

氟化钙-氟化钡混晶制备与光学性能表征

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摘 要: 通过直接沉淀法制备氟化钙-氟化钡($\text{CaF}_2\text{-BaF}_2$)混晶多晶料。采用坩埚下降法, 通过设计合理的工艺条件(真空度: 10^{-3} Pa, 下降速率: $0.2\sim 1$ mm/h; 轴向温度梯度: $40\sim 70$ °C/cm; 径向温度梯度: $50\sim 70$ °C/cm, 降温速率: 25 °C/h), 生长出不同原料配比的 $\text{CaF}_2\text{-BaF}_2$ 混晶。用 X 射线衍射仪、双折射率仪、红外分光光度计对 $\text{CaF}_2\text{-BaF}_2$ 混晶性能进行表征, 并研究其光学性能。结果表明: $\text{CaF}_2\text{-BaF}_2$ 混晶尺寸为 $\phi 20$ mm \times (175~180) mm, 晶体透过率为 70%~80%, 其本征双折射率略低于 CaF_2 单晶。

关键词: 氟化钙; 氟化钡; 混晶原料纯度; 双折射; 透过率

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Preparation and Optical Characterization of Calcium Fluoride-Barium Fluoride Mixed Crystal

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Abstract: The polycrystalline materials of calcium fluoride-barium fluoride ($\text{CaF}_2\text{-BaF}_2$) were prepared by a direct precipitation method. The $\text{CaF}_2\text{-BaF}_2$ mixed crystals at different ratios of raw materials were grown by the Bridgman method. The parameters of the growth used were the vacuum degree of 10^{-3} Pa, the decline rate of $0.2\sim 1$ mm/h, the axial temperature gradient of $40\sim 70$ °C/cm, the radial temperature gradient of $50\sim 70$ °C/cm, and the cooling rate of 25 °C/h. The performance of the $\text{CaF}_2\text{-BaF}_2$ materials was characterized by X-ray diffraction, birefringence analysis and Fourier transform infrared spectroscopy, respectively. The optical properties of the $\text{CaF}_2\text{-BaF}_2$ mixed crystal were also analyzed. The results show that the size of the $\text{CaF}_2\text{-BaF}_2$ is $\phi 20$ mm in diameter and 175~180 mm in length. The transmittance of the mixed crystals is 70%~80%. The intrinsic birefringence of the mixed crystals is less than that of CaF_2 single crystal.

Key words: calcium fluoride; barium fluoride; mixed crystals; purity of raw materials; birefringence; transmission

1 Introduction

The stages of developing integrated circuits (ICs) are divided by small-scale, large-scale, and even great-scale. The ICs can be applied in various fields such as aerospace engineering, defense engineering, etc.^[1]

Lithography as one of the most mature methods to prepare ICs has undergone four stages, g line (436 nm), i line (365 nm), far ultraviolet (UV) (248 nm, KrF laser), and deep ultraviolet (DUV) (193 nm, ArF laser).^[2-3] The wavelength reduction at each stage represents the de-

velopment of the ICs, the lithography range of DUV laser is from 193 nm to 121 nm now^[4]. The CaF_2 crystals are widely used as optical medium materials and important lithography lens elements due to its remarkable properties such as high and stable transmission at the ultraviolet region, broad transmittance range (from far UV to mid-IR), high laser damage threshold, low refractive index, low stress birefringence, and corrosion resistance.^[5-7]

As the lens of the lithography system, the lens surface of the two polarizations has different refractive indices,

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and the light generates the bifurcations when the light passes through the lens. Meanwhile, the polarization component of light through the crystal can be formed when accumulated into different phases, thereby generating the phase distortion. The above phenomena will lead to an addition in image sharpness and resolution.^[8] There are two solutions to eliminate the effect of birefringence. One solution is to reduce the use of CaF_2 crystal, and design a more complex optical system. The intrinsic birefringence effect has a low symmetry in the general direction of propagation, but it has multiple symmetries in some specific direction. The birefringence can be reduced by cross-coupling lens. The other is the composition of CaF_2 and other crystal materials. MF_2 ($M = \text{Ca}, \text{Ba}, \text{Sr}$) crystals have the same cubic structure, and the similar physical and chemical properties. The compensation effect of the intrinsic birefringence can reduce the birefringence^[9], and improve the resolution of the lithography systems at 193 nm and 157 nm.

