Nonlinear Optical Properties Of Mixed Oxides $CsB^{V}MoO_6$ (B^{V}=Nb,Ta)

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Inorganic NLO crystals are especially promising for such a purpose because of their resistance to high-power radiation beams. Here we focus on the defective pyrochlores based on mixed oxides of MoO_3, Ta_2O_5, Cs_2O, Nb_2O_5 which were synthesized recently[1]. However, variation in the chemical composition and ionic disorder lead to a large number of crystalline modifications and complicate the studies of NLO properties for many inorganic materials. To assist in these studies, it would be helpful to perform a rapid theoretical screening of the optical properties for possible crystalline modifications. It can be solved by quantum-chemical calculations. One of the methods available is the coupled-perturbed Hartree-Fock (Kohn-Sham) method CPHF/KS, which was implemented in CRYSTAL program[2]. Here we predict SHG activity of defective pyrochlore crystals $CsB^{V}MoO6$ (B^{V}=Nb,Ta) by CPHF/KS method using HF and DFT/PBE0 formalism within two basis sets. To estimate the accuracy of these predictions, we benchmark our methods on the crystals of KH_2PO_4 (KDP), $LiNbO_3$, $(NH_2)_2CO$ (urea), and α-SiO_2 where reliable experimental are data available. Additionally, we studied the influence of the statistical disorder arising due to the different occupations of d-metal sublattice positions by atoms Mo or B^{V} on the NLO properties. We calculated both linear optical properties (refractive indices and linear polarizabilities) and nonlinear ones (first hyperpolarizabilities and nonlinear optical tensors) for different isomers $CsNbMoO_6$ and $CsTaMoO_6$ at different levels of theory. The results obtained allow to make the following conclusions: (1) the best agreement of the calculated nonlinear optical parameters with experiment is achieved in the case of calculations at the DFT/PBE0 level with the POB-TZVP basis;(2) agreement between the calculated quantities and the experimental data is accomplished when the dimensionless relative NLO activity $\rho=\eta_i/\eta_X$ is used for this comparison (η_i is the ratio of powers of the single and double frequency rays for the unknown compound, η_X is the same ratio for the reference compound); (3) the calculated NLO characteristics $\rho(CsNbMoO_6/LiNbO_3)$=0.0161 and $\rho(CsTaMoO_6/LiNbO_3)$=0.0219; (4) the symmetry of the sublattices of disordered atoms significantly affects the SHG parameters of the crystal and the values of the calculated parameters for sublattices of different symmetry can differ by an order of magnitude.

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