CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

CrystEngComm

PAPER

Effect of supersaturation levels on the segregation coefficient of deuterium in $K(H_{1-x}D_x)_2PO_4$ crystals using Raman spectroscopy

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shaohua Ji,*[abc] Bing Teng,*[ac] Weijin Kong,[a] Degao Zhong,[ac] Xun Sun[b] and Zhengping Wang[b]

The deuteration level of $K(H_{1-x}D_x)_2PO_4$ (DKDP) crystals was measured by Raman spectroscopy and non-critical phase matching (NCPM) temperature experiment. Our results indicate that the PO_4 vibration peak of the DKDP crystals shifted towards lower wavenumbers with increasing the deuterium concentration. A different deuterium content was found between crystals grown from similarly deuterated solutions but varying degree of supersaturation. The NCPM temperature experiments confirm that the deuterated partition difference was about 10% when the deuteration level was medium (30% - 70%) at different supersaturation levels. We found that 1% deuterium content corresponds to 0.61 ℃ NCPM temperature difference.

Introduction

Deuterated dihydrogen phosphate crystals (DKDP) are often used as optical components because of their excellent optical properties including a large nonlinear optical coefficient and high UV transmittance.[1-4] The deuteration level is an important parameter that significantly affects many essential properties of DKDP crystals such as the refractive index, electro-optical properties, thermal properties, cell parameters and the laser induced threshold.[8-15] Deuteration also affects the application of NCPM and fourth harmonic generation (FHG) in DKDP crystals.[5-7]

DKDP crystals can be grown via either the point-seed method or the traditional growth method.[16-18] Compared to the traditional growth method, the growth period attributable to supersaturation can be decreased by about 85% when using the point-seed method. The deuterium partition coefficient, however, may differ from the one obtained using the traditional growth method. Indeed, the partition (segregation) coefficient between the crystal and solution depends on the degree of supersaturation and temperature.[19-21] In 1974, the distribution coefficient of deuterium of DKDP crystals grown using the traditional method was investigated.[22] However, there are no reports about the deuterium partition coefficient of DKDP crystals grown using the point-seed rapid method at high supersaturation.

Raman Spectroscopy is an effective way to determine deuteration levels in DKDP crystals. The shift of the PO_4 vibration peak can clearly be attributed to H/D isotope substitution. In 1997 Yaksin et al. suggested that the Raman shift could be used to determine the deuteration degree of DKDP crystals.[23] In 2004 T. Huser et al. found that the dependence of the Raman shift on the degree of deuteration is almost linear and that a $1cm^{-1}$ wavenumber shift of the PO_4 vibration peak corresponds to a 2.68% variation of the deuteration level.[24] In 2013 B. Liu et al found that the intensity of the strongest peak of DKDP crystals grown using the rapid growth method with different deuterium contents decreases first before it reaches its minimum. The mole percentage of the deuterium content in the crystal was about 74% when the Raman intensity reached a minimum, and the relationship between Raman intensity and deuterium content is not linear.[25]

The effect of supersaturation on growth morphology is well known, but not yet well understood, since when a system becomes supersaturated, other parameters change in turn, especially in solution of poorly soluble compounds. Considering the lack of knowledge of the effect of supersaturation on the deuterium partition coefficient, further studies are desirable. In this paper, traditional growth DKDP crystal and rapid growth DKDP crystal were controlled strictly grown with similar parameters except for supersaturation. And the deuterium segregation mechanism of rapid growth $K(H_{1-x}D_x)_2PO_4$ crystal, for the first time to our knowledge, is described and confirmed by Raman spectroscopy and NCPM FHG experiment. Our study may contribute to the application and improvement of DKDP optical components in NCPM FHG.

