ at 323.15 K. The calculated thermal-conductivity components of single-crystal BaWO₄ are 2.256 W m⁻¹ K⁻¹ along the [001] direction and 2.324 W m⁻¹ K⁻¹ along the [100] direction at 323.15 K, as shown in Fig. 6.

TABLE II. Vickers microhardness of BaWO₄ crystal.

Load (kg)	Vickers microhardness (MPa)	
	(001) Crystallographic plane	(100) Crystallographic plane
0.010	1471	1893
0.025	1461	1883
0.050	1393	1814

F. Microhardness

Hardness is the resistance offered by a material to localized plastic deformation caused by scratching or indentation. Vickers microhardness is indentation hardness, which is determined from the formula³¹

$$H_v = 18.18P/d^2, \quad (11)$$

where H_v , P , and d are the Vickers microhardness number (in megapascal), applied load (in kilogram), and diagonal length of indentation (in millimeter), respectively.

The microhardness of the BaWO₄ crystal was measured for loads of 0.010, 0.025, and 0.050 kg on the (100) and (001) crystallographic planes. The measured results are listed in Table II. It can be seen that the value of hardness decreases as the load increases and the hardness of the (100) plane is higher than that of the (001) plane. Generally speaking, the microhardness of single-crystal BaWO₄ is low, which means that the single crystal is soft and more easily processed.

IV. CONCLUSION

The thermal properties of single-crystal BaWO₄ were carefully studied by measuring the melting point, molar enthalpy of fusion, molar entropy of fusion, thermal expansion, specific heat, thermal diffusion coefficient, and thermal conductivity. The DSC measurement shows that the crystal possesses large molar entropy of fusion and that the liquid-solid interface should be smooth. The thermal-expansion measurements show that the crystal has only two independent principal components of the thermal-expansion coefficient tensor. The average linear thermal-expansion coefficients are $\alpha_a = 10.9526 \times 10^{-6}/\text{K}$, $\alpha_b = 10.8069 \times 10^{-6}/\text{K}$, and $\alpha_c = 35.1063 \times 10^{-6}/\text{K}$ over the temperature range from 303.15 to 1423.15 K. The specific heat of the crystal is little changed at measured values of 115.56–130.96 J K⁻¹ mol⁻¹ in the temperature range of 323.15–1173.15 K. The thermal-conductivity tensor components of the crystal along the [001] and [100] directions are 2.256 and 2.324 W m⁻¹ K⁻¹, respectively, at 323.15 K, which suggest that the crystal has good thermal-conductivity properties. Finally, the microhardness of the crystal was measured on the (001) and (100) crystallographic planes and the results show that it is a soft material that should be easily processed and polished.

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