Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Crystal Growth 283 (2005) 108–114
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Synthesis of large optically clear $AlPO_4$-5 single crystals

F.Y. Jiang[a,b,1], J.P. Zhai[a], J.T. Ye[a], J.R. Han[b], Z.K. Tang[a,*]

[a]*Department of Physics and Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*
[b]*State Key Laboratory of Crystal Materials, Shandong University, Jinan, China*

Received 6 May 2005; received in revised form 8 May 2005; accepted 13 May 2005
Available online 25 July 2005
Communicated by D. P. Norton

Abstract

We report the effects of gel composition and crystallization condition on the hydrothermal synthesis of optical-clear large $AlPO_4$-5 crystals. By using a gel with excessive Al species and high HF content, large perfect hexagonal-shaped $AlPO_4$-5 crystals (size 1.25 mm × 0.65 mm) were obtained, at a synthesis temperature of 453 K with a crystallization period of 36 h. The optical quality of the crystals is sensitive to the crystallization temperature and time duration.

PACS: 83.80.P; 81.10

Keywords: A1. Hydrothermal synthesis; A3. Crystal growth; B1. AFI; B2. Large $AlPO_4$-5 crystals

1. Introduction

Since the first report of crystalline microporous aluminophosphate ($AlPO_{4\text{-}n}$) in 1982 [1], many research works have been carried out on this new-type molecular sieve materials. In this family, the $AlPO_4$-5 (IZA structure code: AFI) is the most extensively studied. An AFI crystal has a hexagonal structure with space group of P6cc. Its framework consists of one-dimensional 12-ring channels (inner diameter 0.73 nm) which are packed parallel to the *c*-axis. An AFI single crystal is electrically insulating, optically transparent from ultraviolet to infrared and thermally stable up to 1173 K. These excellent physical properties, plus their unique opened pore structures, offer an excellent template to fabricate host–guest nanostructured composites. Vietze et al. [2,3] incorporated organic dye molecules (Pyridine 2) into the channel of $AlPO_4$-5 crystals by in situ inclusion during the synthesis, and observed single-mode laser emission at 687 nm. Tang et al. [4,5] fabricated ultra-small single-walled carbon nanotubes with a diameter as

*Corresponding author.
E-mail addresses: fyjiang@ust.hk (F.Y. Jiang), phzktang@ust.hk (Z.K. Tang).
[1]Permanent address: Yantai University, Yantai, China.

0022-0248/$ - see front matter
doi:10.1016/j.jcrysgro.2005.05.069

small as 0.4 nm inside the channels of $AlPO_4$-5 crystals by carbonizing the occluded organic template tripropylamine (TPA), and subsequently observed the superconductivity of the single-walled carbon nanotubes. Caro et al. [6] have reported the nonlinear optical properties of *p*-nitroaniline-loaded $AlPO_4$-5 crystals. Both for fundamental research and practical applications arising from the novel properties of these host–guest nanostructures, synthesis of large-sized AFI crystals with high optical quality is essential. However, it is not easy to synthesize optical-quality AFI single crystals with reasonably large dimensions owing to some critical issues in crystal growth.

Several groups have reported growth methods of $AlPO_4$-5 [9], $CrAPO_{4\text{-}5}$[7], and $MgAPO_{4\text{-}5}$ [8] single crystals with a crystal length up to 1.4, 1.0, and 1.7 mm, respectively. However, all those crystals have a very high aspect ratio (long but very thin) which is not favorable in practical applications. In this paper, we report a method of synthesizing large $AlPO_4$-5 single crystals with a diameter of 0.65 mm and a proper aspect ratio. The crystals are of perfect hexagonal morphology and high optical quality. To our best knowledge, they are the largest AFI crystals reported so far.

2. Experimental procedure

$AlPO_4$-5 crystals were synthesized using a hydrothermal process using starting gels with composition of $x Al_2O_3{:}P_2O_5{:}y TPA{:}500H_2O{:}z HF$. The source reagents were tri-isopropylate aluminum (98 wt%, Aldrich), orthophosphoric acid (85 wt%, Aldrich), TPA (98 wt%, Aldrich), hydrofluoric acid (40 wt%, Fluka) and deionized water. The typical synthesis procedure is as follows: (1) preparing the tri-isopropylate aluminum gel solution by dissolving tri-isopropylate aluminum into deionized water and stirring for 12 h; (2) adding dropwise diluted orthophosphoric acid into the gel solution and stirring for 2 h; (3) adding TPA into the mixed gel solution and stirring for 2 h; (4) adding diluted HF solution into the mixed gel solution followed by a further stirring for 2 h; (5) filling a Teflon-lined stainless-steel autoclave with the prepared gel solution, and aging for a period of time; (6) putting the autoclave into a preheated oven, and maintaining it at a temperature of 180 °C for 5–36 h; and (7) after crystallization, quenching the autoclave in cold water and separating the product by decantation, with the crystals washed and dried at 353 K overnight.

As-synthesized crystals were characterized by X-ray powder diffraction (XRD) using a Philips PW1830 diffractometer. The morphology and optical quality of the crystals were studied by scanning electron microscopy (Philips XL30) and optical microscopy.

3. Results and discussion

In order to grow large, optical-clear $AlPO_4$-5 crystals, we had done a series of experiments to investigate the influence of the synthesis parameters such as gel composition, the process of gel preparation, the crystallization conditions, etc. on the size and quality of the product crystals. Here we limit our discussion to the key factors that affect the crystal size and quality.

3.1. Gel composition

In order to study the effect of gel composition on the synthesis of AFI crystals, we selected the synthesis condition as follows: gel aging time 2 h, crystallization temperature 453 K, and crystallization time 12 h. We synthesized three batches of crystals to investigate the influence of the Al_2O_3/P_2O_5 ratio, TPA content, and HF content, respectively. Every batch has five samples with different gel compositions, and they were synthesized under the same condition synchronously. The results are summarized in Table 1. Below we discuss each of the essential factors influencing the final result.

3.1.1. The ratio of Al_2O_3/P_2O_5

In most experiments reported in the literature, the molar ratio of Al_2O_3/P_2O_5 is usually set to be unity or smaller than unity. In other words, an excessive orthophosphoric acid is used in the reaction gel. In our experiments, we found that only small-sized crystals can be synthesized under