ISSN 0020-1685, Inorganic Materials, 2006, Vol. 42, No. 2, pp. 171–175. © Pleiades Publishing, Inc., 2006.
Original Russian Text © E.A. Tkachenko, P.P. Fedorov, S.V. Kuznetsov, V.V. Voronov, S.V. Lavrishchev, V.E. Shukshin, I.V. Yarotskaya, N.G. Kononova, 2006, published in Neorganicheskie Materialy, 2006, Vol. 42, No. 2, pp. 207–211.

Synthesis of Scandium Orthoborate Powders[1]

E. A. Tkachenko*, P. P. Fedorov*, S. V. Kuznetsov*,
V. V. Voronov*, S. V. Lavrishchev*, V. E. Shukshin*,
I. V. Yarotskaya, and N. G. Kononova*****

** Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, Moscow, 119991 Russia*
*** Lomonosov State Academy of Fine Chemical Technology, pr. Vernadskogo 86, Moscow, 119571 Russia*
**** Institute of Mineralogy and Petrography (Novosibirsk Branch), Siberian Division, Russian Academy of Sciences, ul. Russkaya 43, Novosibirsk, 630058 Russia*
e-mail: tkatchenko@ns.crys.ras.ru

Received June 23, 2005

Abstract—Two polymorphs of scandium orthoborate, $ScBO_3$, are synthesized by adding aqueous ammonia to aqueous solutions of scandium nitrate and boric acids and calcining the resulting precipitates. Dehydration of the precipitates reaches completion below 300°C, and further heating leads to highly exothermic crystallization near 750°C. The synthesized $ScBO_3$ powders consist of submicron-sized particles.

DOI: 10.1134/S0020168506020117

INTRODUCTION

Indium and rare-earth orthoborates (including $ScBO_3$) activated with Ce^{3+}, Pr^{3+}, Tb^{3+}, or Eu^{3+} have attracted considerable attention as materials for scintillators [1, 2] and phosphors [3–5], in particular for the ultraviolet spectral region. Scandium rare-earth borates are attractive host materials for diode-pumped lasers [6–8]. Cr^{3+}-doped scandium borate is of interest as a gain medium for 787- to 892-nm tunable lasers [9]. Orthoborate-based materials offer a high UV transmittance, high optical damage threshold, and good chemical stability and mechanical strength, in particular, at high temperatures [10, 11].

Scandium borate is the only compound in the Sc_2O_3–B_2O_3 system [12]. It crystallizes in the calcite structure (sp. gr. $R\bar{3}c$ [10, 13–15]), is isostructural with $InBO_3$ and the high-temperature form of $LuBO_3$ [15], and melts congruently at 1600–1610°C [6, 12].

Levin [12] described another form of $ScBO_3$, prepared by liquid quenching, but failed to index its x-ray diffraction (XRD) pattern. We will designate it β-$ScBO_3$, in contrast to the calcite phase α-$ScBO_3$. Single crystals of α-$ScBO_3$ are commonly grown from high-temperature solutions [6, 9, 16].

Techniques for the preparation and characterization of RBO_3 powders were described in [5, 10–13, 17–21].

Rare-earth orthoborates can be synthesized by reacting rare-earth oxides with boric anhydride or boric acid at 850–1300°C [5, 20, 21] for several hours with intermediate grindings. The effectiveness of this process is limited by the high volatility of boric anhydride above 1000°C, which impedes the preparation of single-phase material.

Steele and Decius [21] reported the synthesis of granular lanthanum, scandium, and indium orthoborates via dissolution of appropriate oxides in nitric acid with boric acid additions, followed by boiling down the solution.

Lou *et al.* [10] and Boyer *et al.* [11] investigated in detail the classic sol–gel process for the preparation of rare-earth borates from appropriate metal alkoxides (based on isopropanol) and a so-called "sol–gel mineral" process: precipitation of hydrous borates from acid solutions via neutralization with ammonia, followed by calcination. Reports on $ScBO_3$ synthesis by these processes are not available in the literature.

Newnham *et al.* [13] reported the preparation of rare-earth borates from rare-earth nitrate solutions by adding an ammoniacal solution of ammonium pentaborate, followed by filtration and calcination of the precipitate at 1200°C. The excess of the forming boron oxide volatilized at 1400°C.