Experimental

Crystal growth and sample preparation

The traditional growth (TG) DKDP crystals were grown from solution with deuteration levels of 17.6%, 61.5%, 74.3%, 78.4%, 86.2% and 98.5%. The rapid growth (RG) DKDP crystals were grown The traditional growth (TG) DKDP crystals were grown from solution with deuteration levels of 17.6%, 61.5%, 74.3%, 78.4%, 86.2% and 98.5%. The rapid growth (RG) DKDP crystals were grown from solution with 17%, 40%, 50%, 60%, 70%, 80% and 90% deuteration levels. The TG DKDP crystals were grown at a supersaturation of 0.15% and RG DKDP crystals at a

[a] College of Physics, Qingdao University, Qingdao 266071, China
[b] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China
[c] Key Laboratory of Photonics Materials and Technology in Universities of Shandong (Qingdao University), Qingdao 266071, China

supersaturation of 2.5%. The solution was filtered using a polysulfide filter with a 0.15-micrometer pore diameter. The crystals are transparent without any visible macroscopic defects as shown in Fig. 1.

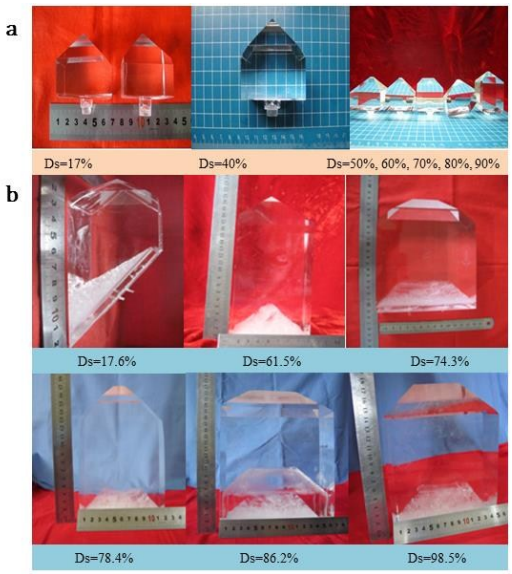

Fig. 1 DKDP crystals grown from different deuterated-level solution (Ds) by RG (a) and TG (b).

For TG DKDP crystals, the growth temperature period governing the H/D exchange is much longer than that of RG DKDP crystals, so along the growth direction (Z-direction) TG DKDP crystal samples and RG DKDP crystal samples were cut and chosen considering their identical growth temperature. In the crystal growth process, supersaturation and temperature were controlled strictly to prevent formation of stray grain.

The deuteration level in solution (D_s) is calculated using the formula below, where n (D) is the mole amount of deuterium and n (H) is the mole amount of hydrogen.

$$Ds(\%) = \{ n(D) / [n(D) + n(H)] \} \times 100\% \quad (1)$$

For TG DKDP crystals, the relationship between deuteration level in solution (Ds) and deuteration level in crystal (Dc) are calculated with the formula below which depends on the growth parameters[22]

$$Dc = 0.68 \times Ds \times e^{0.00382Ds} \quad (2)$$

However, this formula is not suitable for calculating the deuteration level in RG DKDP crystals because the supersaturation levels of the two growth methods are very different (0.15% for TG and 2.5% for RG calculated by formula 3). Supersaturation levels were controlled by reducing the temperature of the growth solution to a constant value which could be calculated as:

$$\sigma = (C-Ce) / Ce \quad (3)$$

Here Ce and C are the equilibrium and actual concentrations of the DKDP salt, respectively. Accordingly, in order to modify formula 2 for higher supersaturation, the PO_4 vibration peak of DKDP crystals grown using the different method measured by Raman spectrum is used as a proven method to determine deuteration in crystals.

Raman Spectrum

All crystal samples are cut from DKDP crystals and processed into 10×10×10mm cubes, with x (100) or y (010) and z (001) direction oriented accurately and polished optimally. Because crystal samples cut from different parts of a crystal would show differences in the Raman spectrum, we ensure that all the samples are cut from relative fixed position corresponding to similar growth temperature periods. They are also processed using identical techniques, and possess identical sizes.

The Raman spectra of the crystal samples were recorded with a high-resolution confocal μ-Raman system (LabRAM HR800) with excitation wavelength of 632.81 nm, and a scanning speed of 1 cm^{-1} in one step. In order to counter the influence caused by H/D exchange process, the measuring point was taken inside the crystal sample on Z (001) with the direction of laser beam parallel to Z (001). The measured spectral range was from 800 to 1100 cm^{-1}.

