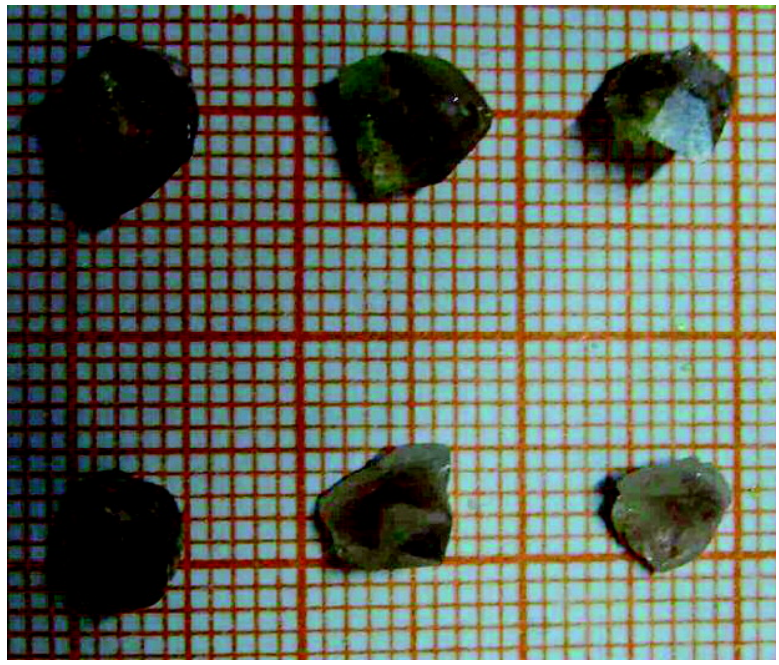
Article

Flux Growth and Characterizations of GaPO Single Crystals

Guogang Xu, Jing Li, Jiyang Wang, Hongyang Zhao, and Hong Liu

Cryst. Growth Des., **2008**, 8 (10), 3577-3580 • DOI: 10.1021/cg7012649 • Publication Date (Web): 13 September 2008



CRYSTAL GROWTH & DESIGN
2008
VOL. 8, NO. 10
3577–3580

Flux Growth and Characterizations of Ga_3PO_7 Single Crystals

Guogang Xu, Jing Li, Jiyang Wang,* Hongyang Zhao, and Hong Liu

State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong 250100, P. R. China

Received December 23, 2007; Revised Manuscript Received July 1, 2008

ABSTRACT: Trigallium phosphate single crystals, Ga_3PO_7, have been grown for the first time by a spontaneous nucleation method using Li_2CO_3-$3MoO_3$ as a flux. The crystal structure was determined by using a four circle X-ray diffractometer. The trigonal unit cell parameters are $a = b = 7.897(3)$ Å, $c = 6.757(6)$ Å, and $Z = 3$ with space group $R3m$. The crystal has a Mohs hardness of 6.5 and a density of 4.874 g/cm^3 as determined by using Archimedes' method. Analysis of differential scanning calorimetry (DSC) and thermogravimetric (TG) shows that the crystal is stable over the temperature range of 25 to 1364.8 °C with no mass change. It has a wide transmission range from 250 to 4300 nm from UV through the IR region. The useful piezoelectric properties have been characterized, and the results show that it is a promising candidate for high temperature piezoelectric applications.

Introduction

Piezoelectric crystals, in particular, α-SiO_2, α-$AlPO_4$, $GaPO_4$, $LiNbO_3$ and $LiTaO_3$, have been extensively investigated. They are used to make sensors, accelerators, energy conversion devices, and so on.[1−3] However, with the rapid development of high-speed electronic, communication and aeronautical technology, current crystals cannot satisfy all the application requirements. The need for new piezoelectric crystals with improved properties, especially high electromechanical coupling factors, high temperature stability, and high frequency stability is growing.

Recently, crystalline trigallium phosphate (Ga_3PO_7) has attracted our attention due to its special crystal structure. Single crystal Ga_3PO_7 was first synthesized by Boudin et al. in 1997 using hydrothermal synthesis at high temperature (773 K) and high pressure (210×10^6 Pa).[4] It crystallizes in a noncentrosymmetric trigonal crystal system with space group $R3m$, which belongs to the same space group as $LiNbO_3$ and $LiTaO_3$, and belongs to one of the 10 polar crystal systems that have excellent optical and electromechanical properties.[5−9] It is a promising candidate for piezoelectric, pyroelectric, and optical applications. Up to now, there have been no other reports of Ga_3PO_7 single-crystal growth and properties characterization except for the above-mentioned work. As is well-known, large size crystals are difficult to obtain using the hydrothermal synthesis method under such severe reaction conditions. Therefore, a search for a better growth method is important in order to produce large size and high quality Ga_3PO_7 crystals for piezoelectric and optical applications.

