

Supporting Informations

Pure and Sc-doped diopside ($\text{CaMgSi}_2\text{O}_6$) vibrational spectra: modelling and experiments

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Atom definitions

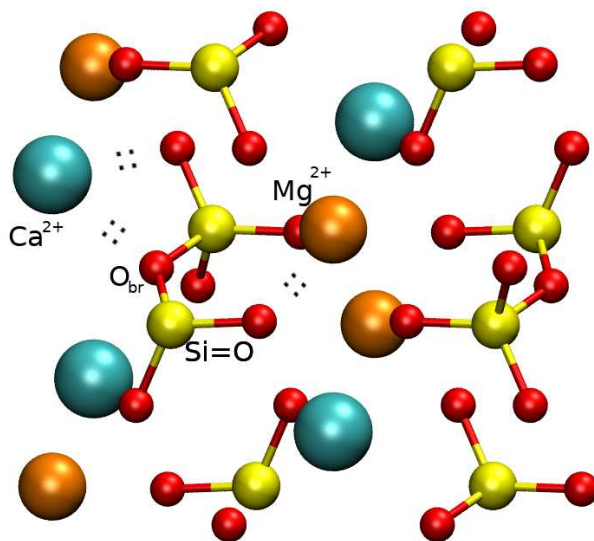


Figure S1: Nomenclature used to define atoms. Mg^{2+} (orange) is accommodated in M1 site and interacts with the oxygens (red) double bounded to Si (yellow) of SiO_4 ($\text{Si}=\text{O}::\text{Mg}$). Ca^{2+} (cyano) is located in M2 site interacting with bridging oxygen ($\text{Si}-\text{O}_{br}::\text{Ca}$) and oxygens double bounded to Si ($\text{Si}=\text{O}::\text{Ca}$).

Distance distributions

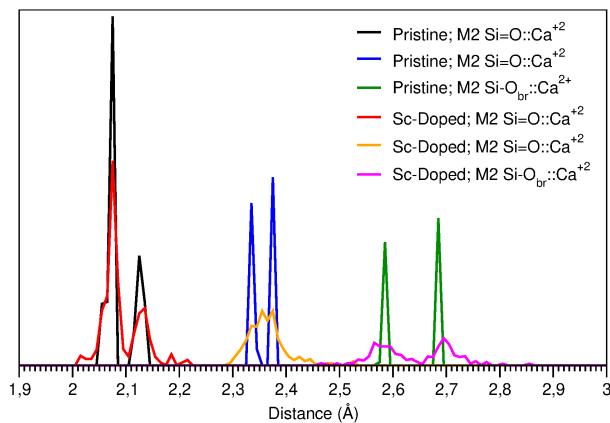


Figure S2: Distance distributions. Distribution of the distances between Mg^{2+} and oxygen atoms at the M1 site and: pristine diopside is in black, and Sc-doped diopside is in red. Distance distributions between Ca^{2+} and oxygen atoms at the M2 site: pristine diopside is coloured blue and green, while Sc is coloured orange and magenta. The presence of scandium (Sc) and vacancies introduces a certain degree of distortion since the distributions become broader, but the main peaks of the distance distributions remain essentially unchanged.

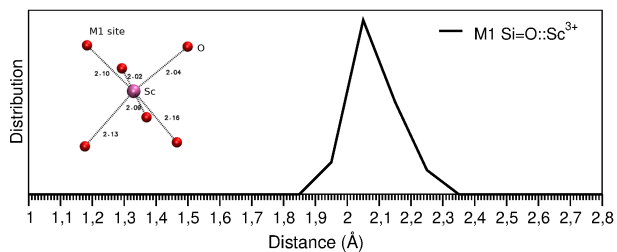


Figure S3: Distance distribution between oxygen and Sc^{3+} in M1 site. In the inset is reported an example of M1 site with Sc coordinated by the 6 oxygen and their distances in Å.

Example of stretching internal coordinates

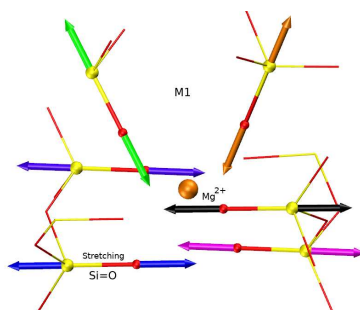


Figure S4: Representation of the 6 stretchings defined as the distance between the Oxygen and Silica atoms involved in M1 site around Mg^{2+} atom.

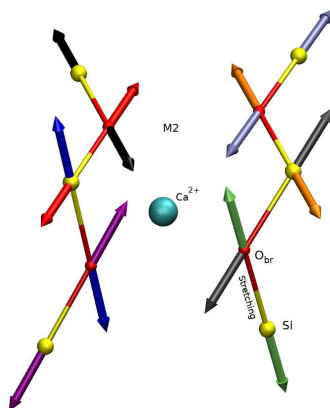


Figure S5: Representation of the 8 stretchings defined as the distance between the Silica and the bridging oxygen atoms involved in M2 site around Ca^{2+} atom.

