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Raman and infrared spectra of minerals from *ab initio* molecular dynamics simulations: The spodumene crystal

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ABSTRACT

Ab initio molecular dynamics simulations with the Car–Parrinello method have been performed on the spodumene crystal at standard conditions and high pressure. Starting from the computed trajectories, accurate Raman and infrared spectra have been obtained and compared with available experimental measurements in the low and high pressure phases. The structural and spectroscopic changes due to the pressure effects are discussed.

1. Introduction

Vibrational (infrared and Raman) spectroscopy gives access to a series of basic information related to the structural and dynamic properties of solid state matter. These include elucidation of bonding properties, molecular orientation and ordering, crystal symmetry, elastic properties, phase transitions and others that are of particular relevance for minerals of interest in earth and planetary science [1–3].

For a correct and more detailed interpretation of complex spectroscopic data, computational simulations, performed starting from the knowledge of the atomic and molecular crystal coordinates of the studied system, are of great help. For instance, reproducing IR and Raman spectra with computational methods is of particular importance to correctly characterize the transformations that take place during phase transitions or chemical reactions. Molecular dynamics simulations, in the classical approach, are usually employed to study the behavior of a system at atomic level, but significant limitations arise from the reduced accuracy of the model potentials when strong interactions take place. For instance, the adopted force field could significantly differ at high pressure from that at standard conditions. *Ab initio* molecular dynamics simulations are able to overcome this problem, since the intermolecular potential is computed during the simulations from first principles. Recently Pagliai et al. [4] have generalized the method proposed by Putrino et al. [5] to compute the Raman spectra, for simulation cells of any symmetry, starting from molecular dynamics trajectories generated by Car–Parrinello (CPMD) [6] simulations. In the generalized version, this method allows the simultaneous computation of infrared and Raman spectra and has been successfully applied to study the vibrational spectra of the naphthalene crystal [4].

In the present paper this method has been applied to reproduce IR and Raman spectra of the spodumene crystal in different thermodynamic conditions, at standard and high pressure (~8.8 GPa). Spodumene is a member of the pyroxene mineral class with chemical formula $LiAlSi_2O_6$ and it crystallizes at standard conditions of temperature and pressure in the monoclinic system (space group $C2/c$) [7]. A phase transition occurs by increasing the pressure to ~3.2 GPa, accompanied by a symmetry lowering to the $P2_1/c$ space group, with a consequent abrupt change in the spectral features [8,9]. The phase transition has been monitored by Raman spectroscopy with diamond anvil cell (DAC) equipment [8]. The crystal structure of $LiAlSi_2O_6$ at standard conditions (0 GPa) and high pressure (8–9 GPa) has been characterized by means of X-ray diffraction studies [9,10]. We will show that Raman and IR spectra of the spodumene crystal can be reproduced in good agreement with experiments by using *ab initio* molecular dynamics simulations.

2. Computational details

The CPMD simulations [11] of the spodumene crystal have been performed using the PBE exchange and correlation functionals [12]. Goedecker–Teter–Hutter (GTH) pseudo-potentials [13–15] have been adopted to describe the core region of all elements, the plane wave expansion has been truncated at 100 Ry and a

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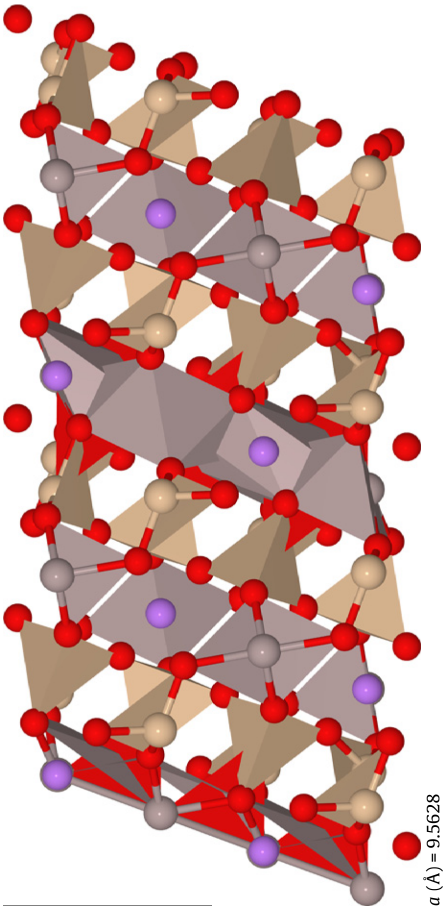
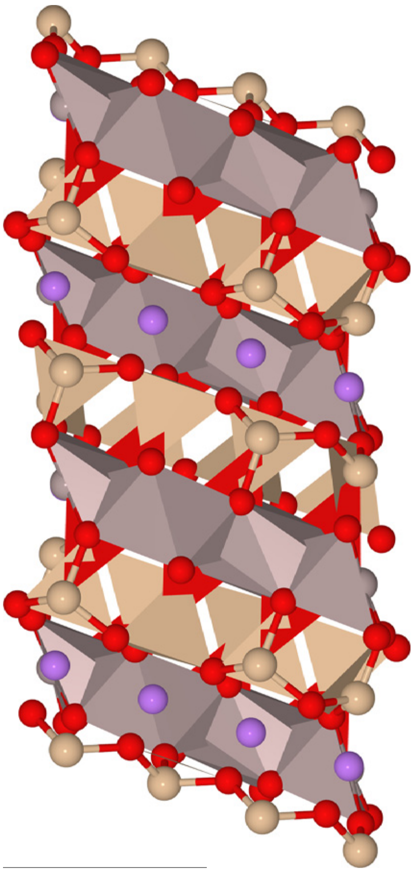
Table 1
Crystal structure and unit cell parameters of spodumene at standard conditions and at the pressure of 8.835 GPa and room temperature. Lithium atoms are shown as violet spheres; gray and cream polyhedra represent aluminum and silicate chains, respectively. The simulation box was twice the primitive cell along the *c* axis.

