Heterogeneous growth of KDP/KT crystal*

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The growth of heterogeneous crystal has aroused a great deal of interest in recent years. In this study, KH_2PO_4 (KDP)/$KTaO_3$ (KT) heterogeneous crystal is acquired based on the KT substrate. Here, we report the observation of the oriented layer-by-layer structure in KDP/KT composite crystal by scanning electron microscopy (SEM). The structure of KDP/KT composite crystal is accurately identified by transmission electron microscopy (TEM) for the first time and we find that the KT crystals dope into KDP crystal in the growth process with the mode of doping. It can be obtained from the analysis of crystal structure that the structure difference leads to the doping growth mode. Our research demonstrates a facile method to fabricate a composite nonlinear optical crystal based on KDP/KT heterostructure, and might shed light on potential applications of the composite nonlinear optical crystal.

Keywords: KDP, KT, heterostructure, nonlinear optical materials

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1. Introduction

The KDP crystal is an irreplaceable multiplier material suitable for nonlinear optical switches, large-aperture high-power lasers, and frequency conversion in inertial confinement fusion (ICF) due to its adequate electro-optical coefficient and convenience in growing to as large as centimeter dimensions.[1–4] One of the most challenging tasks on KDP materials is the growth control since we can hardly study the exact mechanism of the growth process. It is expected that the atomic structure at the crystal-solution interface plays a primary role in the composition, growth, and morphology of the crystal due to the growth of crystal occurring at this boundary.[5] The surface/interface structure of KDP crystal has a significant influence on the growth of crystal and the formation of defects. A power-law growth model of KDP crystal, with the activity-based driving force used, has been put forward. Computational fluid dynamics (CFD) was used to evaluate the thickness of a diffusion layer around the crystal.[6] A combination of CFD and multiblock model was applied to modelling KDP crystal growth in the suspension crystallizer. The CFD simulations were translated to a proper form and used as input data for the multiblock model.[7]

Nowadays heterojunction crystal growth has presented its potential and become the focus of attention in crystal growth study. However, heterojunction crystal growth usually brings the problems of lattice mismatch and substrate constraint. The lattice mismatch usually appears in semiconductor material, which results from the two materials with different lattice constants. Woodall *et al.* have studied the electrical behavior of GaInAs/GaAs dislocation system.[8] Sharma *et al.* have grown InP epilayer on InSb substrate and studied the electrical transport in the heterostructure.[9] Li *et al.* have demonstrated that the difference between light emitting diodes (LEDs) is due to the difference in quality between MgZnO and ZnO layers grown on different lattice mismatch substrates.[10] The GaN/InGaN materials grown on sapphire substrates, Si substrates and SiC substrates have been extensively studied. Wang J X *et al.* have used the α-plane InGaN interlayer to improve the property of α-plane GaN grown on sapphire substrates.[11] Liu *et al.* have prepared GaN/InGaN multiple quantum wells on Si substrates and investigated the influences of stress on the properties.[12] Nishikawa *et al.* have studied the current-voltage characteristics of InGaN/GaN vertical conducting diodes grown on SiC substrates.[13] In the present work, KT is used as the seed crystal for growing KDP crystal. We focus on the study of the lattice mismatch in the KDP/KT heterojunction.

In this work, an intriguing KDP/KT composite crystal is investigated. The morphology of KDP crystal is found to be dependent on KT seed crystal. For the difficulty resulting from the structural instability of KDP under a high-energy electron beam of microscope, few studies on electron microscopy imaging have been reported. In our previous work, laser irradiation precipitation of nonlinear optical KDP crystal has been reported.[14] For the first time, transmission electron microscopy evidence illustrating the KDP/KT heterojunction is

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presented. Our work provides a novel entry point for preparing the KDP/KT heterojunction crystal.

