

Structural, electronic and vibrational properties of the calcite phase of CaCO_3 : An experimental and theoretical study

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The calcite phase of the calcium carbonate (CaCO_3) is an important material for optical devices (such as light polarization filters) due to some of its optical properties, such as the birefringence. However, the CaCO_3 is also a peculiar material because, due to the way that the Ca^{2+} and CO_3^{2-} ions arrange themselves in the lattice, it can form polymorphs like the calcite, the aragonite and the vaterite structures, that are also important in biological processes. For this reason, there is a great interest in the scientific community on the knowledge of the structural, electronic, optical and vibrational properties of this material, once the published data on this subject is rather scarce in the literature. In this work, we have studied the optical and vibrational properties of some samples of mineral calcite CaCO_3 by the UV-Visible absorption and the Fourier-Transform Infrared spectroscopies, as well as by Raman scattering techniques. In order to analyze the obtained experimental results, we have calculated the structural, electronic and vibrational properties of calcite CaCO_3 , by using the Density Functional Theory (DFT) within the Local Density Approximation (LDA), gradient conjugated techniques and the plane-wave pseudopotential method (Abinit code) [1]. We have used both the Troullier-Martins, as well as Projector-Augmented-Wave (PAW) pseudopotentials [2]. The theoretical optical absorption was obtained by means of the Linear Response method in the Casida approach as implemented in the DP code [3], and the phonons were obtained by the Density-Functional Perturbation Theory [1]. Our theoretical results are in good agreement with the obtained experimental ones as well as those experimental data available in the literature. From the obtained results, we found that, at room temperature, the calcite CaCO_3 is an indirect gap material ($E_g = 5.80 \pm 0.01$ eV), which involves a $E_u(\text{TO})$ phonon with 159.3 meV, detected in both infrared data and in theoretical calculations. Moreover, due to the obtained values for its dielectric function, $\epsilon_1^{\text{latt}}(0) = 9.08$, we can classify this material as a low-K one, good for optical devices.

Keywords: Optical absorption, TDDFT, vibrational modes, calcite, total energy calculations.

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[1] X. Gonze, *et al.*, Comput. Phys. Commun. **180**, 2582 (2009).

[2] A. R. Tackett, N. A. W. Holzwarth and G. E. Matthews, Comput. Phys. Commun. **135**, 329 (2001).

[3] V. Olevano, L. Reining and F. Sottile, DP package, <http://dp-code.org>, 1998-2004.

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