In this work, polycrystalline materials of CaF_2 - BaF_2 were prepared with calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), barium carbonate (BaCO_3) and sodium fluoride (NaF) as raw materials by a direct precipitation method. In addition, the structure and performance of the polycrystalline materials were analyzed.

2 Experimental

2.1 Raw materials

$\text{Ca}(\text{NO}_3)_2$ (99.99%), BaCO_3 (99.99%), and NaF (99.99%) were used as raw materials in the experiments. $\text{Ca}(\text{NO}_3)_2$, BaCO_3 and NaF were prepared as an aqueous solution with an appropriate concentration in accordance with $\text{Ca}_{1-x}\text{Ba}_x\text{F}_2$ where $x = 0.75$ or 0.85 . The solution was firstly stirred at a high speed, and then washed by deionized water and centrifuged at 11 000 r/min. The resultant powdered product was obtained after dried at 160°C . The raw material for the fluoride crystal growth cannot be used directly due to the presence of moisture and oxides producing some impurities. A small amount of PbF_2 as a scavenge was added to the powder and put into a furnace. The furnace was heated in HF gas for 10 h to remove the moisture, and then N_2 was given into the furnace to remove residual HF gas. Finally, CaF_2 - BaF_2 polycrystalline materials in two ratios were obtained with the raw materials in a high purity of 99.999%.

2.2 Crystal growth

The CaF_2 - BaF_2 mixed crystals were grown by Bridgman method. The processing parameters are as the flowing. The vacuum degree was 10^{-3} Pa. The decline rate was 0.2–1 mm/h. The axial temperature gradient was $40\text{--}70^\circ\text{C}/\text{cm}$. The radial temperature gradient was $50\text{--}70^\circ\text{C}/\text{cm}$. The freezing rate was $25^\circ\text{C}/\text{h}$. The annealing temperature was $1\ 100^\circ\text{C}$. The thermostat was 10 h, and the cooling rate was $1\text{--}20^\circ\text{C}/\text{h}$. Fig. 1 shows the CaF_2 - BaF_2 mixed

crystals in two different ratios with the size of $\phi 20$ mm in diameter and 180 mm in length.

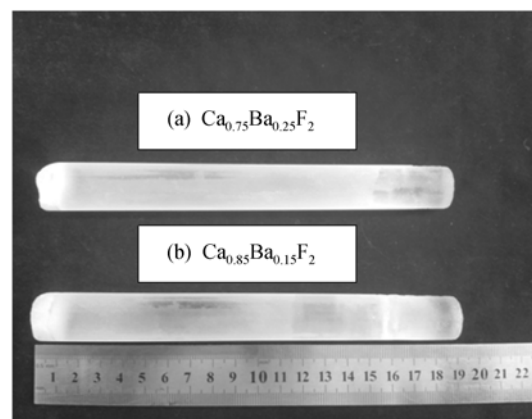


Fig. 1 CaF_2 - BaF_2 mixed crystals

2.3 Characterization

The structure of the as-grown crystal was determined by a mode D/max-Ultima IV X-ray diffractometer (Science Co., Ltd., Japan) ($\text{Cu K}\alpha_1$ radiation; curved graphite crystal monochromatic filter; the operating voltage was 40 kV; operating current was 20 mA; scan rate was $4^\circ/\text{min}$; the step length was 0.06°). The transmittance curve of the two CaF_2 - BaF_2 mixed crystals were measured by a model IRprestige-21 Fourier transform spectrometer (Shimadzu Co., Ltd., Japan). The birefringence of two CaF_2 - BaF_2 mixed crystals and CaF_2 single crystal were measured by a mode ABR-10A automatic birefringence measurement system.

