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# The Surface Morphology and Photoluminescence Properties of ZnO Crystals Synthesized by Flux Method

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**Abstract:** Transparent pale yellow ZnO crystals with different hexagonal morphology, such as hexagonal caps and hexagonal lamellae, have been successfully synthesized in molten hydrous NaOH-LiOH. The phase structure of the as-grown crystals was investigated by means of X-ray powder diffraction. Detailed surface morphology of the crystals was studied using optical microscopy and scanning electron microscopy. Elemental analysis of the synthesized crystals was performed using energy dispersive X-ray spectrum. The photoluminescence spectrum was employed to characterize the obtained crystals. Some ultraviolet, blue, green and red emission peaks were observed in the photoluminescence spectrum.

**Key words:** ZnO; NaOH-LiOH; surface morphology; crystal; photoluminescence

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## 混合碱液法生长的氧化锌晶体表面形貌及光致发光性质

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**摘要:** 从 NaOH 和 LiOH 的混合碱液中生长了具有不同六方形貌的淡黄色 ZnO 晶体。采用 X 射线粉末衍射的方法对晶体的物相进行了分析, 利用光学显微镜和扫描电镜对晶体的形貌进行了表征, 同时利用电子探针能谱仪对晶体的组分进行了分析。从晶体的室温光致发光谱图中可以观测到 380, 445, 512, 652 nm 处存在与晶体结构和缺陷相关的发射峰。

**关键词:** ZnO; NaOH-LiOH; 表面形貌; 晶体; 光致发光

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## 1 Introduction

Zinc oxide (ZnO) has a wurtzite crystal structure and belongs to the  $P63mc$  space group. Recently, a great deal attention has been paid to ZnO due to the widely application, including phosphors, ferrites, varistors, surface elastic wave filters, ammonia gas sensors, semiconductors, luminescent materials and ferromagnets<sup>[1-2]</sup>. ZnO single crystals have been successfully synthesized by many methods such as the hydrothermal method<sup>[3-6]</sup>, the chemical vapor transport method<sup>[7-8]</sup>, the flux method<sup>[9]</sup>, etc.

In the present work, we report on the structural, morphological and optical properties of transparent pale yellow ZnO crystals that were prepared from molten hydrous NaOH-LiOH using the flux method. The advantages of this growth method include low growth temperature, less growth time and low-cost equipment.

## 2 Experiments

Transparent pale yellow ZnO crystals, with hexagonal capped and hexagonal lamellar morphology, were successfully grown by the spontaneous nucleation method in molten hydrous NaOH-LiOH. Crystal growth was carried out in a resistance box furnace. The furnace temperature was controlled by an FP23 controller. The preparation procedure consists of the following steps: (1) solid NaOH, solid LiOH, ZnO powder and deionized water in a molar ratio of 10:1:2:13 were sequentially put into a silver crucible. Both the NaOH and the LiOH were guaranteed grade reagents, and the ZnO was an analytical grade reagent. (2) The mixture, along with the silver crucible, was placed in an alumina crucible, which was then put into the furnace. (3) The mixture was heated to 713 K and held at this temperature for 34 h. After heating, the melt was allowed to cool down to room temperature naturally. The resulting pale yellow ZnO crystals were extracted by dissolving the flux away in water.

X-ray powder diffraction (XRD) was used to determine the phase structure of the as-grown crystals. The detailed surface morphology of the synthe-

sized crystals was investigated by means of optical microscopy and scanning electron microscopy. The chemical composition and photoluminescence properties of the obtained crystals were determined by using energy dispersion spectroscopy and photoluminescence spectrum measurements, respectively.

## 3 Results and Discussion

### 3.1 The Phase Structure of As-grown Crystals

X-ray powder diffraction was used to characterize the phase structure of the as-grown ZnO crystals at room temperature. The XRD data were recorded on a Japan Bruker model D8/advance X-ray diffractometer system with graphite-monochromatized Cu  $K\alpha$  radiation ( $\lambda = 0.15418$  nm), using a diffractometer scan step size of  $2\theta = 0.02^\circ$ , and dwell time of 1 s/step, over a  $2\theta$  range of  $10^\circ \sim 80^\circ$ .