Using indium borate as a test system, we developed a method for the preparation of nanocrystalline powders through so-called borate rearrangement [17, 18]. During heating, hydrous borate precipitates loose water and turn into an amorphous state. As a result, crystallization occurs upon a significant superheating, is accompanied by active heat release, and leads to the formation of very small particles.

---

[1] Presented in part at the XI National Conference on Crystal Growth, Moscow, Russia, December 14–17, 2004.

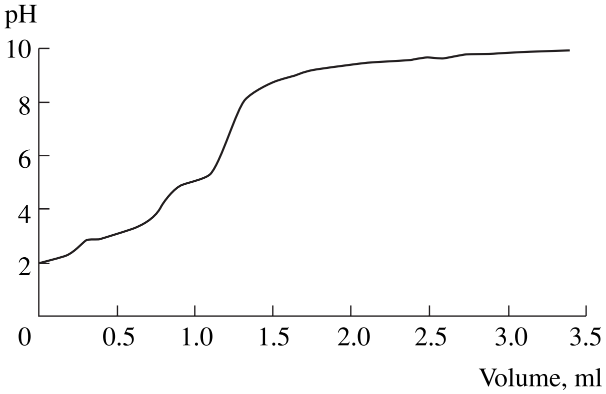

Fig. 1. Solution pH as a function of the volume of added aqueous ammonia for the titration of a scandium borate nitrate solution (precipitation of a precursor to α-$ScBO_3$).

The purpose of this work was to prepare scandium orthoborate powders by this method.

EXPERIMENTAL

As starting chemicals, we used reagent-grade scandium nitrate $Sc(NO_3)_3 \cdot 4H_2O$, reagent-grade boric acid H_3BO_3, OSCh 12-3 boric anhydride B_2O_3, analytical-grade aqueous ammonia (RF State Standard GOST 3760-79), and distilled water. Metaboric acid, HBO_2, was prepared by dehydrating boric acid at 150°C. We obtained the metastable form HBO_2-II with lattice parameters $a = 7.12$ Å, $b = 8.84$ Å, $c = 6.77$ Å, and $\beta = 93.3°$ (JCPDS PDF, 22-1109).

An $Sc(NO_3)_3$ solution (0.029 ± 0.001 M) was prepared by heating scandium nitrate powder in distilled water (50–60°C). Boric acid solutions were prepared by dissolving B_2O_3 in boiling water (0.161 M in terms of H_3BO_3) and by dissolving HBO_2 in cold water (0.227 M). The scandium nitrate solution and one of the acid solutions were poured together, and the mixture was titrated by aqueous ammonia until the formation of a gel-like precipitate. During titration, we monitored the solution pH (Hanna Instruments Checker) as a function of the volume of added NH_4OH (Fig. 1). The precipitate was collected on a two-layer ashless blue ribbon filter paper, repeatedly washed with water, and left to dry in air for 2–3 days.

Thermal analysis (DTA + TG + DTG) was carried out with a MOM Q-1500 system in air. Samples were placed in alundum crucibles and heated to 1000°C at a rate of 10°C/min. XRD measurements were performed on a DRON-2 powder diffractometer with CuK_α radiation. Raman spectra were recorded on a Spex Ramalog 1403 (1-41) spectrometer under excitation with the 488-nm argon laser (ILA 120) line. Powder morphology was examined by scanning electron microscopy (SEM) on a JEOL-5910. To prevent specimen charging, a gold layer was evaporated onto the powder.

RESULTS AND DISCUSSION

Our results demonstrate that both forms (α and β) of $ScBO_3$ can be prepared by precipitation from aqueous solutions followed by calcination, depending on the

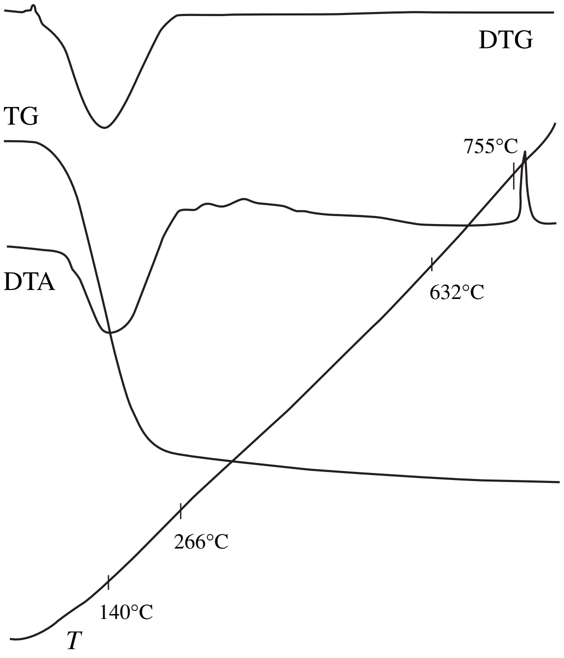

Fig. 2. Thermal analysis of solvated scandium borate prepared using B_2O_3; sample weight of 304.5 mg, heating to 1000°C.