Schematic flow of the algorithm

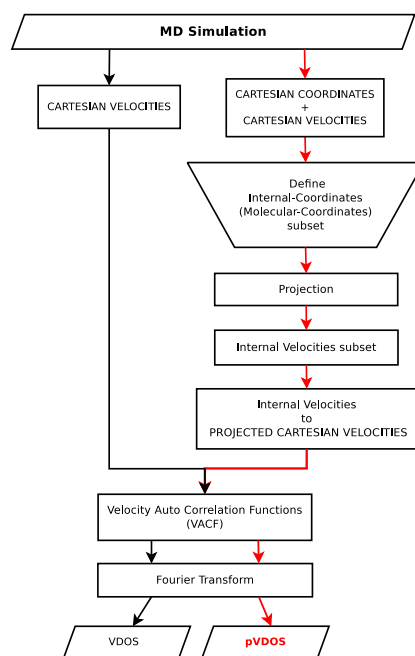


Figure S6: Schematic flow of the algorithm for evaluating VDOS and pVDOS. The algorithm begins with coordinates and velocities obtained from ab initio molecular dynamics (MD) simulations. The VDOS (black path) is calculated through the Fourier Transform of the autocorrelation function of the original atomic velocities. To evaluate the pVDOS (red path), a subset of internal coordinates (IC) is defined. To this aim, it is necessary to know the Cartesian coordinates of the involved atoms. The algorithm projects the Cartesian velocities into the subspace defined by these ICs to obtain the subset of internal velocities. The internal velocities are then reconverted to Cartesian velocities. These projected coordinates contain only the contributions along the selected internal coordinates, filtering out other contributions. The pVDOS (red) is then calculated through the Fourier Transform of the autocorrelation function of these projected (purified) Cartesian velocities.

pVDOS details

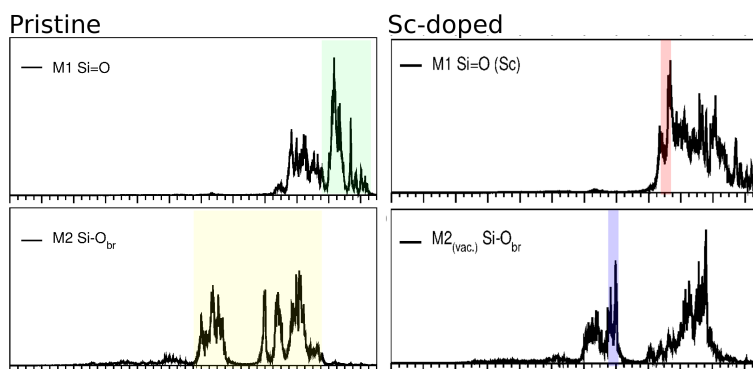


Figure S7: Pristine and Sc-doped pVDOS comparison. Top: pVDOS for Si=O stretching of M1 in pristine (left) and in Sc-doped diopside (right). Bottom: pVDOS for Si-O_{br} stretching of M2 site of pristine diopside (left) and the vacant M2 site in Sc-doped diopside (right)

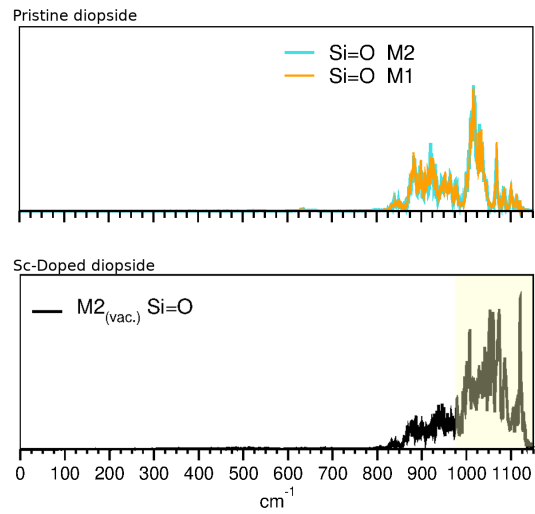


Figure S8: Top: Pristine diopside pVDOS along Si=O stretch of M1 (orange) and M2 (cyan) sites show no significant differences. Bottom: Sc-doped diopside pVDOS along Si=O stretch of vacant M2 sites. The bands are shifted towards higher frequencies (yellow area).