Fig. 1 shows the XRD patterns of the ZnO crystals synthesized in molten hydrous NaOH-LiOH under ambient pressure. X-ray analysis indicates that all the peaks can be indexed to the standard JCPDS Card File 36-1451 for wurtzite ZnO. No additional peaks were found, which means that the as-grown crystals are well crystallized in the wurtzite structure. In Fig. 1, the relative intensity of the peaks corresponding to the (100), (002), (101), (110) and (103) planes was different for the hexagonal lamellar and the hexagonal capped crystals. The crystal growth environment was different at different places in the growth system. This variation affects the relative growth rate of these planes, which in

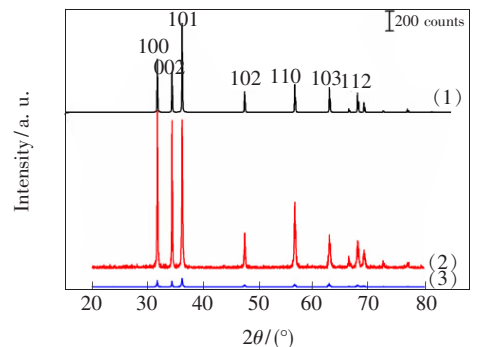


Fig. 1 X-ray powder diffraction pattern of transparent pale yellow ZnO crystals, (1) standard XRD card of single crystal ZnO, (2) hexagonal lamellar crystals, and (3) hexagonal capped crystals.

turn leads to a variation in the crystal morphology. This supposition can be proved by the different relative intensities of the X-ray powder diffraction peaks<sup>[10]</sup>.

### 3.2 Surface Morphology and Composition of Hexagonal Capped Crystals

The detailed surface morphology of the hexagonal capped ZnO crystals was investigated by using optical microscopy and scanning electron microscopy. Fig. 2 showed the optical microscopy images of the hexagonal capped crystals. From these images, conspicuous striations along certain directions and curved growth-sector boundaries were observed on the crystal surfaces. Fluctuations in the crystal growth system, such as variations of temperature and melt convection, can lead to temporary changes in growth rate, and thus affect the whole growth front, forming inhomogeneous layers parallel to the interface. Since the inhomogeneous layers appear in a quasi-periodic sequence, the striations exhibit a quasi-periodic structure. The growth-sector boundary is curved due to the fluctuating relative growth rate of two neighboring faces as the crystal grows.

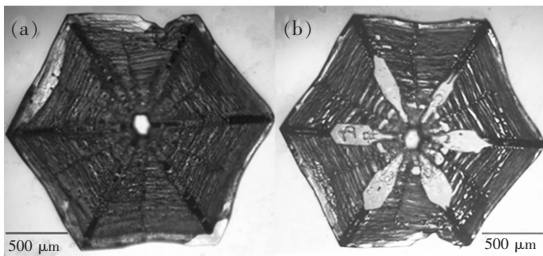


Fig. 2 Optical images of the as-grown hexagonal capped ZnO crystals observed from different directions

To investigate the surface morphology of the hexagonal capped crystals in detail, a scanning electron microscopy was employed. From Fig. 3, it can be seen that there were some regular hexagonal pits around the edges of the capped crystals. The quasi-periodic boundaries can also be clearly observed. The energy dispersion spectroscopy data acquired by the scanning electron microscopy from the hexagonal capped crystal surface is shown in Fig. 4. It revealed that the crystal surface contains four different elements: zinc, oxygen, aluminum and sodium. The effect of aluminum shedding on the morphological

and structural properties of the crystal can be neglected due to its low frequency of occurrence. Pure ZnO crystals should be colorless, but the as-grown crystals were pale yellow. This abnormal coloration may be caused by the presence of sodium in the growth system.

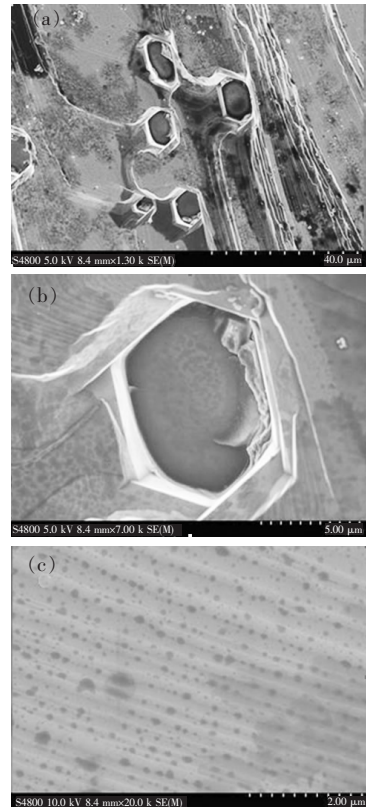


Fig. 3 Scanning electron microscopy images of detailed surface morphology of the hexagonal capped crystals