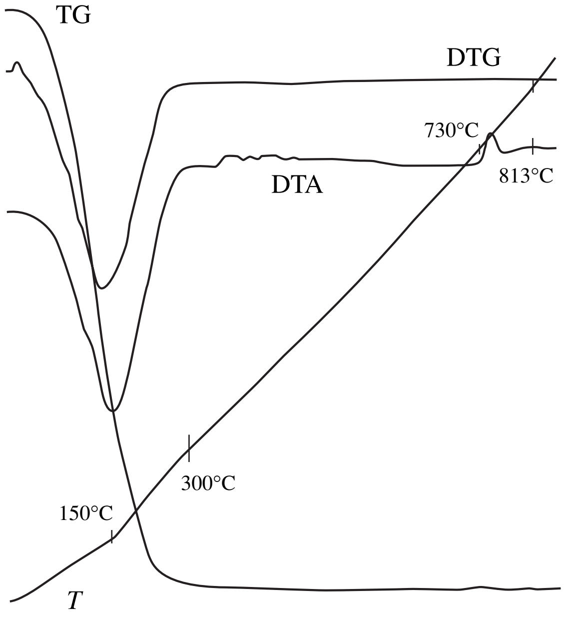

Fig. 3. Thermal analysis of solvated scandium borate prepared using metaboric acid; sample weight of 207 mg, heating to 1000°C.

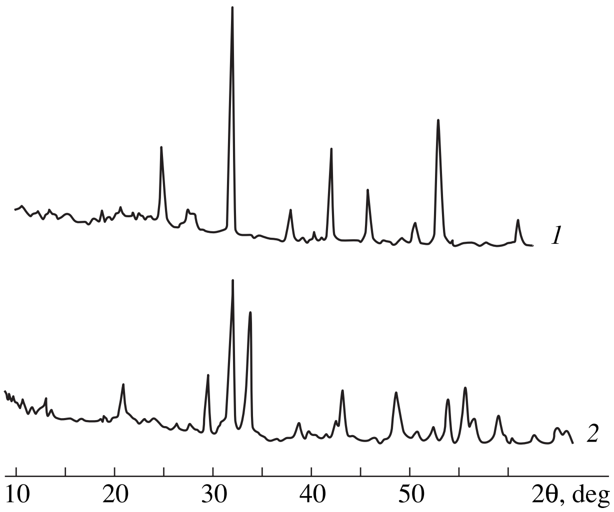

Fig. 4. XRD patterns of scandium orthoborate samples: (*1*) α-$ScBO_3$, prepared using HBO_2; (*2*) β-$ScBO_3$, prepared using B_2O_3.

acid solution used. We obtained α-$ScBO_3$ using HBO_2 and β-$ScBO_3$ using B_2O_3 as a starting reagent.

Titration of the nitrate solution of scandium and boric acids with aqueous ammonia leads to the formation of a white gel-like precipitate, which settles to the bottom in several hours. The process reaches completion at pH 8.2 (Fig. 1). The precipitate thus obtained is x-ray amorphous.

According to thermal analysis results (Figs. 2, 3), the precipitate looses nearly all of the water in the range 150–300°C. The sample prepared with the use of B_2O_3 (Fig. 2) looses 94 wt % on heating to 300°C and an additional 2 wt % on heating to 632°C. At 755°C, an exothermic event begins. For the sample prepared using HBO_2 (Fig. 3), the weight loss in the range 150–300°C is 96%, and the exotherm begins at 730°C.

The XRD patterns taken after heating the samples to 1000°C in DTA scans are displayed in Fig. 4. The sample prepared with the use of B_2O_3 has the calcite structure (α-$ScBO_3$). The lattice parameters computed with Powder-2 in space group $R\bar{3}c$ (rhombohedral symmetry) agree with those reported by Levin [12]: a = 4.736 Å, c = 15.34 Å. The XRD pattern of the sample prepared with the use of HBO_2 is very similar to that reported by Keszler and Sun [15] for β-$ScBO_3$, but we failed to index it or to determine the lattice parameters.