NCPM FHG experiments

Both the DKDP crystals were processed along the type-I NCPM direction, which was 90º relative to the z-axis (Θ=90º) and at 45º relative to the x-axis (Φ=45º). The geometric dimensions of the DKDP crystal samples were 14.8×14.8×7 mm^3. The transmitting faces of the crystals were polished but not coated. The experimental setup for NCPM FHG and cutting type of the crystals is the same as the one mentioned in ref. [26].

Results and discussion

Raman Spectroscopy

The observed main features are the shifts of the PO_4 vibration peak of the KDP crystal around 912.9 cm^{-1} and the shift toward shorter wavenumber as deuteration levels increase. As shown in Fig.2 and Fig.3, the Raman spectra of the DKDP crystals grown by the two methods were obtained with different deuteration levels. The deuteration levels of the TG DKDP crystals (Dc) were 12.8%, 52.9%, 67.1%, 71.9%, 81.5% and 97.6%. They were determined using formula 2 and the respective deuteration levels in solution (Ds): 17.6%, 61.5%, 74.3%, 78.4%, 86.2% and 98.5%. When the deuteration level in solution was about 17%, the PO_4 vibration peak was at 906.7 cm^{-1} and 908.8 cm^{-1} for TG and RG DKDP crystals respectively. This indicated that the deuterium content of TG DKDP crystals is 5.6% higher than that of RG DKDP crystals.[24] When the deuteration level in solution approaches a certain number, the PO_4 vibration peak splits into two peaks.[24, 27] When the deuteration level in solution increases to 61.5% and 60%, the position of the PO_4 vibration peaks are 894.9 cm^{-1} and 897.1cm^{-1} for TG and RG crystal respectively. This means that the deuteration level of the TG DKDP

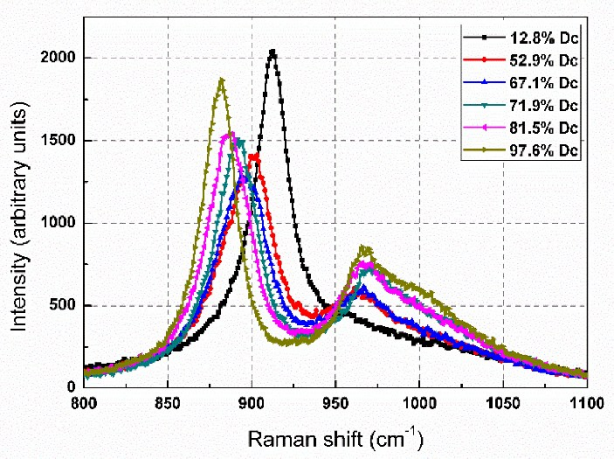

Fig. 2 Raman spectrum of TG DKDP crystals.

Table 1 Position of Raman vibration peak of DKDP crystals grown from different deuterated-level solution by TG and RG.

Deuterated-level in crystal (TG) /%	0	12.8	52.9	67.1	71.9	81.5	97.6	—
PO_4 vibration peak of DKDP crystals /cm^{-1}	912.9	906.7	894.9	887.7	885.5	880.7	876.3	—
Deuterated-level in solution (RG) /%	0	17	40	50	60	70	80	90
PO_4 vibration peak of DKDP crystals /cm^{-1}	912.9	908.8	905.7	901.7	897.1	891	886.7	881.9

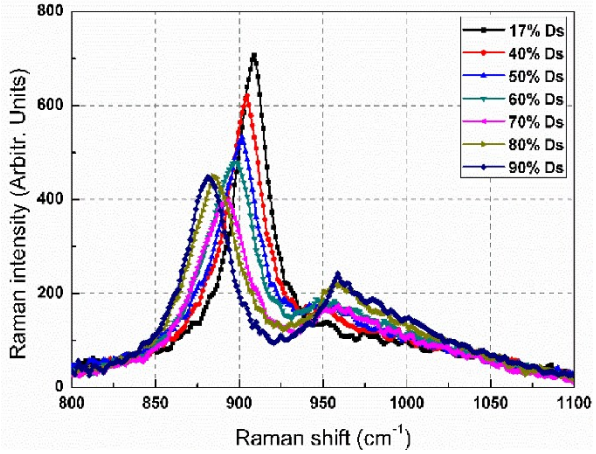

Fig. 3 Raman spectrum of RG DKDP crystals.

