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Growth, characterization and the fourth harmonic generation at 266 nm of $K_2Al_2B_2O_7$ crystals without UV absorptions and Na impurity

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ABSTRACT

We utilize a combined technology to grow relatively pure $K_2Al_2B_2O_7$ crystals without sodium and UV absorptions aroused by Fe^{3+} ions. It is found that under reducing atmosphere, iron impurities can no longer substitute into the Al^{3+} sites in the crystal lattice. Thus, the as-grown crystals are free from the abnormal UV absorption from 200 nm to 300 nm. At the same time, KF flux prevents the inclusion of sodium into the crystal contrasted with the generally used NaF flux. Lattice parameters of the as-grown crystals were refined by powder X-ray diffraction and compared with those grown from NaF flux. Based on the measured refractive indices, new Sellmeier equations were derived from refractive index dispersion curves. Finally, FHG experiment of a QCW Nd:YAG laser at 266 nm demonstrated an output power of 440 mW, which is the highest record achieved in KABO crystal so far.

1. Introduction

Generation of ultraviolet (UV) and deep UV coherent lights with regard to their promising applications in high-resolution spectroscopy, semiconductor photolithography and modern laser processing is of increasing importance [1–3]. Up to now, frequency conversion by using nonlinear optical (NLO) crystals is the only way to extend the discrete IR and visible solid-state lasers into the UV region. Thereby, searching for new efficient NLO crystals in the UV region has attracted more and more attentions since the appearance of the first high-performance NLO borate crystal, the low-temperature phase of BaB_2O_4 (BBO) [4]. Subsequently, another famous borate NLO crystal LiB_3O_5 (LBO) [5] was discovered and both of them demonstrated superior properties to satisfy the practical frequency conversion requirements from the visible to near UV regions. However, crystals available for the deep UV coherent lights are still lacking due to the inappeasable prerequisites both on the absorption edge and phase matching conditions. Take the fourth harmonic generation (FHG) of Nd-based lasers for example, promising candidates are limited to the following several crystals: $K_2Al_2B_2O_7$ (KABO) [6,7], $KBe_2BO_3F_2$ (KBBF) [8], $RbBe_2BO_3F_2$ (RBBF) [9], $CsLiB_6O_{10}$ (CLBO) [10], and $YAl_3(BO_3)_4$ (YAB) [11]. All of them suffer from respective shortcomings such as the growth difficulty (KBBF, RBBF, YAB), toxicity during growth (KBBF, RBBF), intrinsic hygroscopic (CLBO) and unfavorable absorption in the UV range (KABO, YAB). Thus, continuous efforts are needed to improve the above crystals for practical FHG applications.

KABO as a new NLO crystal was firstly reported in 1998 [6,7]. It was considered capable of producing FHG of Nd-based lasers at 266 nm due to its moderate birefringence and good NLO properties. However, there are two main inherent disadvantages of KABO crystal preventing its applications in high power UV light generations. Firstly, the commonly used NaF flux will bring in considerable Na^+ ions substituting K^+ positions into the crystal lattice. This may result in several potential disadvantages, *e.g.* low optical homogeneity and instability of the crystal structure, in view of some formerly reported demonstrations [12,13]. Secondly, the abnormal absorptions arising in the 200–300 nm region reduce the conversion efficiency seriously. Much effort has been made to probe into the origin of these UV absorptions and recently Liu et al. presumed that the Fe^{3+} ion substituting Al^{3+} into the lattice caused the absorption [14]. This viewpoint was supported by the succeeding *d–d* transition spectral studies of high concentration Fe-doped KABO crystals [15]. Based on the crystal chemistry intuition, one of the present authors (Li) proposed that when the Fe^{3+} ion in the melt can be reduced into lower valence, *e.g.* Fe^{2+}, which may be prevented from entering the grown crystal due to both effects of the differences in ionic radii and valences of Fe^{2+} from Al^{3+} ion. Preliminary growing tests based on this idea gave encouraging results with the obtained crystal showing greatly reduced UV absorption [14,16].

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In this paper, we report on the recent progress of KF-based flux growth of pure KABO crystal without UV absorption. Bulk KABO crystals without Na impurities and UV absorptions were grown successfully from the optimized KF-based flux under reducing atmosphere. Characterizations of the as-grown crystals were performed contrastively with those grown from NaF flux. FHG performance shows that the as-grown KABO crystals with neither Na-doping nor UV absorption are promising for the frequency conversion applications in UV region.

2. Experiments

2.1. Crystal growth

KABO crystal used in the experiments was grown by the typical top-seeded solution growth (TSSG) technique. The starting materials, analytically pure KF, Al_2O_3, H_3BO_3 and prefabricated KABO polycrystalline powders, were mixed homogeneously in certain proportions. The charge was heated in a Pt crucible in a resistive heating vacuum furnace filled with protecting gases. The temperature of the furnace was gradually raised up to 850 °C and kept at that temperature for 24 h. It was then cooled down to 810 °C around the saturation temperature which was confirmed by testing crystals. The temperature lowering rate during the crystal growth process was 0.1–0.2 °C/day and the rotating speed was 15–20 r/min. After growing for about two weeks, bulk KABO crystals with largest dimensions of $35 \times 25 \times 10\ mm^3$ were obtained successfully (Fig. 1a). Avoidance of the Fe^{3+} UV absorption was achieved by maintaining reducing atmosphere ($10\%H_2/90\%N_2$) throughout the growth period.