3 Results and discussion

3.1 Crystal ratio of raw materials

According to Burnett, *et al.*,^[10] the double refractive index and wavelength of the CaF_2 and BaF_2 can be expressed by:

$$\Delta n = (n_{<-110>} - n_{<001>}) \quad (1)$$

where Δn is the intrinsic birefringence of CaF_2 and BaF_2 crystal; $n_{<-110>}$ is the double refractive index of the $<-110>$ direction and $n_{<001>}$ is the double refractive index of the $<001>$ direction.

In order to reduce the refractive index, x in $\text{Ca}_{1-x}\text{Ba}_x\text{F}_2$ mixed crystal is

$$x \approx |\Delta n_{\text{CaF}_2} / (\Delta n_{\text{CaF}_2} - \Delta n_{\text{BaF}_2})| \quad (2)$$

where Δn_{CaF_2} is the intrinsic birefringence of CaF_2 crystal and Δn_{BaF_2} is the intrinsic birefringence of BaF_2 crystal.

According to the intrinsic birefringence data of CaF_2 and BaF_2 , $\text{Ca}_{1-x}\text{Ba}_x\text{F}_2$ ratio of raw materials were determined when $x = 0.25$ or 0.15 . As a result, the corresponding mixed crystal at 193 nm is $\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$, and the corresponding mixed crystal at 157 nm is $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$.

Some raw materials for the preparation of a fluoride

crystal usually contain moisture and may result in some growth defects and opaque appearance of the crystal. When the crystals were grown at $>800\text{ }^{\circ}\text{C}$, fluoride reacted with water to form a refractory oxide or sulfide, and the large crystal defects were generated during the crystal growth, which affects the crystal quality.^[11] The polycrystalline material was prepared by the direct precipitation method in this work. By changing the composition of the polycrystalline material, we could obtain the polycrystalline material with the homogeneous phase structure and high purity. The purity of polycrystalline material could be further improved *via* deoxidation and fluorination treatment of reducing the impurities.

3.2 XRD analysis

Fig. 2 shows the XRD spectra of CaF_2 - BaF_2 mixed crystals. Compared to the standard card of CaF_2 and BaF_2 single crystals, the diffraction peak position and intensity of as-grown CaF_2 - BaF_2 mixed crystals are similar as those of the CaF_2 and BaF_2 crystals. Therefore, the mixed crystals obtained can be determined as CaF_2 - BaF_2 mixed crystal.

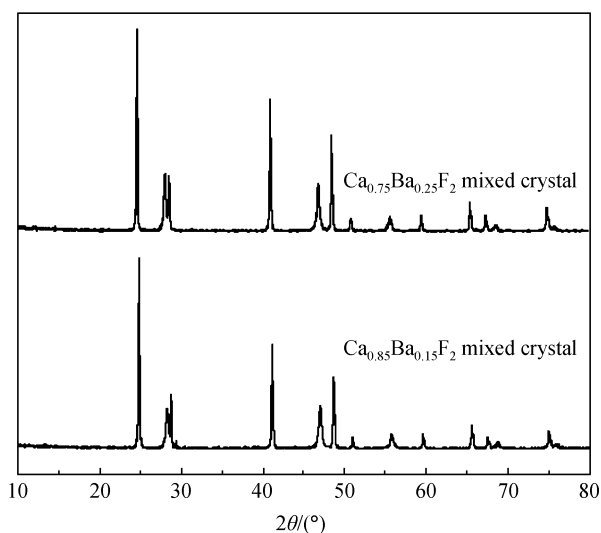


Fig. 2 XRD spectra of $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$ and $\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$ mixed crystal

3.3 Crystal transmission

Fig. 3 shows the transmittances of $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$ and $\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$. In the range of $400\text{--}4\,000\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$), the transmittances of $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$ and $\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$ mixed crystals are both 70%–80%. There is a clear absorption peak at $2\,500\text{ cm}^{-1}$, which could be caused by CO_2 . In the preparation process of polycrystalline materials, the presence of CO_3^{2-} was introduced by BaCO_3 , and then the CO_3^{2-} could generate CO_2 when the polycrystalline materials were heated during the crystal growth. In addition, there was also a small amount of CO_2 from the atmosphere, causing the infrared absorption. A high vacuum charge protective atmosphere can reduce the defects

