crystals

Editorial

Crystal Growth of Multifunctional Borates and Related Materials

Nikolay I Leonyuk

Department of Crystallography and Crystal Chemistry, Moscow State University, 119992 Moscow, Russia; leon@geol.msu.ru

Received: 15 March 2019; Accepted: 19 March 2019; Published: 21 March 2019

Keywords: crystal growth; crystallography; crystal chemistry; borates; multifunctional materials

Crystalline materials play an important role in modern physics and electronics. Therefore, the demand for crystals with functional properties is increasing strongly, due to the technical advance in different fields: telecommunications, computer devices, lasers, semiconductors, sensor technologies, etc. At the first stage, natural minerals (e.g., quartz) were widely used as piezoelectric and optical material. Later on, after the creation of the first laser, interactions between lasers and materials have been investigated: radiation at the double the frequency of a ruby laser was observed as the fundamental light passing through a quartz crystal [1]. This phenomenon became a substantial contribution to the field of quantum electronics and nonlinear optics. However, natural single crystals usually have insufficient purity, size, occurrence, and homogeneity, or do not even exist in nature. That is why the material scientists began to develop important basic materials with the desirable properties. As an example, at the beginning of the 1960s, this resulted in Czochralski growth of $Y_3Al_5O_{12}$ crystals, referred to as YAG, which is the progenitor of the large group of synthetic materials belonging to the structural type of natural garnet family $A_3B_2(SiO_4)_3$ [2]. Owing to a reasonable growth technology, these crystals and their numerous derivatives including transparent nano-ceramics are dominating the elemental base for solid-state laser engineering and various practical applications.

In the meantime, natural and even highly technological synthetic crystals have reached the limit of their potential for fast-progressing science and engineering. The creation of new crystals with predictable structures and, therefore, desirable physical characteristics is restrained by the theoretical, methodological, and technical problems connected with their crystallization from multicomponent systems. Among them, more than 1000 representatives of the anhydrous borate family are listed in the Inorganic Crystal Structure Database [3]. These compounds are characterized by the great variety in their crystal structures, caused in the linkage of planar BO_3–triangles and BO_4–tetrahedra as fundamental structural units. This also leads to glass formation in viscous borate-based melts. Therefore, investigations of "conditions–composition–structure-properties" relationships can help to develop the technology of single crystal components for high performance electronic and optical devices for industrial, medical and entertainment applications. These research works have quickly opened a new field of materials science.

Most of the borate materials attract considerable attention owing to their remarkable characteristics and potential applications. For instance, they demonstrate nonlinear optical and piezoelectric effects (CsB_3O_5, LiB_3O_5, $CsLiB_6O_{10}$, $KBe_2BO_3F_2$, $Sr_2Be_2BO_7$, $K_2Al_2B_2O_7$, $Ca_4GdO(BO_3)_3$, β-BaB_2O_4, $R_2CaB_{10}O_{19}$, $RM_3(BO_3)_4$, where R – rare-earth elements; M – Al, Cr, Ga, Fe, Sc) [4–6], etc., luminescent (RBO_3) [7–9] and magneto-electrical properties ($RFe_3(BO_3)_4$, $RCr_3(BO_3)_4$, $HoAl_3(BO_3)_4$, $TbAl_3(BO_3)_4$) which appear to be multiferroic materials, i.e., they can be used as magnetoelectric sensors, memory elements [10–13], etc.

Comparatively recently, great attention has been paid to orthoborate crystals co-doped with Er and Yb is associated with their potential as efficient active media solid-state lasers emitting in the spectral range 1.5–1.6 μm [14,15]. Due to high phonon frequencies (more than 1000 cm^{-1}), efficient energy transfers from Yb to Er ions take place in these crystals that is one of the crucial conditions for efficient laser action in Er-Yb co-doped materials. First of all, the laser sources in this spectral range are of great interest because of the several reasons: (1) Their emission is eye-safe since it is absorbed by cornea and does not reach retina; (2) it has low losses in atmosphere and quartz fibers; (3) room temperature sensitive detectors exist in this spectral range. Diode-laser pumping with high brightness and efficiency and long lifetime implies opportunities for the development of compact laser sources with unprecedented out parameters in different modes of operation for practical applications. Mode-locked lasers emitting in the spectral range 1.5–1.6 μm with high repetition rate are especially useful as pulse generators for high bit rate optical networks.

Single crystalline thin layers of (Er,Yb):$YAl_3(BO_3)_4$, Er:$YAl_3(BO_3)_4$ and Yb:$YAl_3(BO_3)_4$ on the undoped borate substrates also are of great interest due to their device potential. Because of the difference in the refractive index of thin film and substrate, grown epilayer exhibits waveguide properties. Potential applications of active waveguides are systems of integrated optics for high-speed signal processing.

