Coordination Chemistry Reviews 374 (2018) 464–496

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Second-order nonlinear optical crystals with mixed anions

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ARTICLE INFO

Article history:
Received 15 May 2018
Accepted 17 July 2018

Keywords:
Mixed anions
Crystal structure
NLO property
Structure-property relationship

ABSTRACT

Crystals with mixed anions refer to inorganic salts containing at least two types of anions or anionic groups, and these anions can be Q^{2-} (Q = O, S, Se, Te) and X^- (X = F, Cl, Br, I), and anionic groups include various B–O groups, $(OH)^-$, $(IO_3)^-$, $(CO_3)^{2-}$, $(SiO_4)^{4-}$, $(NO_3)^{3-}$ and $(PO_4)^{3-}$. Recently, in view of the insufficiency and strong requirements of second-order nonlinear optical (NLO) crystals, especially ones in the deep ultraviolet (DUV) and middle and far-infrared (MFIR) regions, the study of NLO crystals have received intensive interest from researchers. For a NLO crystal candidate, desirable properties include large NLO coefficients, high laser-induced damage threshold values, phase matchabilities and wide transparent windows. The availability of the former two properties is especially problematic since the structural factor influences them in reverse order. To balance them, it is necessary to introduce different anions into the structure to induce them to function differently. Under the guidance of anionic group theory and the functional moiety concept, many NLO crystals with mixed anions have been obtained. However, to date, a systematic survey of this topic has not been carried out. In this review, recently reported NLO crystals with mixed anions are summarized, the contents of which are mainly focused on their crystal structures and NLO behaviors, together with the relationship between these two aspects. It is hoped that this work will provide a useful perspective on the most promising NLO candidates.

Contents

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https://doi.org/10.1016/j.ccr.2018.07.013
0010-8545/

1. Introduction

Second-order nonlinear optical (NLO) crystals can be applied to the identification of chemicals and explosives, detection of DNA and cancer, imaging of drugs, laser display, laser printing, photoetching and other processes [1]. Considering societal development and the increasing requirements for NLO crystals, it is necessary to explore crystals with outstanding NLO properties, especially those with large NLO coefficients, high laser-induced damage thresholds (LIDTs) and phase matchability. According to the transparent ranges, NLO crystals can be classified into four subgroups; namely, those in the deep ultraviolet (DUV), ultraviolet (UV), visible and near-infrared (Vis-NIR), and middle and far-infrared (MFIR) regions. UV and Vis-NIR NLO crystals have been maturely developed, and the most representative ones of those are β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO), KH_2PO_4 (KDP) and $KTiOPO_4$ (KTP). Although several DUV and MFIR NLO crystals have been commercialized, such as $KBe_2BO_3F_2$ (KBBF), $AgGaS_2$ (AGS) and $ZnGeP_2$ (ZGP), they are far from meeting market requirements, owing to their inherent disadvantages. Therefore, it is important