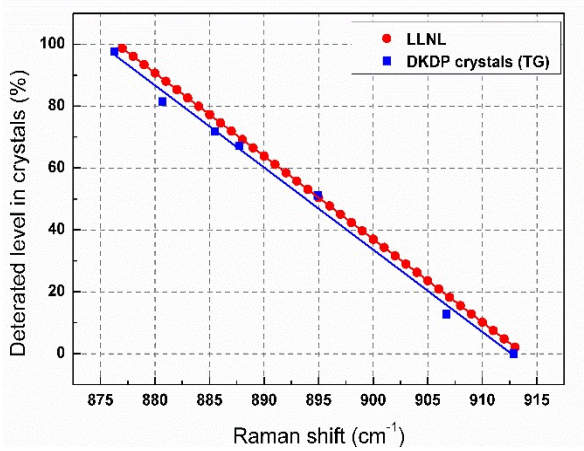

Fig. 4 The relationship between Raman shift and deuteration level in TG DKDP crystals in comparison with the LLNL results.

crystal is 5.9% higher than the RG DKDP crystal. When the deuteration level (Ds) reaches 86.2% and 90%, the PO_4 vibration peaks were at 880.7 cm^{-1} and 881.9cm^{-1} for the respective TG and RG crystals. Hence, the deuterium content of TG crystals is 3.2% higher compared to the RG crystal. Fig. 2 and Fig. 3 indicate that the deuteration level in the crystal is lower than that in solution for higher supersaturation levels. In addition, the deuterium segregation coefficient is also determined by the deuteration level in solution. The PO_4 vibration peaks are shown in Table. 1. The relationship between the position of the Raman vibration peak and the deutetion level in TG DKDP crystal is linear. Hence, the formula below can be derived, where Dc' is the deuteration level in TG DKDP crystals (in %) and R is the spectral mean of the PO_4 vibration in cm^{-1}.

$$Dc' = -2.656cm \times R + 2423.7 \quad (4)$$

The Raman shift and the deuteration level relation for the TG crystals was plotted for our crystals and compared with the Lawrence Livermore National Laboratory (LLNL) results – see Fig.4. The Raman shift of the PO_4 vibration peak indicates that there is about 3% deuteration difference. The difference may be caused by the test condition. Based on the observed dependence of the PO_4 peak position on the degree of deuteration, the deuteration level of the RG crystal can be calculated knowing the PO_4 vibration peak shown in Table 1 using formula 4. As shown in Fig. 5, empirical formula is the classic solidification theory, which is reported in 1974.[22] However, this solidification theory is based on TG DKDP crystal grown under a small supersaturation. Now rapid growth method develops fast and attracts a lot of attention owing to its short growing period, but the deuterium segregation mechanism of RG K(H1-xDx)2PO4 crystal grown at a high supersaturation, is not well known. Similarly, the relationship between deuteration level of RG

DKDP crystals and solution was calculated - see Fig. 5. There is a different trend compared to the empirical formula (formula 2) used to calculate deuterium distribution coefficients of TG DKDP crystals. When the deuteration level in solution is below 30% or above 70%, the deuterium distribution difference between solution and crystal is less than 6%. Moreover, this difference increases to about 10% in a 30% to 70% deuterated solution. The results show that deuterium segregation varies for solutions with different deuteration levels as they are affected by supersaturation levels. High (>70%) or low (<30%) deuteration level solutions, the coefficient of deuterium segregation is similar to that obtained with the empirical formula. Due to the fact that H or D occupies a large area, they can enter the lattice more easily in these deuterated solutions. Supersaturation levels have a significant impact on the deuterium distribution when the solution is at a medium deuteration level. Our result suggests that the influence

