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Linear and nonlinear properties of ultraviolet fluorine crystal: A first-principles study

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ABSTRACT

The electronic structure and optical properties of Deep Ultraviolet (DUV) nonlinear optical crystal $BaMgF_4$ and $KBe_2BO_3F_2$ have been studied in the framework of many-body perturbation theory as well as hybrid functionals. For the electronic properties, the hybrid functionals method makes significant improvement on description of electronic band gap for both crystals. However, the results still underestimate the band gap comparing with the *GW* results. By considering the self-energy of electrons, electronic band gap and the optical band gap are both described well comparing with the experimental results, which is crucial for prediction the performance of DUV crystals in the DUV region. In addition to the remarkable self-energy effect, the macroscopic dielectric function and related optical properties, such as refractive index $n(\omega)$, excitation coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, energy-loss function $L(\omega)$, and reflectivity $R(\omega)$ have been calculated by solving Bethe–Salpeter equation (BSE). By comparing the RPA results and BSE results, we found that the excitonic effects play an important role in description of optical properties, which is absence in the previous work. Furthermore, taking advantage of $2n+1$ theorem, the nonlinear optical susceptibility have been calculated as well. As all key factors that determine the performance of DUV nonlinear crystals have been addressed theoretically, our present work pave the way using first-principle theory to assist the crystal engineering for other candidates of DUV nonlinear optical crystal.

1. Introduction

Deep-ultraviolet (DUV) laser below 200 nm attract great interest in photoemission spectroscopy, laser spectroscopy, semiconductor photolithography, micromachining and photochemical synthesis [10,27]. DUV all-solid-state laser through direct frequency-doubled present great application merits and markets for its simplicity, stability, narrower spectral bandwidth, better beam quality and easier maintenance compared to other DUV coherent light devices.

There are several nonlinear optical (NLO) crystals, such as BBO, CLBO and LBO can produce DUV laser by nonlinear frequency conversion [17,19]. However, for DUV region below 200 nm, they can only be used with sum-frequency mixing, which makes the laser system complex and efficiency low. So the ferroelectric fluoride named $BaMgF_4$ and $KBe_2BO_3F_2$ which show a wide transparency range and good nonlinear optical properties attract great attention [26,3]. Their cut-off wavelength in the DUV side is up to 125 nm and 150 nm respectively [21,8]. In the last decade, both of the two fluoride had been investigated by theoretical and experimental methods. Theoretically, Lin et al. performed the density functional theory (DFT) with both local density approximation (LDA) and generalized gradient approximation (GGA) to investigate the crystal structure, electronic properties, linear and nonlinear optical properties of the two crystals [12,7,11,9]. Moreover, using the anionic group theory, the mechanism of the linear and nonlinear optical effects was elucidated as well. Experimentally, Buchter et al. demonstrated the periodically reversed ferroelectric domains of $BaMgF_4$, which make it theoretically possible to produce 125 nm DUV radiation through the quasi-phase-matching (QPM) method [1]. Recently, Chen et al. measured the second, third-order nonlinear optical characterizations as well as self-phase modulation of $BaMgF_4$ through Z-scan method [4].

Although the $BaMgF_4$ and KBBF are good candidates for the applications of DUV all-solid state laser, both of them has their own *pro and cons*. For KBBF, it is too fragile to grow because of its

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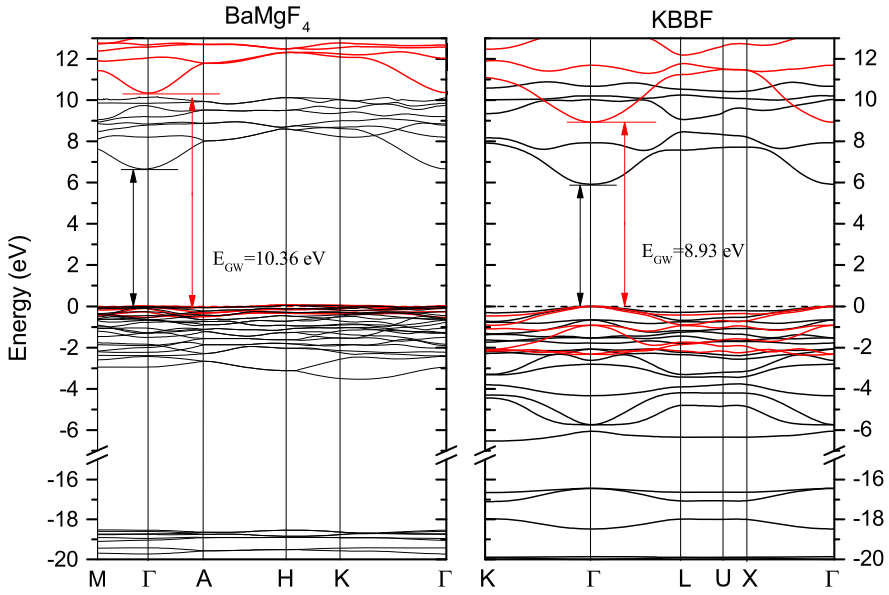

Fig. 1. (Color online) Band structure of $BaMg_4$ (a) and KBBF (b) along; the high symmetry line; the solid black lines are LDA results and the solid red lines are *GW* results. Fermi level is set at the top of the valence bands for both LDA and *GW* results.

