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Characterization of ⟨0 1 0⟩ directed KAP single crystals grown by Sankaranarayanan–Ramasamy (SR) method

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ABSTRACT

Single crystals of potassium acid phthalate (KAP), a semi-organic compound, have been grown at an average growth rate of 4 mm/day from aqueous solution by using the uniaxial crystal growth method of Sankaranarayanan–Ramasamy (SR). Transparent, cylindrical KAP crystal of size 70 mm length and 15 mm diameter was grown. The grown crystals were characterized by etching and UV–vis NIR analysis. HRXRD analysis indicates that the crystalline perfection of SR method-grown KAP is good. The KAP crystals grown by SR method have 9% higher transmittance than conventional method-grown crystal. The microhardness test was carried out on the (0 1 0) face and a load-dependent hardness was observed. TG–DTA evaluated the thermal properties of the grown crystal. KAP was found to be thermally stable up to 290 °C. The dielectric constant and dielectric loss of the crystal were studied as function of frequency and temperature.

1. Introduction

Potassium acid phthalate ($K(C_6H_4COOHCOO)$) crystal is a promising material for the qualitative and quantitative X-ray analysis of light elements like Al, Mg, Si, etc., in a long- and middle-range spectral area. It is also a good monochromator [1,2]. Its cleavage faces find applications as substrates for the growth of highly orientated film of conjugated polymers with high non-linear optical susceptibility with non-hygroscopic nature. Recently, KAP crystals have assumed an important role in the epitaxial growth of orientated poly DCH, a conjugated polymer that shows a very large ($\chi^{(3)} = 10^{-1}$ esu) and fast NLO susceptibility [2]. Effects of hydrogen bonds on optical non-linearities of complex crystals have been studied [3–6]. The conventional solution-grown crystals have different planes and facets. The phase matchable portion is only useful for applications and other portions will be wasted after cutting the crystals with the phase matching angle (θ). It is important to realize that the choice of phase matching configuration also influences the effective strength of the non-linearity, because it determines the directions of the involved electric fields with respect to the crystal axes. Many phase-sensitive non-linear processes, in particular parametric processes such as frequency generation, parametric amplification and oscillation, as well as four-wave mixing require phase matching to be efficient. For devices like frequency doublers or optical parametric amplifiers, phase matching needs to be achieved, otherwise the conversion efficiency would be very low. In this point of view, Sankaranarayanan–Ramasamy method [7–9] has given the solution, and it is possible to grow bulk size single crystals along a desired orientation needed for device fabrication.

The authors (N.B. and P.R.) have already grown KAP single crystals by SR method and the results of birefringence study and UV–vis NIR analysis of SR-grown KAP were discussed in the earlier report [10]. In our present investigation we report the etching, Vicker's microhardness, HRXRD, UV–vis NIR analysis, dielectric and thermal analysis studies on conventional method-grown and SR method-grown KAP crystals.

2. Bulk growth of KAP

The crystal making ingredients were the same both for conventional and SR method-grown KAP crystals. The KAP saturated solution was made from Merck (GR-grade) chemical reagents dissolved in Millipore water of resistivity 18.2 MΩ/cm^{-1}. The reported solubility of KAP is 12.5 g in 100 ml of water at 30 °C

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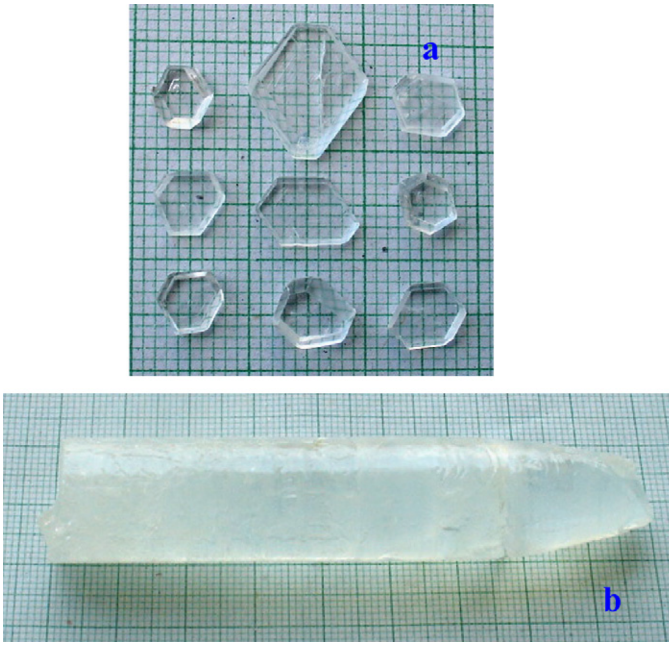

Fig. 1. (a) Conventional and (b)SR method-grown KAP single crystals.