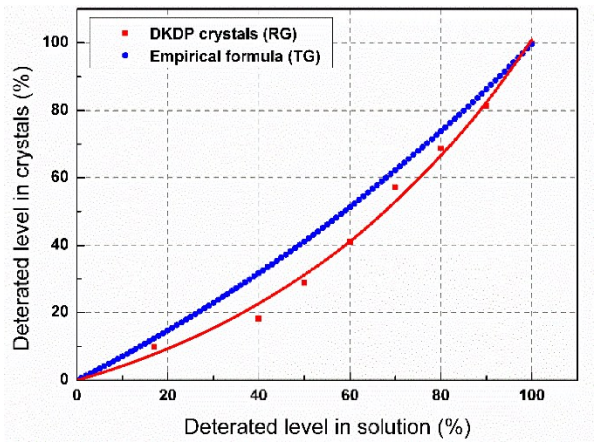

Fig. 5 The dependence of deuterated-level in crystals grown by RG on the deuteration level in solution and empirical formula which is applicable to TG crystals.

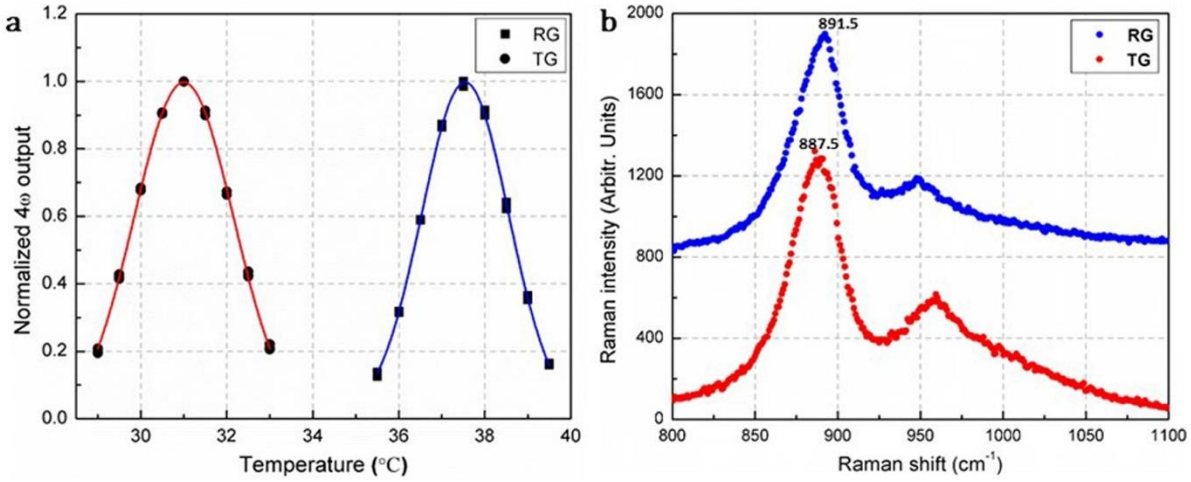

Fig. 6 NCPM temperature (**a**) and Raman spectrum (**b**) of TG and RG DKDP crystals grown from 74.5% deuterated solution

of supersaturation is small when the solution shows high deuterated levels. For example, the 95% deuterated KDP crystal grown at a high supersaturation can be used as a photoelectric switch. The variation of supersaturation levels can affect deuterium segregation during crystal growth and cause both deuteration level changes and inhomogeneous distribution of deuterium in DKDP crystals.[28] For NCPM FHG, the variation of deuteration levels would cause deviations of both the exterior angle and the NCPM temperature.[29-31] Based on our experimental results the formula describing RG crystals at a supersaturation level of 2.5% can be fitted as shown in Fig.5 using

$$Dc = 0.385 \times Ds \times e0.00963Ds$$

Here Dc and Ds are the deuteration level of RG DKDP crystals and its solution, respectively. This result shows that the deuterium level relationship between crystal and solution is not linear for RG crystals. The R Square value of this formula is 0.994, which suggests the deuterium level correlation obtained for RG crystal is reliable. Compared to the empirical formula (formula 2, shown in Fig. 5), the deuterium distribution difference increases when the supersaturation is higher - especially for medium deuteration. Our results suggest DKDP crystals should be grown at moderate supersaturation to maintain both accurate high deuteration levels and homogeneity of deuterium, especially for 70% deuterated KDP crystals when NCPM FHG is used.