In this paper, we report that transparent Ga_3PO_7 single crystals have been successfully grown for the first time by a spontaneous nucleation method using Li_2CO_3-$3MoO_3$ as a flux, and some useful physical properties are investigated.

Experimental Section

A solute of polycrystalline Ga_3PO_7 was first prepared using a standard solid-state reaction method. The raw materials are 4 N pure reagent Ga_2O_3 and analytically pure reagent $NH_4H_2PO_4$. The chemical reactions taking place in the platinum crucible are

$$3Ga_2O_3 + 2NH_4H_2PO_4 = 2Ga_3PO_7 + 2NH_3\uparrow + 3H_2O\uparrow \quad (1)$$

The solvent Li_2CO_3-$3MoO_3$ was adopted as a flux, which was obtained using analytically pure Li_2CO_3 and MoO_3 in stoichiometric proportions.[10−12] The chemical reactions taking place in the platinum crucible are

$$Li_2CO_3 + 3MoO_3 = Li_2Mo_3O_{10}(LMO) + CO_2\uparrow \quad (2)$$

The mass ratio between solute and solvent is 1:5. The mass of the starting chemical reactants Ga_2O_3, $NH_4H_2PO_4$, Li_2CO_3 and MoO_3 are 11.98, 4.90, 12.0 and 70.14 g, respectively. The crystal growth experiments were performed in an electric vertical furnace controlled by a FP-21 digital microprocessor temperature programmer-controller in air. The starting materials were completely mixed and put into a 100 mL Pt crucible covered with a lid. They were heated in the electric resistance furnace from room temperature up to 1050 °C at a ramp rate of 100 °C h^{-1} and held at this temperature for 24 h to homogenize the mixture. Subsequently, a transparent melt was obtained. The melt was slowly cooled at a rate of 1−2 °C h^{-1} from 900 to 500 °C. After this, the crucible was cooled to room temperature at a rate of 100 °C h^{-1}. The growth period covered more than 10 days including heating up and homogenization time. The as-grown single crystals were removed from the flux with dilute nitric acid.

Phase identification of the crystals was performed using a Seifert X-ray powder diffractometer (XRD) using Cu Kα radiation at room temperature over a 2θ range of 10° to 65°. The crystal structure was determined using a Bruker APEX2 CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were performed using a NETZSCH STA 409C thermal analyzer with a heating rate of 10° min^{-1}. Transmittance spectra were measured using Hitachi U-3500 spectrophotometer and NEXUS 670 FTIR spectrophotometer over the range of 190−2000 nm and 2000−4300 nm, respectively. The piezoelectric and dielectric constants of a (100) faced crystal wafer covered with silver electrode were characterized using a ZJ-3A Berlincourt-type quasi-static d33 m and an Agilent 4294A Impedance analyzer. The density of the Ga_3PO_7 crystal was measured using Archimedes' method. The hardness of the Ga_3PO_7 crystal was determined using the Mohs hardness scale.

Results and Discussion

The flux growth is particularly favorable because it has many advantages in comparison with other crystal growth methods. It readily allows crystal growth at a temperature below the melting point. In addition, crystal grown from flux has regular morphology and lower dislocation density.

Compared with the hydrothermal synthesis method, flux growth using water-free solvents offers a way to exclude the source of OH^- groups, which can improve physical properties

* To whom correspondence should be addressed. E-mail: jywang@icm.sdu.edu.cn; xgg_79@yahoo.com.cn.

10.1021/cg7012649 CCC: $40.75
Published on Web 09/13/2008

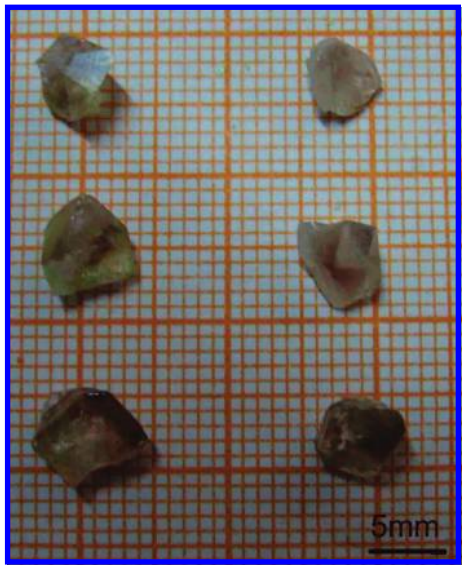


Figure 1. Optical photograph of typical as-grown crystals.