Table 1
Calculated fundamental bandgaps (given in eV) of $BaMgF_4$ and $KBe_2BO_3F_2$ comparing with other calculation.

Crystals	Electronic band gap		
	DFT	HSE06	*GW*
$BaMgF_4$	6.55(6.66)	9.50	10.36
$KBe_2BO_3F_2$	5.92(5.66)	8.92	8.93

strong layer tendency along the *z*-axis, make it hard to grow thicker then even 2 mm [2]. Besides, the composition used to grow the crystal is toxic. For $BaMgF_4$, the birefringence of this crystal is too small (0.02) to directly archive the birefringent phase matching in the DUV region. Since the difficulty of crystal growing and the limitations of the experiment, theoretical investigation could be a promising tool to assist the crystal engineering to find candidates possess more attractive properties. However, the 'bandgap problem' due to the absence of self-interaction effect as well as the 'independent-electron picture' of random-phase approximation for calculating linear optical properties, make the DFT-level calculations not accurate enough to predict the electronic gap nor optical gap for new DUV nonlinear optical crystals [23,20,18]. For the 'bandgap problem', there are three scheme to overcome it, which are Hubuardd U method, hybrid functionals and *GW* corrections. The first one is most efficient but only suitable for the localized orbitals such as *d*, *f* electrons of the system; the second one is also system dependent and the determination of mixing factor β make this scheme is not 'purely' *ab initio*; and the last one is more 'physical' than above two methods, however, the consumption of the computation is unbearable for big systems. For the linear optical calculation, the independent particle approximation, known as RPA, make the theory not suitable for describing the process between N and $N+1(N-1)$ systems. As a result, the *GW* method and corresponding *BSE* method become natural for calculating the properties of such materials. To the best of our knowledge, there is no systematical calculations of electronic and optical properties based on many-body theory for the existing two wide-gap nonlinear optical crystals. Therefor, in this work, the calculations based on many-body theory were performed for the electronic and optical properties of the two crystals. The hybrid functionals calculations

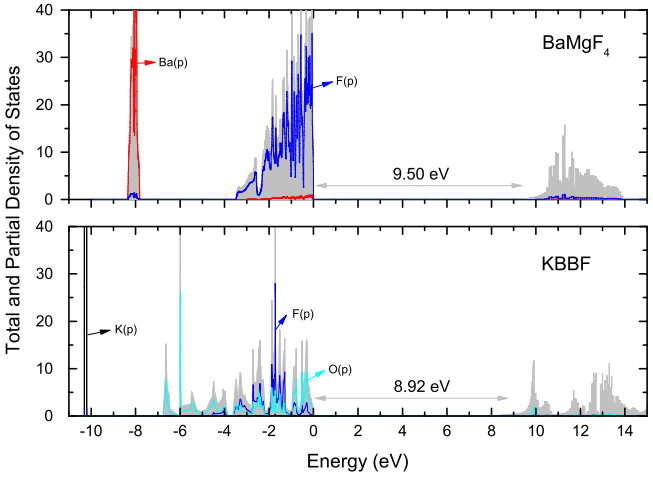

Fig. 2. (Color online) Total and partial density of states of $BaMg_4$ and KBBF.

were performed as well for comparison reason. This study not only confirm the validation of the many body theory on description for the DUV optical crystal, but also give a scenario, which is independent of experimental measurements, to further assisting the searching for new prominent DUV nonlinear optical crystals.

2. Computational details

The calculations are performed within density functional theory, using a plane waves pseudopotentials method as implemented in the ABINIT package [5]. The exchange-correlation energy functional is evaluated within the local density approximation (LDA) as parametrized by Perdew and Wang [16]. The all-electron potentials are replaced by norm-conserving pseudopotentials generated according to the Troullier–Martins scheme [22]. With Ba(5 s,5p,6 s), Mg(3 s), F(2 s,2p) electrons are considered as valence states for $BaMgF_4$ and K(3 s), B(3 s), Be(3 s) and O(3 s) electrons for KBBF. The wave functions are expanded up to a kinetic energy cutoff of 50 Hartrees. Integrals over the Brillouin zone (BZ) are approximated by sums on a $6\times6\times6$ Monkhorst–Pack mesh of special *k*-points [14]. The second-order