Journal of Crystal Growth 310 (2008) 5341–5346

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth and characterization of KDP crystals with potassium carbonate as additive

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ARTICLE INFO

Article history:
Received 20 November 2007
Received in revised form
30 May 2008
Accepted 3 September 2008
Communicated by J. de Yoreo
Available online 17 September 2008

PACS:
77.84.Fa
74.62.Dh

Keywords:
A1. Growth rate
A1. Metastable zone width
A1. Optical properties
A1. Solution growth
A1. X-ray diffraction
B2. Dielectric materials

ABSTRACT

Potassium carbonate (K_2CO_3) as a new additive was added into the potassium dihydrogen phosphate (KDP) solutions in different molar ratios. The metastable zone width of KDP solution with 5 M% K_2CO_3 was determined and compared with the pure system. A good-quality KDP crystal with 5 M% K_2CO_3 additive was grown by the slow cooling method from aqueous solution by the rotation of the seed crystal with the in-house built rotation assembly. Dielectric measurements were carried out on pure and doped KDP crystals at various temperatures ranging from 313 to 423 K by the conventional parallel plate capacitor method, and it indicates that 5 M% K_2CO_3 addition leads to low dielectric constant value dielectrics. The addition of 5 M% K_2CO_3 and proper rotation of seed crystal (40 rpm) improves the quality of the crystal. The high-resolution X-ray diffractometry (HRXRD) analysis shows that the crystalline perfection of the crystal grown in these optimum conditions is extremely good without having any internal structural grain boundaries and mosaic nature. The crystals grown by these optimum conditions show positive effects in the various characterization techniques. The effect of additive on the growth, nucleation kinetics, structural, nonlinear optical, laser-induced damage threshold and optical properties have been investigated by the studies on pure and K_2CO_3-doped (in different concentrations viz., 1, 5 and 10 M%) KDP crystals grown under identical conditions.

1. Introduction

Currently, KH_2PO_4 (KDP) and $KD_xH_{1-x}PO_4$ (DKDP) are the only available nonlinear crystals needed for laser radiation conversion in laser fusion system. Laser fusion research needs large plates of nonlinear crystals for electro-optic switches and frequency converters. The properties of potassium dihydrogen orthophosphate (KDP) and its analogs include transparency in a wide region of the optical spectrum, resistance to damage by laser radiation and relatively high nonlinear efficiency, in combination with reproducible growth to large size and easy finishing [1].

In order to grow large crystals of size 40–60 cm the rapid-growth technique has been developed greatly in recent years; the growth rates can be more than those obtained with the traditional techniques. So, it is necessary to study the dynamics of the medium's effect on the growth, and to understand the relation of the growth conditions, the solution stability, growth mechanism and properties of the crystals. The beneficial effect of additives on the growth process and properties of crystals has been applied in recent years [2–4]. The most efficient additives are reagents with those metal ions that have the same properties as the bulk solutions, or the solution auxiliary that can change the properties of solution, such as viscosity, surface tension, etc., but they should not affect the optical qualities of crystals.

Various additives influence the physical properties of the crystals like growth kinetics [5,6] and surface morphology of the crystal faces [7,8]. The capture of an impurity in a crystal during its growth from a solution is the combined effect of various factors: the solubility of the host and the impurity phase, character of the mother phase, interaction between the host and the impurity molecules, relative size of impurity and host ions, similarity in the crystallographic structure of the two phases, relative size of the impurity and the host ions and other crystallization conditions [9]. The impurity effect depends on the impurity concentration and supersaturation, temperature and the pH of the solution.

One of the major growth inhibitors in the KDP system is the transition metal ions like Fe and Cr which are inherently present. For the great majority of elements, segregation coefficient k has a tendency to decrease with increasing impurity concentration in

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doi:10.1016/j.jcrysgro.2008.09.019

the solution. The decrease is particularly strong in the second group of cations: increasing the initial Co^{2+}, Mn^{2+} and Ni^{2+} concentrations by one to two orders of magnitude reduces k by one to three orders of magnitude. However, this effect, typical of metal (M^{2+}) cations, is much weaker in the case of trivalent cations, which occupy the same interstitial position in the structure of KDP [10]. Our previous investigations reveal that the optimal addition of trivalent La^{3+} ions considerably prevents these bivalent ions from entering into the crystal lattice and results in reduced defects and dislocations [11]. In order to identify other useful additives, which can have similar effects as La^{3+}, we have chosen potassium carbonate (K_2CO_3) as an additive in the present investigation. K_2CO_3-added KDP crystals were grown from the aqueous solution with a simple apparatus that can be applied in certain forced convection configurations to maintain a higher homogeneity of the solution.

With the aim of improving the quality of KDP crystals with better nonlinear optical properties for both academic and industrial uses, an attempt has been made in this present work to grow the KDP crystals by doping it with divalent anionic soluble impurity K_2CO_3 in different molar ratios. The effect of seed rotation on the crystalline perfection is also studied.