Thus, borate crystals with huntite type structure including their derivatives are attractive for different technological applications because of their favorable physical and chemical properties like stability, high transparency, high thermal coefficient, and in particular a very high non-linear optical coefficient, making it the ideal active medium for realizing self-doubling diode pumped solid-state lasers. Wide isomorphous substitutions in *R* positions make it possible to extend new generation functional devices based on these solids.

In this Special Issue, different aspects of multifunctional borate materials are discussed: from ortho- and oxyorthoborates to compounds with condensed anions and from their nonlinear optical and laser properties to piezoelectric characteristics. For example, J. Dawes and coworkers investigated liquid-phase epitaxial growth of the neodymium-doped $YAl_3(BO_3)_4$ optical waveguides as potential active sources for planar integrated optics [16]. E. Cavalli and N. Leonyuk also analyzed the emission properties of the same orthoborate family [17]. Selected excitation, emission, and decay profile of rare earth-doped $YAl_3(BO_3)_4$ crystals were measured and compared with those of the concentrated compounds. The effects of the energy transfer processes and the lattice defects, as well as the ion-lattice interactions are considered taking into account the experimental results. J. Buchen at al. compared twinning in $YAl_3(BO_3)$ and $K_2Al_2B_2O_7$ crystals, which may degrade crystal quality and affect nonlinear optical properties [18]. Space-resolved measurements of the optical rotation related to the twin structure were made, in order to compare the quality of these ortho- and polyborate crystals to select twin-free specimens. The piezoelectric ringing phenomenon in Pockels cells based on the beta barium borate crystals was analyzed by G. Sinkevicius and A. Baskys [19]. It was estimated that piezoelectric ringing in this metaborate crystal occurred at the 150, 205, 445, 600, and 750 kHz frequencies of high voltage pulses. F. Chan et al. also reported single crystal growth and electro-elastic properties of α-BiB_3O_6 and $Bi_2ZnB_2O_7$ crystals with the largest effective piezoelectric coefficients being in the order of 14.8 pC/N and 8.9 pC/N, respectively [20]. Finally, G. Kuzmicheva et. al. reviewed structural aspects and crystallochemical design of orthoborates belonging to huntite-type family [21]. Particular attention was paid to methods and conditions for crystal growth, affecting a crystal real composition and symmetry. A critical analysis of literature data made it possible to formulate unsolved problems in the materials science of rare-earth orthoborates, mainly scandium borates, which are distinguished by an ability to form internal and substitutional (lanthanide and Sc atoms), unlimited and limited solid solutions depending on the topological factor.

Complex investigation of phase formations in multi-component borate melts and the study of crystal growth conditions for novel high-temperature borates will provide a scientific base for development of growth technologies with device potential. On the other hand, investigations of crystal "conditions–composition–structure–properties" relationships in complex borate melts with anion polymerizations can help to create a physico-chemical base for crystal growth technology of high performance electronic and optical devices and components with a variety of industrial, medical, and entertainment applications. In the meantime, these relationships can help to estimate an affinity of synthetic borate materials with their natural prototypes and structural analogs.

The structural stability of many silicates, phosphates, and germanates also depends on the delocalization of formal charges of the A_nO_m (A = Si,Ge,P) anions as a result of their polymerization. The regular variations in their structural motifs make it possible to forecast (optimistically, more or less) new phase systems for the synthesis of advanced materials as well, because currently most of these single crystals are not available in good size or quality. A further analysis of these inorganic polymer structures will set out judicious ways towards a better understanding of the growth mechanisms of multifunctional crystals, and this Special Issue is intended to fill this gap in the field.

Acknowledgments: The Guest Editor thanks all the authors who made this Special Issue possible and the *Crystals* publishing staff for their assistance.