NCPM FHG temperature experiments

To confirm the reliability and validity of formula 5, both the NCPM temperature and Raman spectrum of two DKDP crystals grown from the same deuteration level solution (74.5%) using different growth methods were measured. The TG and RG DKDP crystals were grown at 0.15% and 2.5% levels of supersaturation, respectively. As shown in Fig. 6a, the NCPM temperature of the RG DKDP crystal is 37.5℃, higher than the 31℃ of NCPM temperature in the TG DKDP crystal. This indicates that the deuteration level of RG DKDP crystals is lower than that of TG DKDP crystals. The results show that deuterium content decreases with increasing supersaturation which results in a

hange of the refractive index.

The Raman spectra of the two DKDP crystals described in Fig. 6b further indicate that the PO_4 vibration peaks are at 891.5 cm^{-1} for the RG DKDP crystal and 887.5 cm^{-1} for the TG DKDP crystal respectively. This corresponds to 55.9% and 66.5% deuteration levels of the DKDP crystals calculated using formula 4. It indicates that H/D exchange is less likely at higher supersaturation when deuteration levels of solutions are about 70%. In addition, a 10.6% deuteration level deviation between them is consistent with the result

shown in Fig. 5. The experiment indicates that the deuteration levels in RG DKDP crystals are similar to those calculated using formula 5. A 1% deuteration degree corresponds to about 0.61℃ NCPM temperature difference.

Conclusions

In this paper, the difference between deuterium distribution in DKDP crystals grown via TG and RG at different supersaturation levels were measured using Raman spectroscopy which can specifically determine PO4 symmetric vibrational mode peak position, corresponding to the substitution of D for H. Our results indicate that the deuterium segregation difference between the two crystal growing methods is about 6% if the deuterated-level in solution is below 30% and above 70%. This difference increases to about 10% when the deuterium content of the solution is between 30% and 70%. This result shows that the coefficient of deuterium segregation depends mainly on supersaturation levels. Higher supersaturation increases the deuterium distribution difference in medium deuterated solutions. The NCPM FHG experiments show that 1% deuterium content corresponds to a 0.61℃ NCPM temperature difference. To obtain high quality as well as highly homogeneous DKDP crystals, the supersaturation levels need to be controlled carefully. Additional research of crystal growth and crystallization mechanism on rapid growth $K(H_{1-x}D_x)_2PO_4$ crystals grown for a series of different supersaturated solutions and other growth parameters is in preparation, with aim of decreasing the deuterium segregation difference and improving the homogeneity of rapid growth DKDP crystals.

Acknowledgements

This work was supported by Postdoctoral Science Foundation of China (Grant No. 2015M582055) and Applied Research Project of Qingdao (Grant No. 2015130).