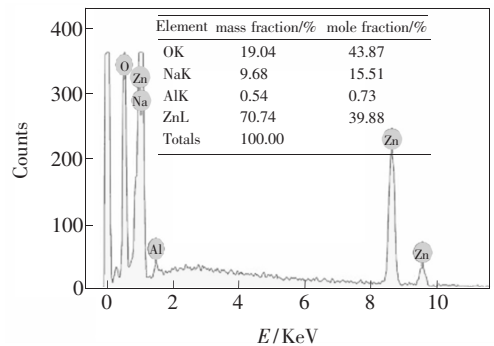


Fig. 4 Energy dispersive X-ray spectrum of the as-grown hexagonal capped ZnO crystals

### 3.3 Surface Morphology and Composition of Hexagonal Lamellar Crystals

Fig. 5 showed the optical microscopy images of the obtained hexagonal lamellar crystals at different times magnification. The detailed surface morphology

of the hexagonal lamellar crystals was investigated by utilizing optical microscopy and scanning electron microscopy at different degrees of magnification. Fig. 5 shows the detailed surface morphology of the hexagonal lamellar ZnO crystals. There are some hexagonal pits

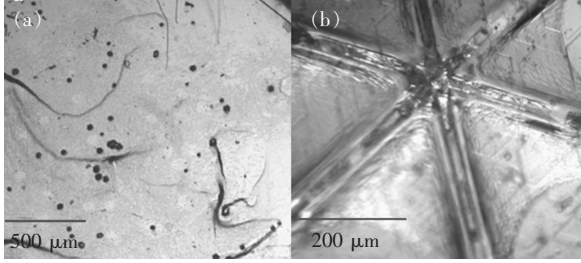


Fig. 5 Optical microscopy images of the obtained hexagonal lamellar crystals at different times magnification

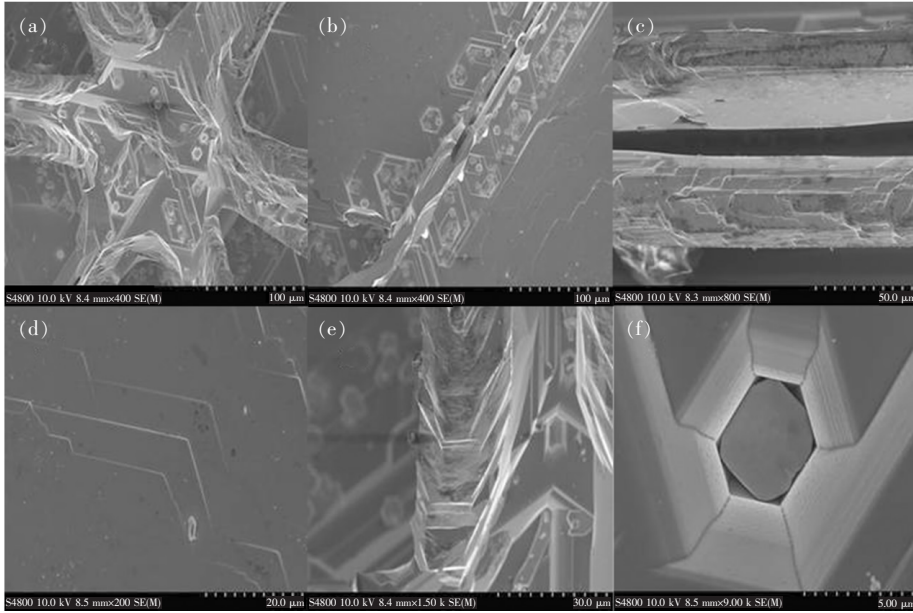


Fig. 6 Scanning electron microscopy images of hexagonal lamellar ZnO crystals of different regions of hexagonal lamellar crystals at different magnification

The energy dispersion spectroscopy was used to determine the chemical composition of the as-grown hexagonal lamellar crystals. The results are shown in Fig. 7. From this figure, it can be seen that the surface chemical composition of the hexagonal lamellar crystals is the same as that of the hexagonal capped crystals. However, the relative elemental content in the hexagonal capped crystals and the hexagonal lamellar crystals is different. The reason may be that the nucleation and growth positions of the two different morphological ZnO crystal types were different in

on the surface of the lamellar crystals, just as observed on the surface of the hexagonal capped crystals. Six quasi-straight growth boundaries are also found on the surface.