2. Experiment

Phosphoric acid (85% H_3PO_4, GR purity) and KOH (GR purity) were used to adjust the pH value of KDP solution. A Mettler pH meter (FE20K, resolution factor 0.01 pH) was used to measure the pH value of KDP solutions at 60 °C. The growth solution was made from KH_2PO_4 (purchased from Beijing Yili Fine Chemicals Co., Ltd., AR purity) and deionized water. Impurity particles were first filtered by filter paper, then removed by filter membranes with pore sizes of 0.45 μm and 0.22 μm, respectively. Growth experiments were carried out in a temperature-controlled (the constant temperature water bath control) standard 1000-ml jar. The saturation temperature was around 51 °C and KDP solution was heated to 80 °C for 24 h to improve the stability of the solution. The seed crystal was a Z-cut cube KT crystal of 4 mm×4 mm×4 mm. The KT seed crystal is purchased from the New Material Institute of Shandong Academy of Science, China. With the pH value of KDP supersaturated solution being 4.5, the KT seed crystal is immersed into the supersaturated solution to grow KDP/KT composite crystal.

Field emission scanning electron microscopy (FESEM, Hitachi S-4800) operated at 1.0 kV was performed to record KDP/KT composite crystal. TEM analysis was carried out on JEM-2100F (JEOL, 200 kV) field emission transmission electron microscopy equipped with a Gatan Ultrascan CCD camera. For TEM measurement, the KDP/KT composite sample was ground in ethanol, then a drop of the mixed solution was placed on an ultra-thin carbon-coated copper grid.

3. Results and discussion

As the pH value of KDP supersaturated solution is 4.5, the integral structure of KDP crystal is obtained (Fig. 1(a)). There are some defects on the surface of KDP crystal. The ions in the original KDP solution continues to migrate to repair the surface defects of KDP crystal, furthermore, to form into an oriented layer structure.

The corner section of the KDP crystal is first repaired and a continuous layer is formed compared with the intermediate section, which is related to the constant migration of KDP solution, indicating that the corner section is beneficial to nucleation. The connected layers have an alignment structure (Fig. 1(b)).

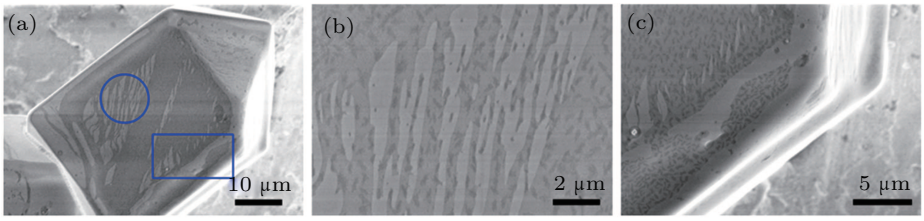


Fig. 1. (color online) (a) SEM image of KDP/KT composite crystal (KT is the seed crystal, growth time is 2 h and pH value of KDP supersaturated solution is 4.5). (b) and (c) Details of the magnified fixed circle area and rectangle area of panel (a), respectively.