The Raman spectra of the two scandium borate polymorphs are shown in Fig. 5. The spectrum of α-$ScBO_3$ (spectrum *2*) shows peaks at 237, 365, 644, 936, 1220, and 1470 cm^{-1}, which correspond to the vibration frequencies of the $[BO_3]^{3-}$ ion in the structure of α-$ScBO_3$ (calcite type). As shown by Voron'ko *et al.* [22], the Raman spectrum of $InBO_3$ differs in the relative intensities of peaks due to $[BO_3]^{3-}$ from the spectra of other orthoborates, e.g., $LuBO_3$. In particular, the totally symmetric mode of the $[BO_3]^{3-}$ anion near 930 cm^{-1} is comparatively weak, which is attributable to the significant covalent contribution to the indium–oxygen bonds. This makes the free $[BO_3]^{3-}$ anion approximation inapplicable in the case of $InBO_3$. As

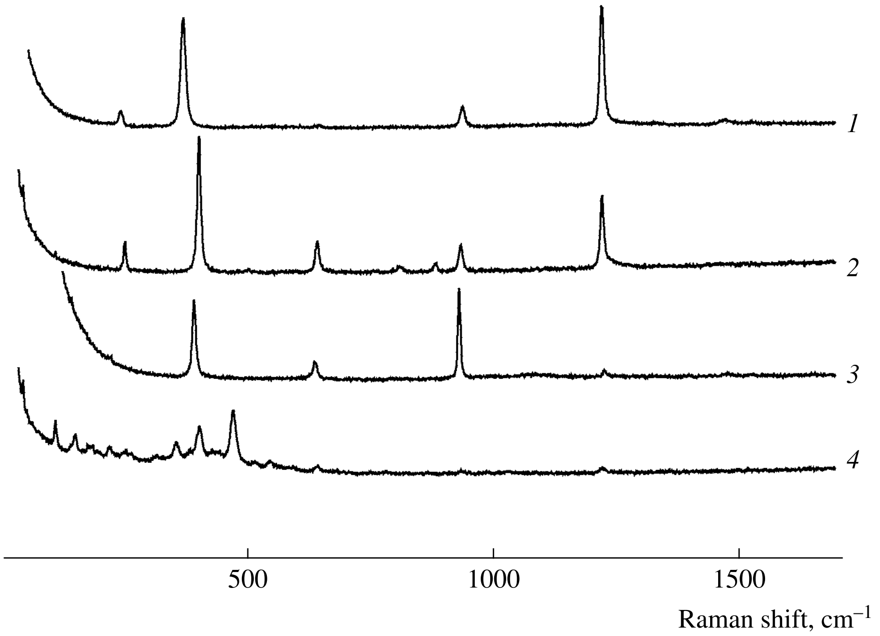

Fig. 5. Raman spectra of (*1*) $InBO_3$, (*2*) α-$ScBO_3$, (*3*) $LuBO_3$ (calcite structure), and (*4*) β-$ScBO_3$.

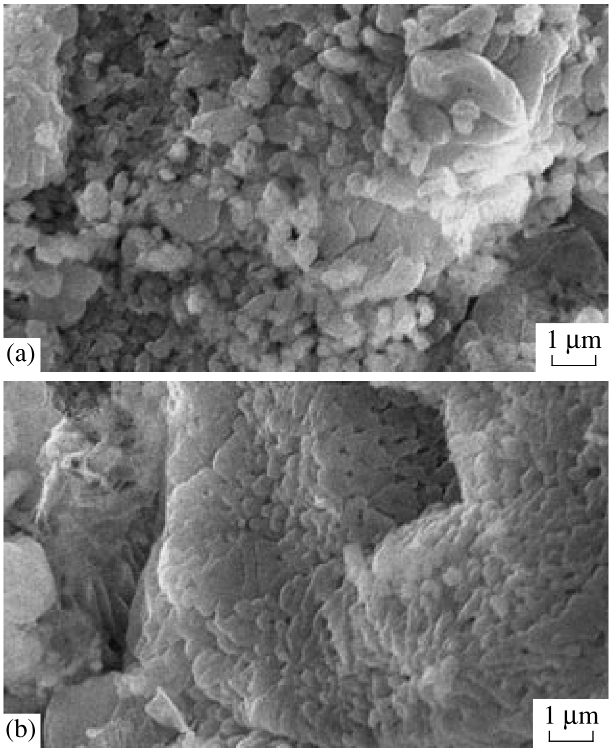

Fig. 6. SEM micrographs of borate powders after heating to 1000°C: (a) α-$ScBO_3$, prepared using metaboric acid; (b) β-$ScBO_3$, prepared using B_2O_3.

seen in Fig. 5, the Raman spectrum of α-$ScBO_3$ (spectrum *2*) is similar in relative intensities to that of $InBO_3$ (spectrum *1*), which attests to predominantly covalent scandium–oxygen bonding.

