Piezoelectric, ferroelectric, optoelectronic and photo-catalytic phenomena from defect levels in hydroxyapatite by first-principles

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Hydroxyapatite (HAp) is an important component of mammal bones and teeth, being widely used in prosthetic implants [1]. However, despite the importance of HAp in medicine (exciting applications involving this material as a high biocompatible materials [1]), several promising new applications involving this material (e.g., in photo-catalysis [2]), depend on how well we understand its fundamental properties. Recent experiments and theoretical studies have shown that HA exhibits piezoelectricity, pyroelectricity, and ferroelectricity [3-8]. A number of theoretical studies of the structure and properties of HA have been carried out [3-6]. It shown the value of the d_{33} piezoelectric coefficient as 15.7 pC N^{-1} in good agreement with the experimental study as described in [7, 8]. Further, experimental evidence suggests that oxygen vacancies play a critical role in the production of surface radicals upon exposure of HAp to ultraviolet (UV) light. However, very little is known about the underlying physical and chemical details.

A hybrid density functional theory (DFT) study of the structural and electronic properties of oxygen vacancies in large HAp supercells within the plane-wave formalism was presented in this work. The vacancies were investigated in large supercells, from which formation energies and electronic transition energies were calculated. The calculations were carried out using DFT, as implemented by the VASP [9]. The exchange-correlation potential was evaluated either using the generalized gradient approximation according to PBE functional or the three-parameter hybrid B3LYP functional, which incorporates a fraction of exact exchange with local and semi-local functional [10]. These methods are also applied to the calculation of defect levels [11].

We found that the vacancies essentially occur in two distinct forms, either as a simple vacant oxygen site (referred to as structures I-IV), or as an oxygen atom replacing two neighbouring oxygen vacancies (bridge structures A-C). The former type of vacancies are deep donors, while the latter are shallow donors with rather low ionization energies. No acceptor states (stable negatively charged defects) were found. Vacancy structures I-IV are more stable in the neutral charge state, while bridge structures A-C are preferred in the double plus charge state. This means that the oxygen vacancy adopts rather different configurations on samples where the Fermi energy is in the upper or the lower half of the band gap. From inspection of the one-electron Kohn-Sham levels, combined with the transition levels obtained from total energies, we find that electron promotion from the valence band top to the donor state of the positively charged structures, involves a zero-phonon absorption of 3.6-3.9 eV.

This transition leads to a spontaneous breaking of either a P-O bridge-bond or an O-H bond, and most likely explains the 3.4-4.0 eV absorption onset for the observation of photocatalysis under persistent UV illumination.

The use of B3LIP allows to consider both electronic excited states of electrons and optical properties, as well as the energy of formation of defects at a high and precise level.

This is not unexpected, since this functionality was developed earlier for the description of molecules, and the studied material based on the hexagonal HAp crystal lattice has a similar molecular structure: it contains isolated PO_4 tetrahedra, columns of calcium atoms and OH hydroxyl channel.

The resulting electronic structure of the band of the top of the valence band turns out to be rather flat, which also confirms the "molecular-like" nature of the internal structure of the HAp.

The effectiveness of the use of the exchange-correlation functional B3LYP in the calculations for pure HAP and defect levels in HAP. Further development and more accurate calculation of these electronic properties and optical photoexciting and photocatalytic processes can be made by correct calculations of the electron – electron correlation of the excited electron states taking into account the Frank-Condon relaxation.

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