Notes and references

1 Y. S. Liu, W. B. Jones, J. P. Chernoch, *Appl. Phys. Lett.*, 1976, **29**, 32.
2 A. Jenkins, *Nat. Photonics*, 2007, **2**, 3.
3 D. Clery, *Science*, 2011, **334**, 445.
4 R. Evens, *Nature*, 1985, **314**, 133.
5 V. I. Bespalov, V. I. Bredikhin, V. P. Ershov, V. I. Katsman, N. V. Kiseleva, S. P. Kuznetsov, *Soviet Journal of Quantum Electronics*, 1982, **12**, 1527.
6 J.J. DeYorea, Z.U. Rek, N.P. Zaitseva, B.W. Woods, J. *Cryst. Growth*,1996, **166**, 291.
7 N. Zaitseva, L. Carman, I. Smolsky, *J. Cryst. Growth.*, 2002, **241**, 363.
8 M. Yamazaki, T. Ogawa, *JOSA*, 1966, **56**, 1407.
9 G. C. Ghosh, G. C. Bhar, *IEEE J. Quantum Electron*, 1982, **18**, 143.
10 C. Belouet, M. Monnier, R. Crouzier, *J. Cryst. Growth*, 1975, **30**, 151.
11 G. Ravi, A. S. H. Hameed, P. Ramasamy, *J. Cryst. Growth*, 1999, **207**, 319.
12 R. J. Nelmes, G. M. Meyer, J. E. Tibballs, *J. Phys. C: Solid State Phys*., 1982, **15**, 59.
13 D. A. V. Kliner, F. Di Teodoro, J. P. Koplow, S. W. Moore, A. V. Smith, *Opt. Commun.*, 2002, **210**, 393.
14 J. Reintjes, R. C. Eckardt, *Appl. Phys. Lett.*, 1977, **30**, 91.
15 D. Bruneau, A. M. Tournade, E. Fabre, *Appl. Opt.*, 1985, **24**, 3740.
16 N. Zaitseva, L. Carman, *Prog. Crystal Growth and Charact*., 2001, **43**, 1.
17 M. Staynova, Chr. Nanev, *Cryst. Res. Technol.*, 1989, **24**, 951.
18 N. Zaitseva, L. Carman, I. Smolsky, R. Torres, M. Yan, *J. Cryst. Growth.*, 1999, **204**, 512.
19 See, for instance, Sunagawa, *I. In Crystals: Growth Morphology and Perfection*; Cambridge University Press: Cambridge, U.K., 2005; p56.
20 Burton, J. A.; Prim, R. C.; Slichter, W. P. Theor, *J. Chem. Phys.*, 1953, **21**, 1987.
21 J. Leroudier, J. Zaccaro, J. Debray, P. Segonds and A. Ibanez, *Cryst. Growth Des.*, 2013, **13**, 3613.
22 G. M. Loiacono, J. F. Balascio, W. Osborne, *Appl. Phys. Lett.*, 1974, **24**, 455.
23 M. A. Yakshin, D. W. Kim, Y. S. Kim, Y. Y. Broslavets, O. E. Sidoryuk, S. Goldstein, *Laser Phys*, 1997, **7**, 941.
24 T. Huser,*C. W. Hollars, W. J. Siekhaus, J. J. Deyoreo, T. I. Suratwala, T. A. Land, *Appl. Spectrosc.*, 2004, **58**, 349.
25 B. Liu, H. Zhou, Q. Zhang, M. Xu, S. Ji, L. Zhu, L. Zhang, F. Liu, X. Sun, X. Xu, *Chin. Phys. Lett.*, 2013, **30**, 067804.
26 S. Ji, F. Wang, L. Zhu, X. Xu, Z. Wang and X. Sun, *Scientific Reports*, 2013, **3**, 1.
27 C. E. Barker, R. A. Sacks, B. M. V. Wonterghem, J. A. Caird, J. R. Murray, J. H. Campbell, K. Kyle, R. E. Ehrlich, N. D. Nielsen, *Proc. SPIE.*, 1995, **2633**, 501.
28 S. Ji, F. Li, F. Wang, X. Xu, Z. Wang, X. Sun, *Opt. Mater. Express.*, 2014, **4**, 997.
29 S. T. Yang, M. A. Henesian, T. L. Weiland, J. L. Vickers, R. L. Luthi, J. P. Bielecki, P. J. Wegner, *Opt. Lett.*, 2011, **36**, 1824.
30 S. Ji, S. Zhang, M. Xu, B. Liu, L. Zhu, L. Zhang, X. Xu, Z. Wang, X. Sun, *Opt. Mater. Express.*, 2012, **2**, 735.
31 S. Ji, F. Wang, M. Xu, L. Zhu, X. Xu, Z. Wang, X. Sun, *Opt. Lett.*, 2013, **38**, 1679.