

[o.m1.p19] Relations Between Structural Features and Crystallization Mechanisms of Non-Linear Optical Borate Materials. N.I. Leonyuk, *Dept. of Crystallography and Crystallochemistry, Geological Faculty, Lomonosov Moscow State University, Moscow 119899, Russia*
 Keywords: crystallization, borates, crystal chemistry.

In this paper, an attempt was made to examine crystallochemically crystal growth processes of the most important borates with device potential, in order to develop advantageous crystal growth technologies for these new materials.

Orthoborates: $RM_3(BO_3)_4$ ($R = Y, La - Lu, In$ or Bi , and $M = Al, Sc, Cr, Fe, Ga$), $RECa_4(BO_3)_4$, $InBO_3$, $BaCaBO_3F$, $Ba_7(BO_3)_3F_5$, $KBe_2BO_3F_2$. The growth of orthoborate crystals is restricted mostly by the transfer of BO_3 triangles from an associated state of strain, due to linked B-O bonds (about 520 kJ/mole), to separated isolated state at the solid/liquid interface. The change in the coordination number of boron atoms from 4 (in complex borate melts) to 3 (in solids) cannot be excluded, and it is also associated with a high energy consumption. A wide range of complex melts, first of all, based on the alkali molybdates and tungstates will be proposed to destroy boron-oxygen polymers and intensify mass transfer in the orthoborate crystallization process. The fluorides will also destroy the polymers, and they would be preferable for the crystal growth of fluorine-containing orthoborates.

Pyro- and metaborates: $Mg_2B_2O_5$, $Cd_2B_2O_5$, $KNbOB_2O_5$, BaB_2O_4 . Isolated B_2O_5 pyroborate dimers and B_3O_6 metaborate rings most likely occur in the borate melts, in particular, if the complex melts contain a rather large cations like Na^+ , K^+ , Mg^{2+} , Cd^{2+} , and even Ba^{2+} . There is a correlation between the fluxed melt composition and the temperature ranges, in which metaborate chains transform into metaborate rings, and the BBO crystallizes in the low temperature modification. To optimize the crystal growth of pyro- and metaborates, the complex melt compositions and temperature ranges for formation of isolated B_2O_5 pyroborate dimers, B_3O_6 metaborate rings and B_nO_{2n} metaborate chains will be discussed.

Polyborates: $Li_2B_4O_7$, LiB_3O_5 , CsB_3O_5 , SrB_4O_7 , $Sr_2Be_2B_2O_7$, $SrLiB_9O_{15}$. In this case, there are substantial restrictions to transport very large B_nO_m polymers from the melts into the crystal structure that practically has the same polyanion configurations with covalent boron-oxygen bonds. A major problem which awaits clarification concerns the detailed mechanism of polyanion reconstruction along the specific liquid polymer/solid polymer interface. In this connection, a role of various cations as a catalysts will be considered to promote these polyborate to crystallize. This assumption is based on the growth of LiB_3O_5/CsB_3O_5 crystals from non-stoichiometric melts with some excesses of Na_2O , K_2O , MoO_3 and WO_3 .

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[o.m1.p20] Polar Phase in Alkaline and Thallium Fluoroberyllates at Room Temperature? C. González-Silgo^a, J. González-Platas^a, J. Rodríguez-Carvajal^b, M.L. Martínez-Sarrión^c & L. Mestres.^c ^a *Departamento Física Fundamental II, Universidad de La Laguna, Tenerife, Spain.* ^b *Laboratoire Léon Brillouin, CEA-CNRS, CE Saclay, France.* ^c *Departamento de Química Inorgánica, Universitat de Barcelona, Spain.*

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Alkaline fluoroberyllates are exceptional cases, inasmuch as they do not have a β - K_2SO_4 structure at room temperature¹. The difficulty in obtaining good single crystals has limited dielectric and structural studies. Recently we have studied² the K_2BeF_4 compound by standard X-ray powder diffraction, thermal analysis and Raman scattering. We have suggested that the room temperature phase belongs to the $Pna2_1$ space group. However, the structure refinement at room temperature (ferroelectric phase) is not exhaustive and the structure at higher temperatures (paraelectric phase) has not been resolved. Cs_2BeF_4 and Rb_2BeF_4 also undergo structural phase transition at higher temperatures but these have not yet been analysed. Both Neutron and X-ray diffraction experiments at room temperature were carried out with polycrystalline samples. The program FULLPROF³ was used for crystal refinement. Several options were used in order to determine structural anomalies: (a) Rigid Body refinement of BeF_4^{2-} tetrahedral groups. (b) Multipattern refinement (c) Stereochemical restraint based on the bond valence rules⁴. Comparison of these results with other A_2BX_4 compounds with a β - K_2SO_4 structure suggests that the frequently observed symmetries could be fully described.

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