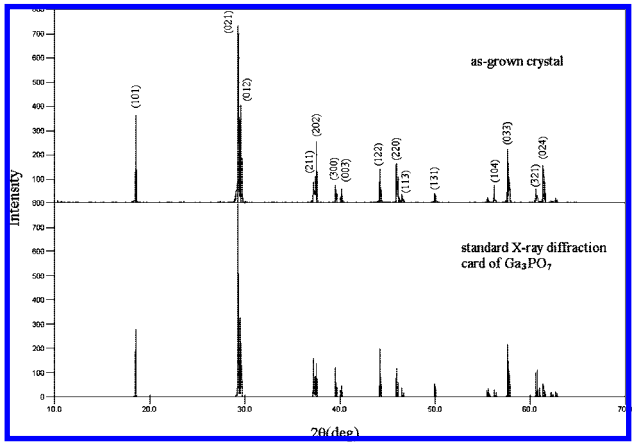


Figure 2. X-ray powder diffraction pattern of the as-grown crystal.

of the crystal especially at high temperature. After the process of slow cooling, well-formed transparent crystals were obtained from the product in the platinum crucible. Some typical as-grown crystals from the flux are shown in Figure 1, the maximum size being 7 × 6 × 3 mm^3. The crystals are transparent and slightly brownish in color. The color may be caused by color centers induced by oxygen vacancies, which can be decreased by annealing at lower temperature. Judging by the appearance of the as-grown crystals, we conclude that large sized crystals can be easily grown by the top-seeded solution growth method using LMO as a flux.

Figure 2 shows the X-ray powder diffraction pattern of the as-grown crystal. The X-ray analysis shows that as-grown the crystals are well formed, and all peaks can be indexed in accordance with the standard JCPDS Card File 87-0530 for Ga_3PO_7. No additional peaks are found.

The Ga_3PO_7 crystal structure had been reported by Boudin et al.[4] To reconfirm the crystal structure, a crystal with dimension of 0.10 × 0.07 × 0.01 mm^3 was selected to collect single-crystal X-ray diffraction data. The compound crystallizes in the trigonal crystal system with a noncentrosymmetric space group *R*3*m*, which is a basic precondition for a potential piezoelectric material. There are no distinct differences in our work from theirs except for the unit cell parameters and bond distance.

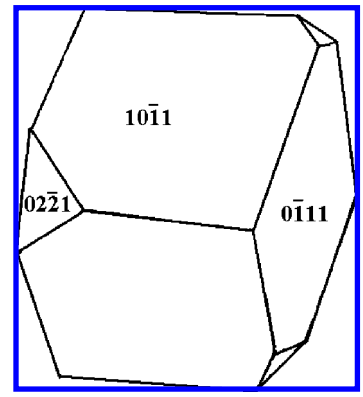


Figure 3. Schematic drawing of Ga_3PO_7 crystal with $\{10\bar{1}1\}$ and $\{02\bar{2}1\}$ faces.

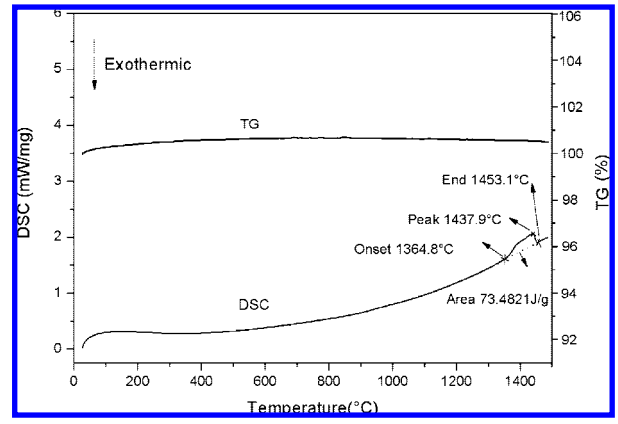


Figure 4. DSC/TG analysis curves of Ga_3PO_7 crystal.

On the basis of X-ray powder diffraction data, the Miller indices of as-grown crystals were investigated using an X-ray crystal orientation apparatus. The crystals were found to be bounded by well-developed $\{10\bar{1}1\}$ and $\{02\bar{2}1\}$ faces, and the calculated interfacial angles between $(10\bar{1}1)$ and $(0\bar{1}11)$; and the $(10\bar{1}1)$ and $(02\bar{2}1)$ are 104.7° and 127.3°, respectively. A schematic drawing of the crystal is shown in Figure 3.

