

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE JUN 2010		2. REPORT TYPE		3. DATES COVERED 00-00-2010 to 00-00-2010	
4. TITLE AND SUBTITLE Hydrothermal Growth and Properties of KBe2BO3F2 (KBBF) and RbBe2BO3F2 (RBBF) Single Crystals			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Clemson University, Center for Optical Materials Science and Engineering Technologies (COMSET), 91 Technology Dr, Anderson, SC, 29625			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADA541135. Presented at the Advanced Photonics and Renewable Energy: 2010 OSA Optics and Photonics Congress Held in Karlsruhe, Germany on June 21-24, 2010. Sponsored by EOARD.					
14. ABSTRACT Centimeter-size KBBF and RBBF single crystals have been grown hydrothermally for NLO applications. Second harmonic generation of 800 nm fundamental light has been demonstrated using both KBBF and RBBF in preliminary studies.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 2	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Hydrothermal Growth and Properties of $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) and $\text{RbBe}_2\text{BO}_3\text{F}_2$ (RBBF) Single Crystals

Colin McMillen¹, Joseph Kolis¹, Chang Liu², Adam Kaminski² and John Ballato¹

¹ *Clemson University and Center for Optical Materials Science and Engineering Technologies (COMSET)
91 Technology Dr., Anderson, SC, 29625, USA*

² *Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011*

*Author e-mail addresses: cmcmill@clemson.edu (CM), kjoseph@clemson.edu (JK),
cliu82@iastate.edu (CL), kaminski@ameslab.gov (AK), jballat@clemson.edu (JB)*

Abstract: Centimeter-size KBBF and RBBF single crystals have been grown hydrothermally for NLO applications. Second harmonic generation of 800 nm fundamental light has been demonstrated using both KBBF and RBBF in preliminary studies.

©2009 Optical Society of America

OCIS codes: 160.4670; 160.4330

1. Introduction

Alkali fluorberyllium borates such as $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) and $\text{RbBe}_2\text{BO}_3\text{F}_2$ (RBBF) are fascinating materials offering nonlinear optical (NLO) capabilities over a very broad range of wavelengths well into the deep-UV [1]. Flux grown KBBF single crystals are particularly well-studied [2,3] and a number of elegant NLO experiments have recently been performed using these crystals. KBBF has proven to be versatile in the visible region, offering efficient sum frequency mixing over the 397-539 nm range [4], as well as the UV and deep-UV regions where it has been used with a prism coupling technique to efficiently generate 266 nm light [5] and several other sub-200 nm wavelengths [6,7], even as low as 156 nm [8]. However, the crystal growth process has proven to be both difficult (crystals are typically grown to only a few mm in thickness) and costly, limiting the mainstream availability of suitable crystals [9]. Hydrothermal growth methods have only recently been pursued as an alternative method to obtain thicker KBBF crystals [10,11], and optical data on these crystals has not yet been reported. So far, RBBF has been relatively unexplored despite its identical structure to KBBF [11,12]. Here, we overview the hydrothermal growth of KBBF and RBBF and present some preliminary optical characterization of these interesting materials.

2. Experimental

KBBF and RBBF crystals were grown hydrothermally in silver lined autoclaves by direct recrystallization of polycrystalline feedstock onto seed crystals using fluoride mineralizers. The feedstock materials were prepared at 700 °C by stoichiometric solid state reactions of KBF_4 , BeO and H_3BO_3 for KBBF and $\text{Rb}(\text{OH})$, BeO, B_2O_3 and NH_4F for RBBF. Seeds were obtained from spontaneous nucleation experiments and suspended from a silver ladder which was placed in the autoclave along with the appropriate feedstock and aqueous KF or RbF mineralizers (1 M concentrations). The region of the autoclave containing the feedstock was heated to 400-450 °C, and the region containing the seed crystals was held 20 degrees cooler. This heating arrangement was maintained for 4-6 weeks until the autoclave was cooled to room temperature and the as-grown crystals were retrieved.

Second harmonic generation from the resulting crystals was characterized using a Tsunami laser (Spectra Physics) having a fundamental beam of 800 nm, 200 fs pulse width, 8 MHz repetition rate and pumped by a 9 W Millennia laser (Spectra Physics). The fundamental beam was focused onto the single crystal using an AR lens ($f = 50$ mm). The second harmonic beam was separated using a short pass filter and its power was measured using a calibrated GaP detector (FGAP71 – Thorlabs). Angle tuning was performed at 150 mW fundamental power to optimize the intensity of the second harmonic.

3. Results and Discussion

KBBF and RBBF crystals have been grown hydrothermally having dimensions over 1 cm on (001) and approximately 4 mm thick. Representative crystals are shown in Figure 1 and were grown with a dissolution (feedstock) zone temperature of 410 °C with the temperature gradient applied as described above. Optically clear growth was observed and growth rates for the crystals pictured in Figure 1 were 0.75 mm/week on (001) and 0.36

mm/week in thickness for KBBF and 0.70 mm/week on (001) and 0.46 mm/week in thickness for RBBF. Both crystals formed as hexagonal plates, but the KBBF crystal did not reach its finished morphology since the seed crystal began as only a plate fragment in this experiment.