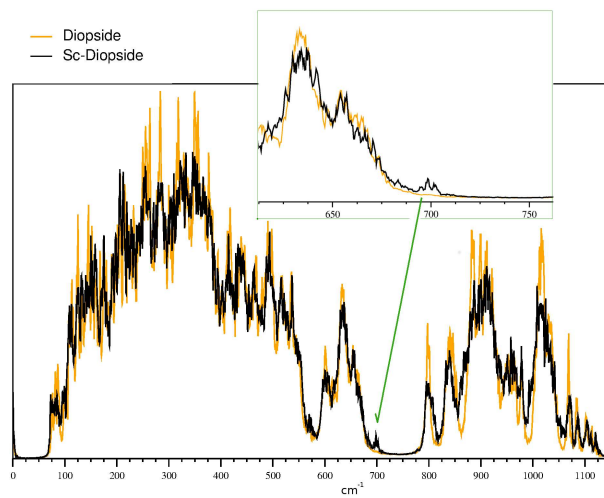


Figure S9: Total VDOS for pure (yellow) and Sc-doped (black) diopside.

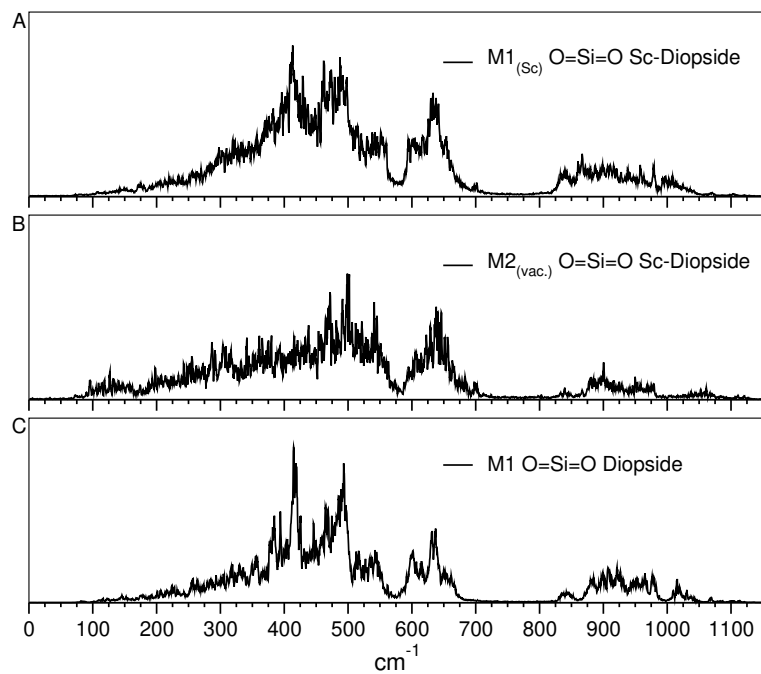


Figure S10: pVDOS obtained by projecting the Cartesian velocities along O=Si=O bendings. (A) pVDOS evaluated taking into account the O=Si=O bendings involved in the 4 M1 sites containing Sc atoms of Sc-doped diopside. (B) pVDOS evaluated taking into account the O=Si=O bendings of the empty M2 sites of S-doped diopside. (C) pVDOS evaluated taking into account the O=Si=O bendings of pristine diopside.

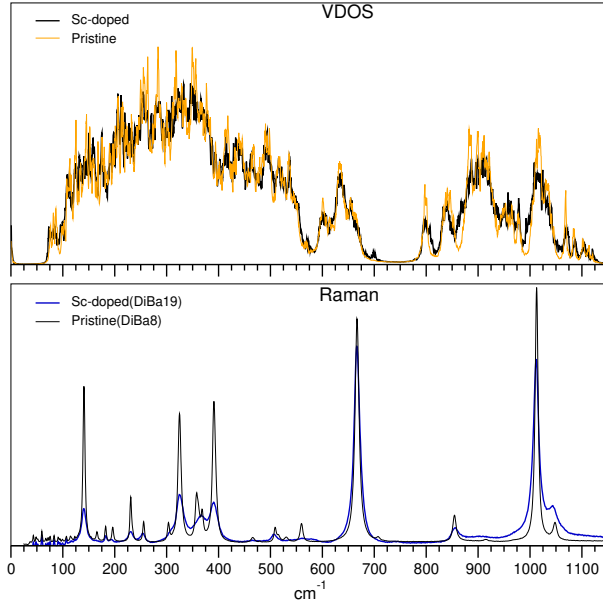


Figure S11: Total VDOS (black, top) and Raman spectra (blue, bottom) of Sc-doped and pristine diopside. The intensity of VDOS, which is related to the distribution of vibrational modes, is not directly comparable to the intensity of Raman, because related to the polarizability the system. VDOS serves as a comprehensive representation of all accessible vibrational frequencies. Raman spectra selectively exhibit frequencies that satisfy the selection rules. It is noteworthy that the frequencies associated with the major peaks in the Raman spectra demonstrate a commendable agreement with the peaks present in VDOS, highlighting the coherence between the two methods. Remarkably, the presence of Sc atoms and vacancies affects in the same measure both calculated and experimental spectra as explained in the main text.