2. Experimental procedure

The KDP (GR grade), K_2CO_3 (GR) from Merck and Millipore water of resistivity 18.2 MΩ cm were used for the study. No further purification was done. The solubility studies were done for pure KDP and KDP doped with small amount (5 M%) of K_2CO_3 as additive. Solubility studies were carried out in a constant-temperature water bath with cryostat facility with an accuracy of ±0.01 °C. Stirring was done using an immersible magnetic stirrer. The solution was stirred continuously for 6 h to achieve stabilization. Solubility was determined by gravimetric analysis for different temperatures (30–50 °C). The solubility curve of pure KDP is shown in Fig. 1.

Metastable zone width is an essential parameter for the growth of large-size crystals from a solution, since it is the direct measure of the stability of the solution in its supersaturated region. Metastable zone width is an experimentally measurable quantity, which depends on number of factors, such as stirring rate, cooling rate of the solution and presence of additional impurities [12–15]. The metastable-zone-width studies of pure KDP and K_2CO_3-added KDP solutions were measured by adopting the polythermal method [13]. The KDP solution (500 ml) saturated at 30 °C was prepared according to the solubility diagram with continuous stirring using the magnetic stirrer. Then the solution was filtered by the filtration pump and Whatman filter paper of pore size 11 μm. Two similar beakers with 250 ml solution each were used, one containing pure KDP solution and the other 5 M% K_2CO_3 was added. Then pure and K_2CO_3-added KDP solutions were kept in a constant-temperature bath with cryostat facility. The solutions were stirred continuously for a period of 6 h for stabilization using the magnetic stirrer. It was slowly cooled at a desired cooling rate of 4 °C/h, until the first crystal appeared, the temperature was instantly recorded. The difference between the saturation temperature and nucleation temperature was taken to be the maximum undercooling Δt_{max}. This gives the metastable zone width of the system. The experiment is repeated for different saturation temperatures, 35, 40, 45, 50 °C, and the corresponding metastable zone widths are measured. Several nucleation runs (7–9 times) were carried out under controlled conditions. Reproducible results with the accuracy of ±0.25% were obtained.

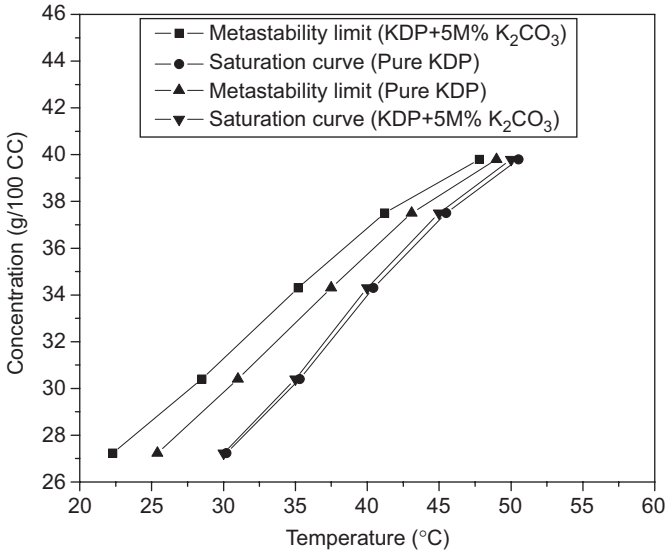

Fig. 1. Solubility curves and metastability limit curves of pure and K_2CO_3-added KDP solutions.

KDP crystal doped with 5 M% K_2CO_3 was grown from aqueous solution with a simple apparatus that can be applied in certain forced convection configurations to maintain a higher homogeneity of the solution. This apparatus consists of bi-directional seed rotation controller coupled with a stepper motor, which is controlled by using a microcontroller-based drive. This controller rotates the seed holder in the crystallizer. The seed crystal is mounted on the center of the platform made up of acrylic material and is fixed into the crystallizer. The seed mount platform stirs the solution very well and makes the solution more stable, which results in better crystal quality. The uniform rotation of the seed is required so as not to produce stagnant regions or re-circulating flows, otherwise inclusions in the crystals will be formed due to inhomogeneous supersaturation in the solution [16].

The crystal growth is carried out in a 5000 ml standard crystallizer used for conventional crystal growth by the method of temperature reduction. The crystallizer temperature is controlled using an external water bath and the temperature fluctuations are less than 0.01 °C. The saturation temperature was 50 °C. The solution was filtered by filtration pump and Whatman filter paper of pore size 11 μm to remove extraneous solid and colloidal particles, which may act as the centers of spontaneous nucleation during growth. After filtration the solution was overheated at 70 °C for 24 h. This duration of overheating was found to be effective to destroy the molecule clusters existing in the solution and to make the solution stable against spontaneous nucleation under a high supersaturation [15,17]. After overheating, the temperature of the solution was reduced slightly above the saturation point and seed crystal was mounted on the platform. The rotation rate of the platform with the crystal was about 40 rpm. From the saturation point, the temperature was decreased at 0.1 °C/day at the beginning of the growth. As the growth progressed the temperature lowering rate was increased. After reaching the room temperature, an optically transparent KDP single crystal of size $45 \times 25 \times 15\ mm^3$ was obtained. The grown crystal is shown in Fig. 2.

For various characterization techniques, pure and K_2CO_3-doped (in different concentrations viz., 1, 5 and 10 M%) KDP crystals were grown by the slow cooling method with stirring under identical conditions.