The thermal stability of the crystal is a very important factor for crystal growth and potential applications. In order to know the thermal behavior of Ga_3PO_7 crystals, DSC and TG were carried out over the temperature range from 25 to 1500 °C. The initial mass of the crystal sample subjected to analysis was 45.22 mg. The DSC and TG curves are shown in Figure 4. The crystal is stable up to 1364.8 °C, and only a weak endothermic peak appears between 1364.8 and 1453.1 °C. The maximum peak temperature is 1437.9 °C. The TG curve shows that the total mass of the crystal is almost invariant in the measurement temperature range. After the measurements were completed, the surface of the crystal sample was observed to be covered by a layer of white powder. All the experimental findings suggest that the weak endothermic peak can be ascribed to the decomposition of the crystal, and that its melting point was not reached.

The crystal had been put into water and dilute nitric acid at room temperature for three weeks, and no changes were observed. It is demonstrated that Ga_3PO_7 crystals are stable and nonhygroscopic. The density of Ga_3PO_7 crystal was measured to be 4.874 g/cm^3 using Archimedes' method, in agreement with the theoretical prediction of 4.807 g/cm^3. The difference between the measured and calculated density is within experimental error.

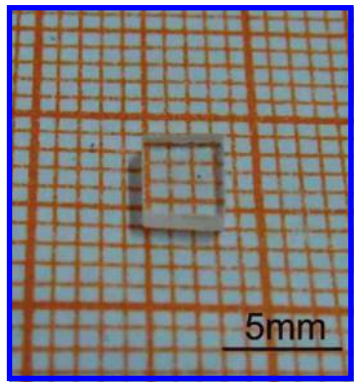


Figure 5. Optical photograph of (101) face wafer cutting from the as-grown crystal.

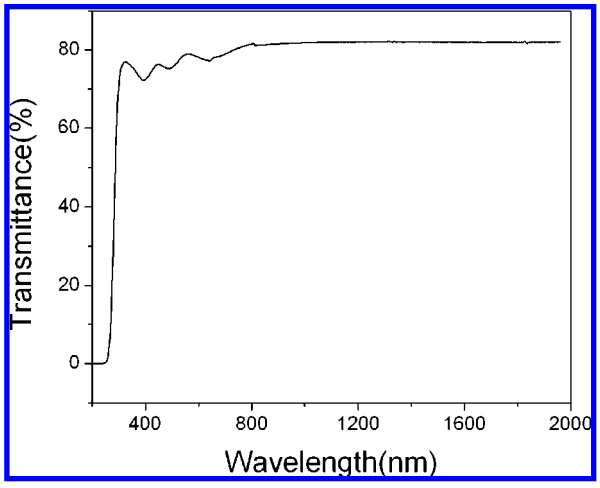


Figure 6. Optical transmittance spectrum of the (101) face wafer in the wavelength of 190−2000 nm.

The Mohs hardness value is about 6.5, which is slightly lower than that of quartz.

Some useful optical and piezoelectric properties were also determined. Figure 5 shows a (101) faced wafer that was cut from the as-grown crystal used for optical transmittance measurement. The room temperature optical transmittance spectra of the crystal are shown in Figures 6 and 7. From Figure 6, it can be seen that the UV transparency cutoff wavelength of the as-grown crystal occurs at 250 nm. The transmittance over the wavelength range of 250−300 nm increases sharply from 0 to 80%. Over the wavelength range from 300 to 2000 nm, the transmittance remains constant at around 80−82%. Figure 7 shows the transmittance spectrum of the same wafer over the range of 2000−4300 nm. It can be seen that the transmittance stays above 85% over the range of 2000−3750 nm, and only some small absorption bands around 3000, 3480, and 3800 nm were found. From the transmittance results, the conclusion can be drawn that the crystal has a wide optical transparency region.

The results of piezoelectric measurements are shown in Table 1 along with data for other piezoelectric materials. From the comparison, we can clearly see that Ga_3PO_7 has the best temperature stability up to 1364.8 °C, and the piezoelectric constant d in the direction perpendicular to the (100) face is 4.5PC/N. Although all the piezoelectric constants cannot be attained because of the small size of the crystal obtained, the piezoelectric effect is still as good as $GaPO_4$ and greater than