From the scanning electron microscopy images shown in Fig. 6, it is apparent that these boundaries are composed of hexagonally symmetric pits, different growth layer thicknesses and narrow crevices. There were solid inclusions in the hexagonally symmetric pits. Due to the fluctuation of the relative growth rate at the neighboring faces of these pits, curved growth boundaries were formed within them. Moreover, some growth striations were found near the narrow crevices (Fig. 6(c)).

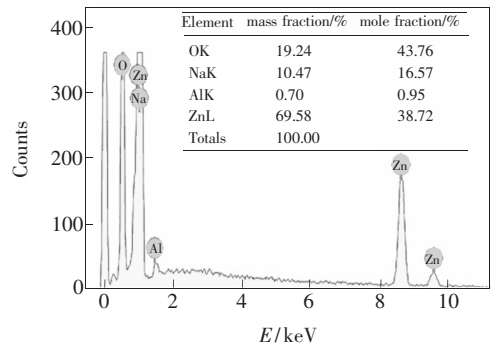


Fig. 7 Energy dispersive X-ray spectrum of the hexagonal lamellar ZnO crystals

the growth system.

### 3.4 The Photoluminescence Property of Synthesized Crystals

Fig. 8 showed the room-temperature photoluminescence spectra of the ZnO crystals grown from molten hydrous NaOH and LiOH, and excited by radiation at a wavelength of 325 nm. Both the hexagonal capped and lamellar crystals show strong UV (380 nm), and weak blue (445 nm) and red emissions (652 nm). The hexagonal capped crystals also show a weak green emission (514 nm). The UV emission, which is centered at about 380 nm, originates from excitonic combination corresponding to the band-edge emission of ZnO<sup>[11-13]</sup>. The blue emission at 445 nm can be attributed to the  $O_i$  transition between defects at the grain boundaries and the valence band, and lattice defects related to oxygen and  $V_{Zn}$ <sup>[14-15]</sup>. The green luminescence peak centered

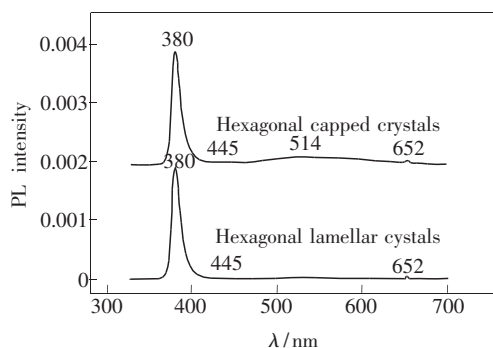


Fig. 8 Photoluminescence spectra of the obtained crystals grown from molten hydrous NaOH and LiOH with different morphology

at about 514 nm may be resulted from singly ionized oxygen vacancy in ZnO, donor-acceptor complexes, anti-site oxygen and surface states<sup>[11,15-18]</sup>. The weak red emission peak at about 652 nm may be related to intrinsic defects in  $O_i$ , defects that form deep energy levels in the band gap<sup>[15]</sup>.

## 4 Conclusion

Transparent pale yellow ZnO crystals of hexagonal capped and hexagonal lamellar morphology were successfully synthesized in molten hydrous NaOH-LiOH under atmospheric pressure. X-ray powder diffraction was used to confirm the phase structure of the obtained crystals. The results indicate that the as-grown crystals are well-crystallized wurtzite ZnO. Both the detailed surface morphology and chemical composition of the synthesized crystals were investigated by means of optical microscopy, scanning electron microscopy and energy dispersion spectroscopy. Some defects were evident, such as growth striations and growth pits that are present on the surface of the as-grown crystals. The morphology of the crystals grown in the same growth system varies as a result of different nucleation location and growth position in the growth system. The photoluminescence spectrum was used to characterize the as-grown ZnO crystals. There are some emission peaks between 380 nm to 652 nm (ultraviolet to red emission) observed in the photoluminescence spectrum.

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