Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Crystal Growth 274 (2005) 555–562
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Study on the growth and characterization of KDP-type crystals

Guohui Li[a,*], Xue Liping[b], Genbo Su[a], Xinxin Zhuang[a], Zhengdong Li[a], Youping He[a]

[a]Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China
[b]The Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received 17 July 2004; accepted 25 October 2004
Communicated by M. Schieber
Available online 30 November 2004

Abstract

Potassium chloride (KCl) as a new additive was added into the potassium dihydrogen phosphate (KDP) solutions in a small amount (5 M%). The solubility curve and metastable zone width of KDP solution with 5 M% KCl were determined and we explained the mechanism of rapid growth of KDP-type crystals with KCl and NH_4Cl as additives, respectively. The clear transparent crystal of KDP with a dimension of $54 \times 54 \times 42\,mm^3$ were grown rapidly by the cooling solution method in 2 days. KDP-type crystals grown were polished at face (0 0 1) for optical measurements. The transmission spectra, Raman spectra, electronic conductivity and the damage thresholds of the crystals were determined and compared, respectively. A new method to determine the deuterium content of DKDP crystal with thermo-gravimetric apparatus is developed in the article which implies the weighing of the initial material and products of thermal decay. This handy method of analysis requires merely 30–50 mg DKDP crystal sample to determine its deuterium content with high accuracy.

PACS: 81.10.Dn; 81.70.Pg

Keywords: A1. Optical properties; A2. Rapid growth; B1. Deuterium content; B1. KCl; B1. KDP-type crystals

1. Introduction

Potassium dihydrogen phosphate (KDP) is one of the first and best-known electro-optic crystals. It is a member of a broad family of isomorphic compounds having a generic composition MY_2XO_4, where {M = K, NH_4 (A), Rb and Cs}, {Y = H and D (deuterium)} and {X = P and As}. The most commonly used materials are KDP and ammonium dihydrogen phosphate (ADP) and their deuterated analogs DKDP and DADP. The crystal structures of KDP isomorphs belong to the same point group $I\bar{4}2m$ at room temperature and

*Corresponding author.
E-mail address: lgh@ms.fjirsm.ac.cn (G. Li).

0022-0248/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2004.10.052

the large crystals can be grown from aqueous or heavy water (deuterated) by cooling solution method.

The very high-energy Nd-glass lasers used for inertial confinement fusion research, need large plates of nonlinear crystals for electro-optic switches and frequency converters. The approximately $40 \times 40\,cm^2$ aperture of lasers under construction in the US and France, require single-crystal boules with linear dimensions in the 50–100 cm range. KDP and its analogs DKDP and ADP are the only nonlinear crystals currently used for these applications due to their exclusive physical properties [1]. The growth rate of such large crystals by traditional techniques is merely 0.5–1 mm/day typical for low-temperature solution growth. Slow growth leads to growth cycles exceeding 1–2 years. The difficulties in providing reliable equipment, the high risk of failure, and defect formation during such long periods result in low yield and high cost of the final crystals. These reasons stimulated the development of new techniques to accelerate the growth without sacrificing the optical quality of large crystals.

Zaitseva et al. of LLNL grew large-scale (40–55 cm) KDP crystals at a rate of 1020 mm/day, the rapid growth method is based on the use of "point seed" [2]. Nakatsuka et al. used external energy to grow KDP crystals of 60 mm in size at high rates of excess of 50 mm/day [3]. However, these new techniques described above require raw material of higher purity, acoustic power and continuous filtration system.

The adjustment effect of additives on the growth process and properties of crystals has been applied in recent years [4–6]. With additives, KDP crystals can be grown rapidly in the traditional crystallizers of simple design for conventional growth. In this present work, KDP crystals were grown from the aqueous solutions added with 5 M% KCl, Podder [7] reported that the presence of KCl in the growth medium is also found to suppress the metal ion impurities to a large extent and increases the growth rate. The increase in the quality of the KDP crystal in presence of KCl is due to the complexation of trace metal ion impurities in solution by Cl ion. These complex metal impurities cannot get into the crystal lattice. The solubility curve and metastable zone width of 5 M% KCl added solution is also measured comparing to the pure system. This new technology can also be applied in the rapid growth of other KDP-type crystals. In this context, we also compared the transmission spectra, Raman spectra, electronic conductivity and the damage thresholds measured in our experiments of the KDP-type crystals grown.

2. Experimental procedure

2.1. Solubility curve and determination of metastable zone width

The solubility curve was measured by means of traditional weight analysis, and we could also measure the avalanche point temperature by watching the appearance of spontaneous crystallization of solutions. The solution was filtered through a 0.15 μm membrane and kept in a 5000 ml vessel with a point seed in the seed hold rotating in the mode of "forward-stop-backward" with a speed of 30 rpm. The solutions were stirred for about 24 h continuously for stabilization and slowly cooled at a desired cooling rate of 4 °C/h until the first crystal speck in the solution appeared and this temperature was recorded. The experiment was repeated for different saturation temperatures like 40, 45, 50, and 60 °C and the corresponding metastable zone widths were measured. The metastable region was shown in Fig. 1. The solubility curve of pure KDP solution was adopted from the report by Yang Shangfeng et al. [4] which is measured by means of traditional weight analysis.

In our experiments, we found that when 5 M% KCl was added into the solution and dissolved, the temperature of KDP crystal saturation was raised because small amount of KCl in water changed the dissolution equilibrium of KDP. So the solubility curve of KDP solution with 5 M% KCl is on the right side of the solubility curve of pure KDP solution. The metastable zone width of KDP solution with 5 M% KCl was doubled and greatly wider than that of pure KDP solution, KDP crystal can be rapidly grown under higher