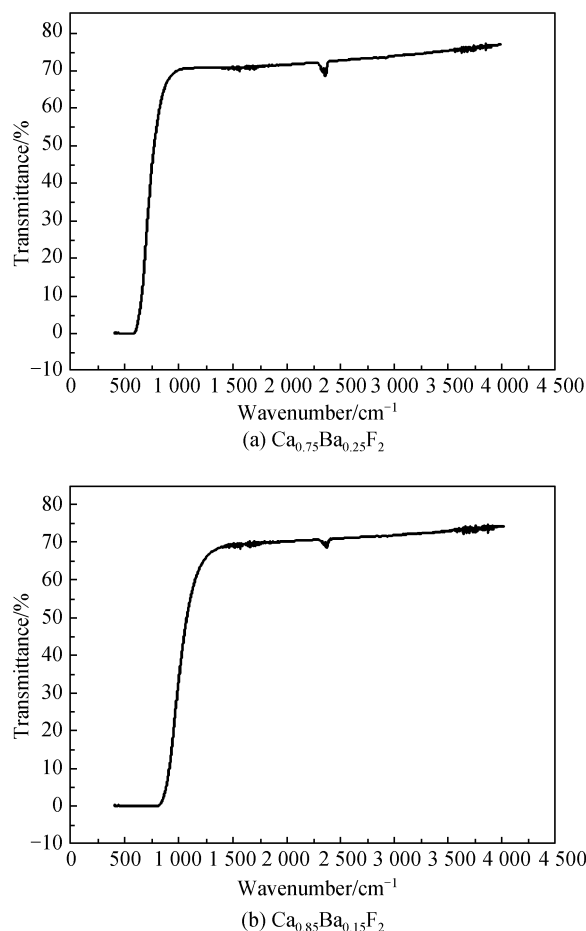


Fig. 3 Transmission curves of CaF_2 - BaF_2 mixed crystals

of the mixed crystal and improve its quality. Also, the transmittance of the mixed crystal could be further improved by the chemical polishing, coating film and other high-precision processing technologies.

3.4 Intrinsic birefringence of the crystal

Table 1 shows the birefringence data of $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$ at 157 nm, $\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$ at 193 nm and CaF_2 . It is seen that the birefringence of CaF_2 - BaF_2 mixed crystals is slightly smaller than that of CaF_2 single crystal due to their similar physical and chemical properties. In the mixed crystal, Ba^{2+} replaces Ca^{2+} in random, leading to a certain degree of distortion of the mixed crystal lattice. The refractive index of CaF_2 and BaF_2 crystals correspond to each other and have the opposite sign,^[9–10] the intrinsic birefringence is reduced due to the compensation effect.

Table 1 Intrinsic birefringence of CaF_2 and CaF_2 - BaF_2 mixed crystals

Crystal	Intrinsic birefringence/(nm·cm ⁻¹)	
	193 nm	157 nm
CaF_2	3.5	11.5
$\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$		10.7
$\text{Ca}_{0.85}\text{Ba}_{0.15}\text{F}_2$	2.8	

4 Conclusions

The polycrystalline materials of $\text{CaF}_2\text{-BaF}_2$ with the high purity and homogeneous phase structure were prepared by a direct precipitation method. The crystal quality could be improved effectively *via* the removal of moisture and impurities in the crystal growth process and control of temperature.

The $\text{CaF}_2\text{-BaF}_2$ mixed crystal with the size of $\phi 20$ mm in diameter and 180 mm in length were obtained by the Bridgman method. The crystal materials are $\text{CaF}_2\text{-BaF}_2$ mixed crystal phase. The raw material composition of CaF_2 and BaF_2 , the proportion of ingredients as well as the process parameters were optimized to improve the optical quality of the mixed crystal materials. The birefringence of the $\text{CaF}_2\text{-BaF}_2$ mixed crystal was less than that of CaF_2 single crystal. For the deep ultraviolet lithography system, $\text{CaF}_2\text{-BaF}_2$ mixed crystals are promising optical materials to improve the resolution of lithography system, and have some application prospects.

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