References

1. Franken, P.A.; Hill, A.E.; Peters, C.W.; Weinreich, G. Generation of Optical Harmonics. *Phys. Rev. Lett.* **1961**, *7*, 118–119. [CrossRef]
2. Monchamp, R.R. The distribution coefficient on neodymium and lutetium in Czochralski grown $Y_3Al_5O_{12}$. *J. Cryst. Growth* **1971**, *11*, 310–312. [CrossRef]
3. *Inorganic Crystal Structure Data Base—ICSD*; Fachinformations Zentrum (FIZ) Karlsruhe: Karlsruhe, Germany; Available online: http://icsd.fiz-karlsruhe.de/ (accessed on 3 March 2019).
4. Chen, C.; Wu, Y.; Li, R. The development of new NLO crystals in the borate series. *J. Cryst. Growth* **1990**, *99*, 790–798. [CrossRef]
5. Leonyuk, N.I.; Leonyuk, L.I. Growth and characterization of $RM_3(BO_3)_4$ crystals. *Prog. Cryst. Growth Charact. Mater.* **1995**, *31*, 179–278. [CrossRef]
6. Leonyuk, N.I. Half a century of progress in crystal growth of multifunctional borates $RAl_3(BO_3)_4$ (R = Y, Pr, Sm-Lu). *J. Cryst. Growth* **2017**, *476*, 69–77. [CrossRef]
7. Gorbel, G.; Leblanc, M.; Antic-Fidancev, E.; Lamaitre-Blaise, M.; Krupa, J.C. Luminescence analysis and subsequent revision of the crystal structure of triclinic L-$EuBO_3$. *J. Alloy. Compd.* **1999**, *287*, 71–78. [CrossRef]
8. Boyer, D.; Bertrand-Chadeyron, G.; Mahiou, R.; Lou, L.; Brioude, A.; Mugnier, J. Spectral properties of LuBO3 powders and thin films processed by the sol-gel technique. *Opt. Mater.* **2001**, *16*, 21–27. [CrossRef]
9. Wei, Z.G.; Sun, L.D.; Liao, C.S.; Jiang, X.C.; Yan, C.H. Synthesis and size dependent luminescent properties of hexagonal $(Y,Gd)BO_3$:Eu nanocrystals. *J. Mater. Chem.* **2002**, *12*, 3665–3670. [CrossRef]
10. Zvezdin, A.K.; Vorob'ev, G.P.; Kadomtseva, A.V.; Popov, Y.F.; Pyatakov, A.P.; Bezmaternykh, L.N.; Kuvardin, A.V.; Popova, E.A. Magnetoelectric and magnetoelastic interactions in $NdFe_3(BO_3)_4$ multiferroics. *JETP Lett.* **2006**, *83*, 509–514. [CrossRef]
11. Begunov, A.I.; Demidov, A.A.; Gudim, I.A.; Eremin, E.V. Features of the magnetic and magnetoelectric properties of $HoAl_3(BO_3)_4$. *JETP Lett.* **2013**, *97*, 528–534. [CrossRef]
12. Kadomtseva, A.M.; Popov, Y.F.; Vorob'ev, G.P.; Kostyuchenko, N.V.; Popov, A.I.; Mukhin, A.A.; Ivanov, V.Y.; Bezmaternykh, L.N.; Gudim, I.A.; Temerov, V.L.; et al. High-temperature magnetoelectricity of terbium aluminum borate: The role of excited states of the rare-earth ion. *Phys. Rev. B* **2014**, *89*, 014418. [CrossRef]
13. Bludov, A.N.; Savina, Y.O.; Pashchenko, V.A.; Gnatchenko, S.L.; Maltsev, V.V.; Kuzmin, N.N.; Leonyuk, N.I. Magnetic properties of a $GdCr_3(BO_3)_4$ single crystal. *Low Temp. Phys.* **2018**, *44*, 423–427. [CrossRef]
14. Tolstik, N.A.; Kisel, V.E.; Kuleshov, N.V.; Maltsev, V.V.; Leonyuk, N.I. Er,Yb:$YAl_3(BO_3)_4$—Efficient 1.5 µm laser crystal. *Appl. Phys. B* **2009**, *97*, 357–362. [CrossRef]
15. Lagatsky, A.A.; Sibbett, W.; Kisel, V.E.; Troshin, A.E.; Tolstik, N.A.; Kuleshov, N.V.; Leonyuk, N.I.; Zhukov, A.E.; Rafailov, E.U. Diode-pumped passively mode-locked Er,Yb:$YAl_3(BO_3)_4$ laser at 1.5–1.6 µm. *Opt. Lett.* **2008**, *33*, 83–85. [CrossRef] [PubMed]
16. Lu, Y.; Dekker, P.; Dawes, J.M. Liquid-Phase Epitaxial Growth and Characterization of Nd:$YAl_3(BO_3)_4$ Optical Waveguides. *Crystals* **2019**, *9*, 79. [CrossRef]

17. Cavalli, E.; Leonyuk, N.I. Comparative Investigation on the Emission Properties of $RAl_3(BO_3)_4$ (R = Pr, Eu, Tb, Dy, Tm, Yb) Crystals with the Huntite Structure. *Crystals* **2019**, *9*, 44. [CrossRef]
18. Buchen, J.; Wesemann, V.; Dehmelt, S.; Gross, A.; Rytz, D. Twins in $YAl_3(BO_3)_4$ and $K_2Al_2B_2O_7$ Crystals as Revealed by Changes in Optical Activity. *Crystals* **2019**, *9*, 8. [CrossRef]
19. Sinkevicius, G.; Baskys, A. Investigation of Piezoelectric Ringing Frequency Response of Beta Barium Borate Crystals. *Crystals* **2019**, *9*, 49. [CrossRef]
20. Chen, F.; Cheng, X.; Yu, F.; Wang, C.; Zhao, X. Bismuth-Based Oxyborate Piezoelectric Crystals: Growth and Electro-Elastic Properties. *Crystals* **2019**, *9*, 29. [CrossRef]
21. Kuz'micheva, G.M.; Kaurova, I.A.; Rybakov, V.B.; Podbel'skiy, V.V. Crystallochemical Design of Huntite-Family Compounds. *Crystals* **2019**, *9*, 100. [CrossRef]