0 GPa ($C2/c$)	8.835 GPa ($P2_1/c$)
	
a (Å) = 9.5628 b (Å) = 8.3882 c (Å) = 5.2186 β (°) = 110.187 Z = 4	a (Å) = 9.2007 b (Å) = 8.2656 c (Å) = 5.0240 β (°) = 108.910 Z = 4

ficticious electronic mass of 700 a.u. has been employed in the simulations.

The simulation box was twice the unit cell along the *c* axis [10]. The cell parameters are reported in Table 1.

All simulation runs have been carried out for 131,072 steps, with a time step of 5 a.u. (0.12 fs) for a total simulation time of ~15 ps in the microcanonical (NVE) ensemble, after a thermalization at 300 K by velocity scaling of about 6 ps. The average temperatures of the simulations of spodumene at standard conditions and at high pressure were 312 ± 19 and 287 ± 18 K, respectively.

The computational method allows to obtain the Raman and IR spectra in conditions of temperature and pressure comparable to those adopted in the experimental measurements. The approach combines Car–Parrinello molecular dynamics with polarization and polarizability calculations and fully includes the anharmonicity of the potential. The procedure consists in two separate steps, where initially the system is simulated at selected thermodynamic conditions and then the polarization vectors and the polarizability tensors are calculated on equispaced configurations extracted from the trajectories. Simulated IR and Raman spectra have been obtained on the basis of 4096 equispaced configurations (1 every 32 steps). The dipole moment vector and the polarizability tensor of the simulation cell have been collected for each configuration, by adopting the procedure described in Pagliai et al. [4].

IR and Raman spectra are calculated by the direct Fourier transform of the polarization vector, **P**, and of the polarizability tensor, $\boldsymbol{\alpha}$, respectively [4].

The IR spectra have been obtained by the following relation:[16]

$$I(\omega)=\left(\frac{\omega\hbar}{2k_BT}\right)\coth\left(\frac{\omega\hbar}{2k_BT}\right)\mathscr{F}(\mathbf{P}(t))\mathscr{F}^{\star}(\mathbf{P}(t)) \qquad (1)$$

where $I(\omega)$ is the IR intensity and $\mathscr{F}$ is the Fourier transform of the polarization vector $\mathbf{P}(t)$.

Partitioning the polarizability tensor $\boldsymbol{\alpha}$ in the isotropic and anisotropic parts [4,5,17],

$$\boldsymbol{\alpha}(t)=\alpha(t)\mathbf{I}+\boldsymbol{\beta}(t) \qquad (2)$$

where $\alpha(t)=\frac{1}{3}Tr[\boldsymbol{\alpha}(t)]$, the Raman intensities, $I_R(\omega)$, can be obtained as:

$$I_R(\omega)=\frac{\hbar\omega}{k_BT\left(1-exp^{-\frac{\hbar\omega}{k_BT}}\right)}\Big[\mathscr{F}(\alpha(t))\mathscr{F}^{\star}(\alpha(t)) + \frac{4}{30}\mathscr{F}(Tr[\boldsymbol{\beta}(t)])\mathscr{F}^{\star}(Tr[\boldsymbol{\beta}(t)])\Big] \qquad (3)$$

3. Experimental details

Raman spectra of microcrystalline powder at ambient conditions were collected using a Renishaw RM2000 micro-Raman apparatus, coupled with a diode laser source emitting at 785 nm. Sample irradiation was accomplished using the 50× microscope objective of a Leica Microscope DMLM. The beam power was about 3 mW, the laser spot size was adjusted between 1 and 3 micrometers. Raman scattering was filtered by a double holographic notch filters system and collected by an air-cooled CCD detector. The acquisition time for each measurement was 10 s. All spectra were calibrated with respect to a silicon wafer at 520 cm^{-1}.

Infrared spectra of microcrystalline powder in KBr pellet were obtained in the 4000–450 cm^{-1} region by using a Perkin–Elmer FT-IRRX/I spectrometer.