Comparative Study of Framework Borates Optical Nonlinearities

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One of the pressing problems of modern crystallography and crystal chemistry is construction of noncentosymmetric crystal structures with high with second-order optical susceptibilities. Good solution to the problem may be using of the boron oxide framework matrix as a host for the high-polarizable metal cations. The recently discovered members of the known family of non-centrosymmetric halogen-pentaborates ($M_2B_5O_9Hal$, M = Ca, Sr, Ba, Pb, Eu, Hal = Cl, Br) with hilgardite-type structure are attractive due to their second harmonic generation (SHG) activity. In particular, lead derivative phases demonstrate SHG comparable with well-known BIBO (BiB_3O_6) crystal. The compounds of this family possess zeolite-like framework structures. As it was shown only metals mentioned above stabilize the structural type of hilgardite. Our attempts to obtain other representatives of this family with the same stochiometry lead to producing another structure type of framework halogen borates – boracites stoichiometry $M_3B_7O_{13}Hal$. They are characterized by a zeolite-like 3D non-centro-symmetric structure. We report comparison of our experimental and theoretical results on SHG efficiency for hilgardite and boracite families' members. The experiments show an order less SHG efficiency for boracites relative to hilgartdites. Computational methods developed by Phillips and Van Vechten and approached by Zhang to complex crystals were performed to explain corresponding difference in optical second-order nonlinearities of the crystals. Sequence of compounds in both families according to their SHG efficiencies conforms to the theoretically predicted values.

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