[11]. Re-crystallization was carried out two times to eliminate any impurities in the KAP crystal. The KAP crystal (Fig. 1(a)) was grown by conventional slow-evaporation solution growth technique (SEST) and a well faceted crystal was chosen for SR method. (010) face was selected in the present study to impose the orientation in the growing crystal. The top of the solution in the glass ampoule was maintained at 40 °C to increase the evaporation rate and this had resulted in a reduction of 5–7 ml in the volume of the growth solution in 1 day. The temperature around the growth region is maintained at 33 °C. The experimental conditions were closely monitored, and we found that the seed crystal started to grow after 8 days. The crystal of 15 mm diameter and 70 mm length has grown in a period of 18 days (Fig. 1(b)). The average growth rate was about 4 mm/day. The grown KAP crystal was cut and polished for further studies. Three runs were made for (010) face. Under identical condition the experiments were highly reproducible.

3. Characterization

3.1. Chemical etching analysis

To etch, (010) face of the KAP crystal was dipped at room temperature in the etchant for a period ranging from 10 to 15 s and then wiped with dry filter paper. Fig. 2(a) illustrates etch-pit patterns produced on the (010) face of the conventional method-grown KAP crystal after etching for 15 s. Etch pits of distorted rectangular shape were observed and the etch-pit density (EPD) was $16.7 \times 10^2\,cm^{-2}$. The etch pits did not disappear upon continuous etching, suggesting that the pits were due to dislocations. Fig. 2(b) represents the etch pits observed for SR-grown KAP and EPD was $8.8 \times 10^2\,cm^{-2}$. Less number of EPD in SR-grown KAP shows that the quality of the crystals grown by SR method is better than conventional method-grown crystal. The presence of dislocations strongly influences many of the properties of crystals. The possible reasons for lower EPD of SR-grown crystals are as follows:

(i) The generation of dislocations is strongly correlated with the formation of inclusions in the crystals. Depending on the shape of the seed crystal, inclusions may also arise. If the important habit faces do not bound the seed, the facets of these will be formed in the early stages of growth. The area between these facets develops terraces parallel to the habit faces. In these areas solvent is easily trapped into the crystal. It has also been observed that dislocations can originate from growth sector boundaries [12]. In SR method, as the growth is only on morphology defined facet the dislocations of the above causes are avoided.

(ii) The reason for bulk of the inclusions getting trapped could be due to fluctuations in supersaturation close to the crystal or due to transition from dissolution to growth. A number of parameters such as variation in supersaturation during the growth, non-uniform growth rates, etc., are responsible for the formation of inclusions. Liquid inclusions getting trapped parallel to the interfaces are due to drastic changes in growth condition [13]. In general, it is observed that almost all the conventional method-grown crystals (ADP, KDP, NaBr, $BaNO_3$, KAl $(SO_4)_2$, LAHF) contain inclusions [13–16]. In SR method as there are no such growth fluctuations or non-uniform growth rates the dislocations of the above causes are avoided.

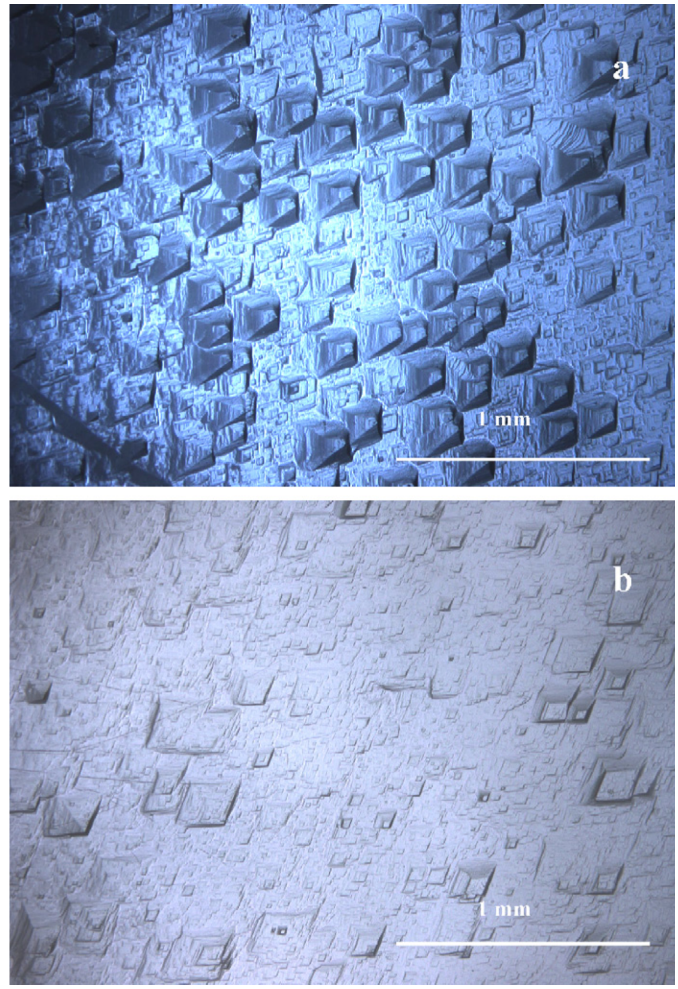

Fig. 2. Etch pattern on (a) conventional and (b) SR-grown KAP.

3.2. Vicker's microhardness analysis

Microhardness studies are carried out using (010) face of the SR method-grown KAP crystal (MITUTOYO MH 120). For each load