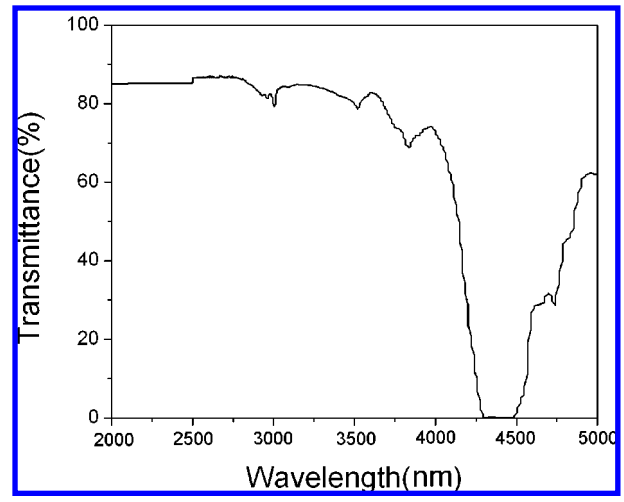


Figure 7. Optical transmittance spectrum of the (101) face wafer in the wavelength of 2000−4300 nm.

Table 1. Properties Comparison of Several Common Piezoelectric Crystals.

crystal	α-SiO_2[2]	α-$AlPO_4$[2]	$GaPO_4$[3]	Ga_3PO_7
crystallographic space group	32	32	32	3*m*
melting point (°C)	1610	1500	1670	
phase changing or decomposing *T* (°C)	573.3	581	933	1364.8
Mohs hardness scale	7	6.5	5.5	6.5
density Kg/m^3	2648	2618	3570	4874
relative dielectric constant	$\varepsilon_{11} = 4.52$	$\varepsilon = 6.0$	$\varepsilon_{11} = 6.5$	$\varepsilon = 4.3$
	$\varepsilon_{33} = 4.64$		$\varepsilon_{33} = 6.7$	
piezoelectric strain constants (10^{-12} C/N)	$d_{11} = -2.3$	$d_{11} = -3.33$	$d_{11} = 4.5$	$d = 4.5$
	$d_{14} = 0.67$	$d_{14} = 1.55$	$d_{14} = 1.9$	

α-SiO_2. Therefore, it is a very promising candidate for use as a high temperature piezoelectric material.

Conclusions

Ga_3PO_7 crystals have been grown by the spontaneous nucleation method using LMO as a flux. The as-grown Ga_3PO_7 crystals are well formed and indexed in the trigonal system with a noncentrosymmetric space group *R*3*m*, which is a basic precondition for a potential piezoelectric material. The crystal morphology is good and bounded by well-developed $\{10\bar{1}1\}$ and $\{02\bar{2}1\}$ faces. The crystal has a Mohs hardness of 6.5 and a density of 4.874 g/cm^3. It has a wide transmission range from 250 to 4300 nm, as observed in the UV through the IR regions. It has high temperature stability up to 1364.8 °C and excellent piezoelectric and dielectric constants when compared with similar materials. Therefore, it is a promising candidate for high temperature piezoelectric devices and optical application.

Acknowledgment. We gratefully acknowledge the financial support from the 973 program of the People's Republic of China (Grant No. 2004CB619002).

Supporting Information Available: X-ray crystallographic file in CIF format for the Ga_3PO_7 single crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Detaint, J.; Philippot, E.; Jumas, J. C. *Proceedings of the 39th Annual Symposium on Frequency Control*; Philadelphia, Pennsylvania, May 29−31, 1985; IEEE: New York, 1985; p 234.

(2) Zhang F. X.; Wang L. K. *Modern Piezoelectricity*; China Science Press: Beijing, 2002.
(3) Krempl, P. W. *Proceedings of 1994 IEEE Ultrasonics Symposium:* Cannes, France, IEEE; November 1994, p 949.
(4) Boudin, S.; Lii, K.-H. *Acta Crystallogr.* **1998**, *C54*, 5.
(5) Fraser, D. B. *J. Appl. Phys.* **1966**, *37*, 3853.
(6) Graham, R. A. *J. Appl. Phys.* **1977**, *48*, 2153.
(7) Weis, R. S.; Gaylord, T. K. *Appl. Phys. A: Mater. Sci. Process.* **1985**, *37*, 191.
(8) Brownridge, J. D.; Shafroth, S. M. *J. Electrost.* **2005**, *63*, 249.
(9) Bhagavannarayan, G.; Budakoti, G. C. *J. Cryst. Growth* **2005**, *282*, 394.
(10) Ozima, M. *J. Cryst. Growth* **1976**, *33*, 193.
(11) Beaurain, M.; Armand, P.; Papet, P. *J. Cryst. Growth* **2005**, *275*, e279.
(12) Li, J.; Wang, J. Y.; Tan, H.; Zhang, H. J. *Mater. Res. Bull.* **2004**, *39*, 1329.

CG7012649