The Raman spectrum of β-$ScBO_3$ (Fig. 5, spectrum *4*) differs drastically from the other three spectra in Fig. 5, suggesting that this borate contains no $[BO_3]^{3-}$ ions in a triangular configuration.

According to SEM results (Fig. 6), the synthesized powders consist of submicron-sized particles. The α-$ScBO_3$ particles (Fig. 6a) are not faceted and exhibit no cleavage, in contrast to what is typical of calcite-structure materials.

The processes observed during heating of scandium borate precipitates seem to be due to so-called borate rearrangement [23, 24], which was observed earlier in $InBO_3$ synthesis [18]. During dehydration, the crystal lattice of borates breaks down, and the material becomes amorphous. Further heating leads to exothermic crystallization, well-observed in the DTA curve. Figure 6b illustrates the transformation of amorphous material into crystalline grains. Since crystallization occurs very rapidly, it is not surprising that the resulting crystalline particles are very small in size. The particle size of $ScBO_3$ can be reduced further by terminating heating immediately after the exothermic event.

$ScBO_3$ synthesis through precipitation of hydrous borates from aqueous solutions followed by calcination was not reported previously. This approach has the advantages of ease for implementation and low energy consumption. The powders thus synthesized can be used both in fabricating phosphors and in preparing charges for the crystal growth of $ScBO_3$ and scandium rare-earth borates.

Thus, borate rearrangement appears to be a viable approach to producing nanoparticles and fine powders of various borates.

ACKNOWLEDGMENTS

We are grateful to A.A. Sobol' (Prokhorov General Physics Institute, Russian Academy of Sciences) for useful discussions and to Rachid Mahiou (Université Blaise Pascal, Clermont-Ferrand, France) for his continuous interest in our work.

REFERENCES

1. Balcerzyk, M., Gontarz, Z., Moszynski, M., *et al.*, Future Hosts for Last and High Light Output Cerium Doped Scintillator, *J. Lumin.*, 2000, vols. 87–89, pp. 963–966.
2. Dorenbos, P., Exchange and Crystal Field Effects on the $4f^{n-1}5d$ Levels of Tb^{3+}, *J. Phys.: Condens. Matter*, 2003, vol. 15, pp. 6249–6268.
3. Lebedev, V.A., Pisarenkov, V.F., Chuev, Yu.M., *et al.*, Study of Energy Transfer from Yb^{3+} to Er^{3+} in Rare-Earth Silicates and Borates, *J. Lumin.*, 1997, vols. 72–74, pp. 942–944.
4. Dotsenko, V.P., Berezovskay, I.V., and Efryushina, N.P., Photoionization and Luminescence Properties of Bi^{3+} in $In_{1-x}Lu_xBO_3$ Solid Solutions, *J. Phys. Chem. Solids*, 1996, vol. 57, no. 4, pp. 437–441.
5. Gaewdang, T., Chaminado, J.P., Garcia, A., *et al.*, Luminescence of Ce^{3+} in the $In_{1-x}Sc_xBO_3$ $(0 \le x \le 1)$ Solid Solutions, *J. Phys. Chem. Solids*, 1994, vol. 55, no. 6, pp. 501–504.
6. Durmanov, S.T., Kuzmin, O.V., Kuzmicheva, G.M., *et al.*, Binary Rare-Earth Scandium Borates for Diode-Pumped Lasers, *Opt. Mater.*, 2001, vol. 18, pp. 243–284.
7. Xifa Long, Xhoubin Lin, Zushu Hu, *et al.*, Optical Study of Cr^{3+}-Doped $LaSc_3(BO_3)_4$ Crystal, *J. Alloys Compd.*, 2002, vol. 347, no. 1/2, pp. 52–55.
8. Leonyuk, N.I., Relation between Structural Features and Crystallization Mechanisms of Non-linear Optical Borate Materials, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.,* 2000, vol. 56, suppl., p. 378.
9. Lai, S.T., Chai, B.H., Long, M., and Morris, R.C., $ScBO_3$:Cr—A Room Temperature Near-Infrared Tunable Laser, *J. Quantum Electron.*, 1986, vol. 22, pp. 1931–1933.
10. Lou, L., Boyer, D., Bertrand-Chadeyron, G., *et al.*, Sol–Gel Waveguide Thin Film of YBO_3: Preparation and

Characterization, *Opt. Mater.*, 2000, vol. 15, no. 1, pp. 1–6.

