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Review

The role of cations in second-order nonlinear optical materials based on π-conjugated $[BO_3]^{3-}$ groups

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ABSTRACT

Nonlinear optical (NLO) materials play a significant role in laser science and technology as they can efficiently expand the fixed (or limited) wavelengths of common laser sources. π-Conjugated $[BO_3]^{3-}$ groups are widely accepted to be one of the most desirable structural groups of NLO materials. A number of NLO materials are composed of $[BO_3]^{3-}$ groups and some of them have been commercially produced and used. The anionic group theory tells researchers what kind of arrangement for anionic groups is beneficial to generate large second-order NLO responses; nevertheless, it does not answer the key question that how to realize the desirable arrangement of anionic groups. Here we systematically review NLO materials with $[BO_3]^{3-}$ groups to provide a deep understanding on the underlying structure-properties relationship between the microscopic electronic configuration of π-conjugated $[BO_3]^{3-}$ groups and macroscopic optical properties of NLO materials. More importantly, some findings can be concluded. Firstly, the cationic MO_xF_y (x = 3, 4, 5, 6, 8; y = 0, 1, 2) polyhedron with three equatorial oxygen atoms are prone to make the $[BO_3]^{3-}$ groups in coplanar and aligned arrangement around the base of a polyhedron, which is beneficial to generate sufficiently large second-harmonic generation and moderate birefringence (or good phase-matchability). Secondly, in some cases the secondary cations (ions with less electronegativy) in one compound have an additional effect on the overall arrangement of $[BO_3]^{3-}$ groups. This work would shed useful insights on how to rationally design and synthesize new superior NLO materials with $[BO_3]^{3-}$ groups.

Contents

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1. Introduction

Nonlinear optical (NLO) materials, as the core devices of solid-state laser systems, can efficiently expand frequency range of common laser sources, which play a significant role in the field of laser-related science and technology, for example, semiconductor manufacturing, photolithography, optical storage, and high-capacity communication networks [1–6]. To be optically applicable, a NLO material must satisfy several fundamental but rigorous requirements on the structure-directing optical properties: wide transparent window, large second-harmonic generation (SHG) response, sufficient birefringence to achieve phase matching, good chemical stability and easy growth of large high-quality single crystals [7]. During the past decades, various NLO materials have been discovered, including borates, carbonates and silicates [8–15]. Among these NLO materials, borates have predominance in applications and some of them, such as β-BaB_2O_4 [16] and LiB_3O_5 [17] are commercially manufactured and used widely for frequency conversion in NLO devices and modern laser systems.

In order to efficiently explore new NLO materials, anionic group theory was proposed by Chen et al. to explain the structure-optical properties [18]. The main points of this theory include: (1) anionic groups are the main contributors to the NLO effect; (2) the macroscopic SHG coefficients can be calculated by summing up the second-order polarizabilities (χ^2) of the constituent anionic groups; (3) the contributions of cations to the macroscopic NLO effect are nearly neglectable. Base on this theory, continued explorations led to a lot of promising NLO borates, such as, $KBe_2BO_3F_2$ (KBBF) [19], $Sr_2Be_2B_2O_7$ (SBBO) [8], $K_2Al_2B_2O_7$ [20,21], β-$Rb_2Al_2B_2O_7$ [22], $BaAl_2B_2O_7$ [20], $YAl_3(BO_3)_4$ [23], $Cd_4BiO(BO_3)_3$ [24], $K_3B_6O_{10}Cl$ [25], $Ba_4B_{11}O_{20}F$ [26], $ABe_2B_3O_7$ (A = K, Rb) [27], $NaSr_3Be_3B_3O_9F_4$ [28], $Ba_3(ZnB_5O_{10})PO_4$ [29], Bi_3TeBO_9 [30], Pb_2BO_3Cl [31], $Pb_2(BO_3)(NO_3)$ [32], $Li_4Sr(BO_3)_2$ [11], $K_3Ba_3Li_2Al_4B_6O_{20}F$ [33], $Li_2B_6O_9F_2$ [34] and $NH_4B_4O_6F$ [35]. In particular, KBBF crystal can generate coherent light covering the region below 200 nm through direct SHG process, which is ascribed to the perfectly coplanar and aligned $[BO_3]^{3-}$ anionic groups in the structure of KBBF according to the anionic group theory.