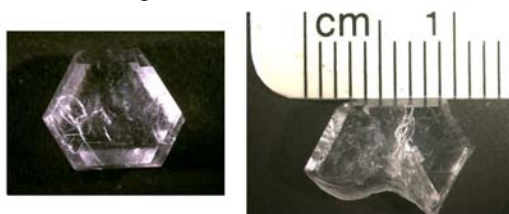


Fig. 1. As-grown RBBF (left) and KBBF (right) crystals.

SHG from the 800 nm fundamental beam was observed as an intense blue light after passing through the target crystal. Intensity of the second harmonic beam increased with increasing fundamental power with no observed power quenching up to 450 mW, as shown in Figure 2. The KBBF (1 mm thick) and RBBF (0.6 mm thick) single crystals in these preliminary studies showed comparable second harmonic intensities despite their differing thicknesses. This is encouraging given the propensity of RBBF to form thicker, less micaceous single crystals.

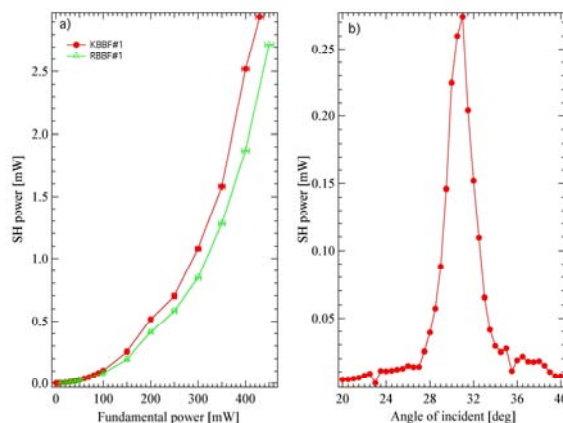


Fig. 2. Second harmonic generation using KBBF (red) and RBBF (green) – a) power curve (left) and b) angle tuning at 150 mW (right).

4. Conclusions

KBBF and RBBF crystals have been grown hydrothermally to sizes exceeding 1 cm. Preliminary optical characterization has been performed on thin crystals. KBBF and RBBF performed comparably and showed no signs of power quenching up to 450 mW. Detailed optical transparency and SHG experiments at other wavelengths are currently underway using thicker crystals.

5. References

- [1] C. Chen, Z. Lin, Z. Wang, "The development of new borate-based UV nonlinear optical crystals," *Appl. Phys. B* **80**, 1-25 (2005).
- [2] D. Tang, Y. Xia, B. Wu, C. Chen, "Growth of a new UV nonlinear optical crystal: $\text{KBe}_2\text{BO}_3\text{F}_2$," *J. Cryst. Growth*, **222**, 125-129 (2001).
- [3] J. Wang, C. Zhang, Y. Liu, J. Zhang, X. Hu, M. Jiang, C. Chen, Y. Wu, Z. Xu, "Growth and properties of $\text{KBe}_2\text{BO}_3\text{F}_2$ crystal," *J. Mater. Res.* **18**, 2478-2485 (2003).
- [4] M. Chattopadhyay, P. Kumbhakar, T. Kobayashi, "Broadband sum-frequency mixing in some recently developed nonlinear optical crystals," *Opt. Engin.* **48**, 124201-1-6 (2009).
- [5] G. Wang, C. Zhang, C. Chen, A. Yao, J. Zhang, Z. Xu, J. Wang, "High-efficiency 266-nm output of a $\text{KBe}_2\text{BO}_3\text{F}_2$ crystal," *Appl. Opt.* **42**, 4331-4334 (2003).
- [6] T. Kanai, X. Wang, S. Adachi, S. Watanabe, C. Chen, "Watt-level tunable deep ultraviolet light source by a KBBF prism-coupled device," *Opt. Express*, **17**, 8696-8703 (2009).
- [7] H. Zhang, G. Wang, L. Guo, A. Geng, Y. Bo, D. Cui, Z. Xu, R. Li, Y. Zhu, X. Wang, C. Chen, "175 to 210 nm tunable deep-ultraviolet light generation based on KBBF crystal," *Appl. Phys. B*, **93**, 323-326 (2008).
- [8] T. Kanai, T. Kanda, T. Sekikawa, S. Watanabe, T. Togashi, C. Chen, C. Zhang, Z. Xu, J. Wang, "Generation of vacuum-ultraviolet light below 160 nm in a KBBF crystal by the fifth harmonic of a single-mode Ti:sapphire laser," *J. Opt. Soc. Am. B*, **21**, 370-375 (2004).
- [9] D. Cyranoski, "China's crystal cache," *Nature*, **457**, 953-955 (2009).
- [10] N. Ye and D. Tang, "Hydrothermal growth of $\text{KBe}_2\text{BO}_3\text{F}_2$ crystals," *J. Cryst. Growth*, **293**, 233-235 (2006).
- [11] C.D. McMillen and J.W. Kolis, "Hydrothermal crystal growth of $\text{ABe}_2\text{BO}_3\text{F}_2$ (A = K, Rb, Cs, Tl) NLO crystals," *J. Cryst. Growth*, **310**, 2033-2038 (2008).
- [12] C.D. McMillen, J. Hu, D. VanDerveer, J. W. Kolis, "Trigonal structures of $\text{ABe}_2\text{BO}_3\text{F}_2$ (A = Rb, Cs, Tl) crystals," *Acta Cryst.* **B65**, 445-449 (2009).