11. Boyer, D., Leroux, F., Bertrand, G., and Mahiou, R., Local Structure of $LuBO_3$ Prepared via Sol–Gel Process and Its Transformation with Temperature: 11B-NMR and *L*-Edge XAS Studies, *J. Non-Cryst. Solids,* 2002, vol. 306, no. 2, pp. 110–119.
12. Levin, E., The System Sc_2O_3–B_2O_3, *J. Am. Ceram. Soc.*, 1967, vol. 50, no. 1, pp. 53–54.
13. Newnham, R.E., Redman, M.J., and Santaro, P.P., Crystal Structure of Yttrium and Other Rare-Earth Borates, *J. Am. Ceram. Soc.*, 1963, vol. 46, no. 6, pp. 253–255.
14. Maximov, E.G., Shport, D.A., and Ivanov, O.V., Microscopical Calculations of Lattice Dynamics of Ionic Crystals and Its Dependence on the Pressure, *Solid State Commun.,* 1997, vol. 101, no. 6, pp. 393–396.
15. Keszler, D.A. and Sun, H., Structure of $ScBO_3$, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, vol. 44, no. 9, pp. 1505–1507.
16. Rudenko, V.V., Flux Growth of MBO_3 Crystals, *Neorg. Mater.*, 1998, vol. 34, no. 12, pp. 1483–1485 [*Inorg. Mater.* (Engl. Transl.), vol. 34, no. 12, pp. 1253–1254].
17. Tkatchenko, E.A., Fedorov, P.P., Kuznetsov, S.V., and Voronov, V.V., Synthesis of Indium and Lanthanum Orthoborates Nanoparticles by Sol–Gel Mineral Technique, *Nanoparticles, Nanostructures, and Nanocomposites: Top. Meet. of the Eur. Ceram. Soc.,* St. Petersburg, 2004, pp. 74–75.
18. Tkachenko, E.A., Fedorov, P.P., Voronov, V.V., *et al.*, Synthesis of Nanocrystalline Indium Borate through Borate Rearrangement, *Zh. Neorg. Khim.,* 2005, vol. 50, no. 5, pp. 754–758.
19. Wei, Zh., Sun, L.D., Liao, Ch.-Sh., *et al.*, Synthesis and Size Dependent Luminescent Properties of Hexagonal $(Y,Gd)BO_3$:Eu Nanocrystals, *J. Mater. Chem.,* 2002, vol. 12, pp. 3665–3670.
20. Huppert, H., von der Eltz, B., Hoffmann, R.D., and Piotrowski, H., Multianvil High-Pressure Synthesis and Crystal Structure of the New Rare-Earth Orthoborates χ-$DyBO_3$ and χ-$ErBO_3$, *J. Solid State Chem.,* 2002, vol. 166, pp. 209–212.
21. Steele, W.C. and Decius, J.C., Infrared Absorption of La, Sc, and In Borates and the Force Constants of Borate Ion, *J. Chem. Phys.*, 1956, vol. 25, no. 6, pp. 1184–1188.
22. Voron'ko, Yu.K., Dzhurinskii, B.F., Kokh, A.E., *et al.*, Raman Spectroscopy and Structure of $InBO_3$, *Neorg. Mater.*, 2005, vol. 41, no. 9, pp. 1119–1124 [*Inorg. Mater.* (Engl. Transl.), vol. 41, no. 9, pp. 984–989].
23. Nikolaev, A.V., *Fiziko-khimicheskoe izuchenie prirodnykh boratov* (Physicochemical Characterization of Natural Borates), Moscow: Akad. Nauk SSSR, 1947.
24. Shvarts, E.M. and Dzene, A.E., *Boraty i boratnye sistemy* (Borates and Borate Systems), Riga: Zinatne, 1978, pp. 101–111.