2.2. Crystal characterization

The Na and Fe contents in KABO crystals were determined by ICP-AES (Varian 710-ES, US). The UV transmittance spectrum from 120 nm to 380 nm of the crystal was measured on a McPherson VUVas2000 spectrophotometer. For powder X-ray diffraction measurements, data was collected at room temperature (25 °C) on a Bruker D8 Advance diffractometer in a transmission mode, using a curved germanium primary monochromatic Cu $K\alpha_1$ radiation (λ=1.54059 Å). The sample was supported by Mylar film, and the data in the 2θ range of 10–120° were collected in a step of 0.0197° with the remaining time 40 s per step under the tube conditions 40 kV and 40 mV.

The refractive indices dispersion of KABO crystal was determined by the minimum-deviation method at different 13 wavelengths between 253.7 and 2325 nm. The measurements were performed on SpectroMaster UV–vis–IR (Trioptics, Germany) at room temperature (about 21 °C). For the FHG experiments, the light source was a high-power Nd:YAG laser (Edgewave IS161-E) with a repetition rate of 10 KHz and pulse duration 10 ns.

3. Results and discussion

The KABO crystal grown from KF-based flux is shown in Fig. 1a. It is recognized that both the volatility and viscosity of KF are higher than the widely used NaF flux [17]. Nevertheless, considering the ionic radius of Na^+ ion is close to that of K^+ ion, substitution of Na^+ ions into the K^+ sites seems unavoidable, which may influence the stability and optical uniformity of the crystal [12,13]. The ICP-AES measurement result confirms that there is as much as 13.6% molar ratio K is replaced by Na in a KABO crystal grown from NaF flux. Contrastively, an optimized $KF–Al_2O_3–B_2O_3$ flux system is free from this problem and the volatility and viscosity can be controlled with appropriate proportions. The powder X-ray diffraction patterns of KABO crystals from both NaF and KF-based flux are shown in Fig. 2. The substitution of K^+ ions by Na^+ ions in the same crystal sites will lead to the decrease of the cell dimensions due to the smaller ionic radius of Na^+ ion, which can be clearly seen from the Bragg peak position shifts towards larger 2θ angles in the X-ray diffraction patterns (Fig. 2, inset). The refinement results via the least-squares method are as follows: crystals grown from NaF

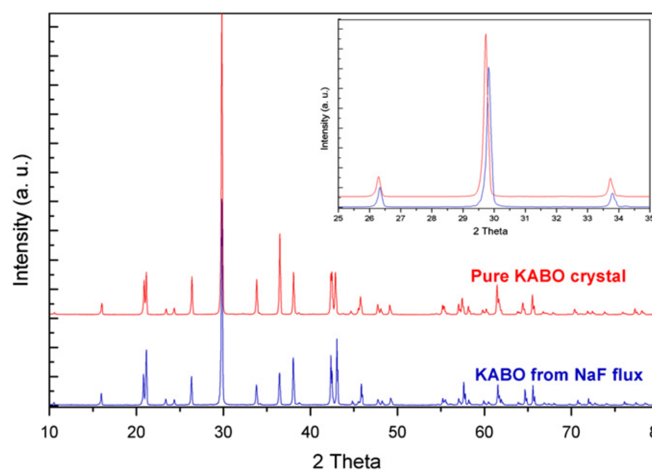

Fig. 2. Powder X-ray diffraction patterns for KABO crystals grown from KF based flux and NaF flux. Insert shows the peak shift between 25° and 35°.

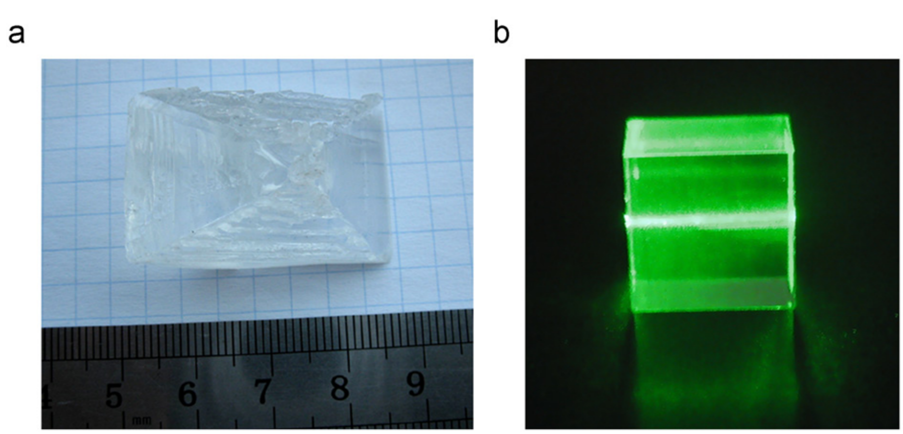

Fig. 1. Photograph of KABO crystals grown from KF-based flux (a) and the scattering pathway under 532 nm lasers (b).