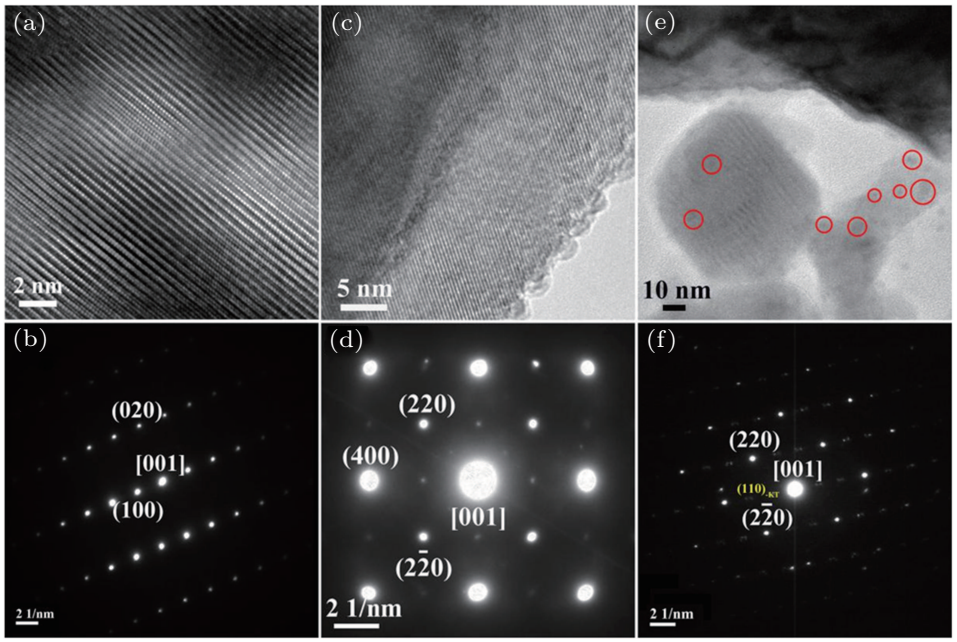


Fig. 2. (color online) (a) and (b) TEM image and electron diffraction pattern of KT crystal, (c) and (d) TEM image and electron diffraction pattern of KDP crystal, and (e) and (f) TEM image and electron diffraction pattern of KDP/KT composite crystal (substrate is KT). The dispersive black dots marked by red circles are KT crystals.

To accurately identify the structure of KDP/KT composite crystal, TEM analysis is carried out for the first time (as shown in Fig. 2). Figures 2(a) and 2(c) show the typical high-resolution TEM images of KT and KDP crystal obtained along the [001] zone axis, respectively. Figure 2(e) shows the TEM image of KDP/KT composite crystal in which the layers are KDP crystals and the black dots (marked as red circle) are KT crystals. The corresponding selected-area electron diffraction (SAED) patterns are acquired from KT crystal, KDP crystal and KDP/KT composite crystal, respectively (shown in Figs. 2(b), 2(d), and 2(f)). Figure 2(f) shows a typical SAED pattern of KDP crystal with some regular weak diffraction spots of KT crystal, indicating that a few KT crystals have been doped into KDP crystal. From these SAED patterns, it can be presumed that the KDP/KT composite crystal is successfully obtained and the compound mode is doping.

Figure 3 shows the crystal structure models of KDP and KT. The KT crystal is of a typical cubic structure consisting of an oxygen octahedron and a K ion, meanwhile a Ta ion is located in the center of the oxygen octahedron and a K ion is surrounded by eight oxygen octahedron (Fig. 3(a)). While a KDP cell consists of four phosphorus oxygen tetrahedrons, four potassium atoms, and eight hydrogen atoms (shown in Fig. 3(b). The difference between two crystal structures with a large mismatch degree of 30.15% leads to a consequence that the KDP crystal growth mode is a new growth pattern, namely the doping mode, instead of the traditional epitaxial growth.

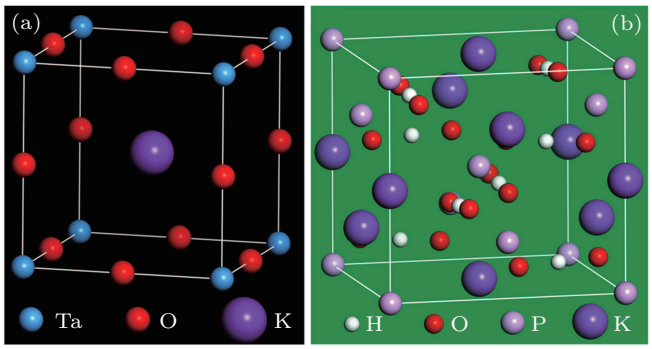


Fig. 3. (color online) Crystal structure models of (a) KT and (b) KDP.

4. Conclusions and perspectives

In this work, we successfully develop a KDP/KT heterojunction with layer-by-layer structure by means of the aqueous solution method with KT crystal serving as the seed crystal. In the process of crystal growth, the ions in the original KDP solution continue to migrate first to repair the surface defects of KDP crystal and then to form into an oriented layer structure. The structure of the obtained KDP/KT heterojunction consisting KDP crystal doped with KT crystal is analyzed by TEM for the first time. It can be obtained from the difference of crystal structure that a large mismatch degree of 30.15% leads to the doping growth mode, indicating the difference between the two crystal structures plays an important role in the composite crystal growth process. This might be conducive to the improvement of the composite crystal growth and the potential applications of the composite nonlinear optical crystal.

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