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Electronic and optical properties of spodumene gemstone: A theoretical study

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Abstract

The spodumene ($LiAlSi_2O_6$) is a natural silicate with monoclinic structure, interesting for a jewel industry and possible application as a scintillator. In this paper we present the electronic structure and some of the basic optical properties of the pure spodumene crystal, as calculated by the first-principles, density functional based, full potential linear augmented plane wave method.

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Keywords: Optical absorption; Spodumene; Electronic structure

1. Introduction

The spodumene is a natural silicate with formula $LiAlSi_2O_6$. It appears in large, nearly perfect crystals in many parts of the world. Its crystal structure belongs to a monoclinic system with the space group $C2/c$ [1]. The transparent varieties of beautiful coloration are considered as semi-precious gemstone: the colorless or yellow (triphane), the pink (kunzite) and the green (hiddenite). The color is due to light absorption by various impurities, mostly Mn, Fe and Cr. Besides, some of the spodumene varieties exhibit striking luminescence, and are used as efficient scintillators. All these properties make the spodumene an interesting optical material for various applications. But, although it has been a subject of some experimental studies so far, there is still lack of theoretical knowledge about its basic electronic and optical properties.

In this paper we present theoretical study of these properties for the pure spodumene crystal, as a first and necessary step towards the future investigation of the impurity effects in the material. As a tool we used a state-of-art, full potential linear augmented plane wave (FP-LAPW) method [2], one of the most elaborate first-principles methods for electronic structure calculations, based on density functional theory [3]. We thoroughly analyzed the obtained electronic structure for the spodumene, identifying the characters of the most important bands around the fundamental gap. Then we calculated a complex dielectric tensor of the spodumene and its optical constants: refractive index and extinction coefficient, as a function of the incident radiation wavelength and discuss the results.

2. Calculation details and structure optimization

The crystal structure of the spodumene is monoclinic, space group $C2/c$, where the Li, Al and Si, O atoms occupy 4e and 8f positions, respectively. Lattice parameters $a = 18.04$ a.u., $b = 9.95$ a.u. and $c = 16.00$ a.u. are relaxed in our calculations. The calculated unit cell volume is found to be 3% larger than the experimental one. All atomic positions within the unit cell are optimized using the damped Newton scheme, until the forces acting on each atom become less than 5.0 mRy/a.u.

The calculation method which has been used is FP-LAPW, implemented into the WIEN2k computer code [4]. Exchange and correlation effects were treated by generalized gradient approximation GGA96 [5]. As a basis set

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the augmented plane waves were used, and the parameter which controls its size was set to RKmax = 7.0. Mesh of 10 k-points in irreducible wedge of Brillouin zone was utilized for k-space summation. The following electronic states were considered as valence states: $1s^2 2s^1$ of Li, $2p^6 3s^2 3p^2$ of Al, $3s^2 3p^1$ of Si, and $2s^2 2p^4$ of O. In our calculations they were treated within the scalar-relativistic approach, whereas the core states were relaxed in a fully relativistic manner.

3. Electronic structure

The resulting electronic structure of the spodumene crystal, in an energy region situated around the band gap, is shown in Fig. 1.

The valence band is dominated by the O electronic states. It consists of two separated bands. A more detailed analysis [6] shows that the lower-energy band is dominated by the O 2s states, while the top mostly consists of the O 2p states. A very bottom of the conduction band is dominated by the Si 3p states, which are followed by the Al 3p states. At higher energies, the Si states dominate the conduction band.

The structure of the electronic bands in the vicinity of the band gap is shown in Fig. 2. It is seen that the conduction band has its energy minimum at gamma point, while the valence band exhibits the energy maximum at the M point in the Brillouin zone. Thus, the band gap in the spodumene crystal is indirect. Its value is calculated to be 5.5 eV.

4. Optical properties

The dielectric function ε of an anisotropic material is a complex symmetric second-order tensor. The imaginary part of the dielectric tensor is directly related to the optical absorption spectrum of the material. It can be computed from the knowledge of the electronic band structure of a solid. In the limit of linear optics, neglecting electron

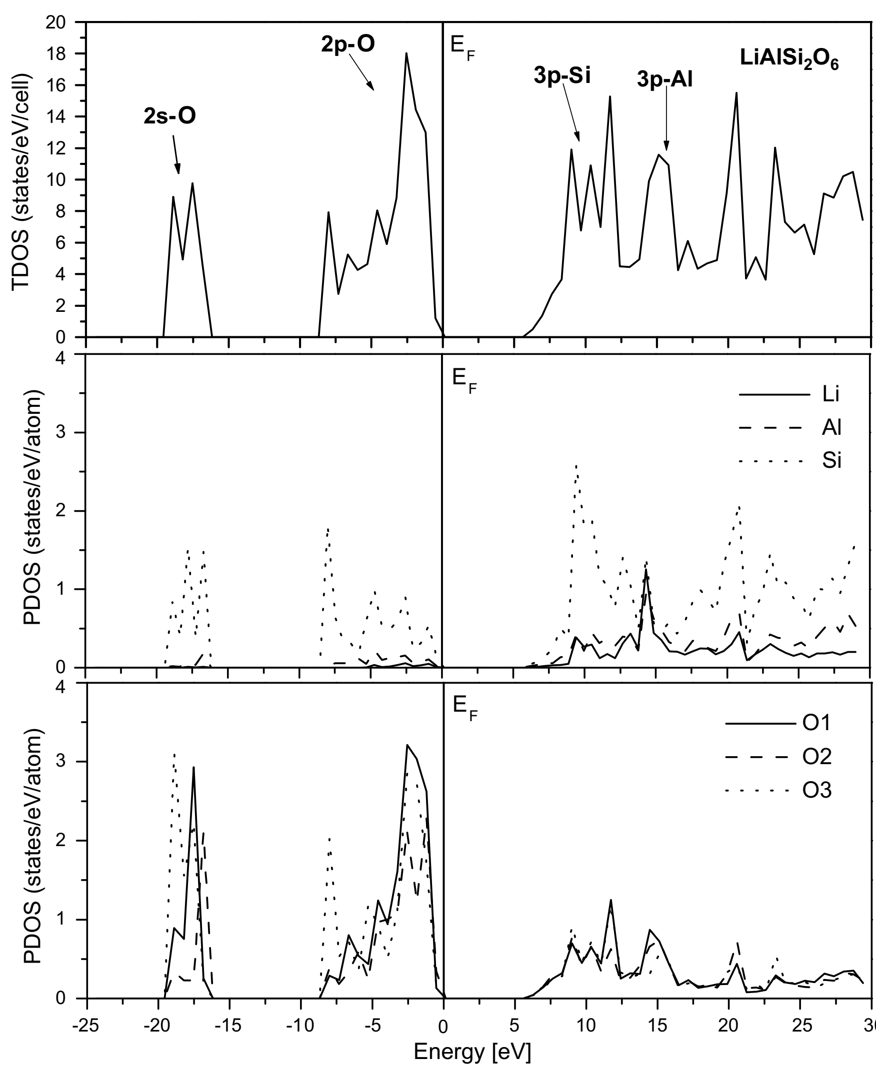

Fig. 1. Calculated total density of states (TDOS) of the spodumene (top), projected DOS (PDOS) for Li, Al and Si atoms (middle), and PDOS for O atoms situated in the three nonequivalent crystallographic sites (bottom). Fermi level is fixed at 0 eV. Predominant orbital characters of some bands are shown.