Poster

New ring-structured high pressure and temperature $CaSiO_3$ polymorph and its stability field

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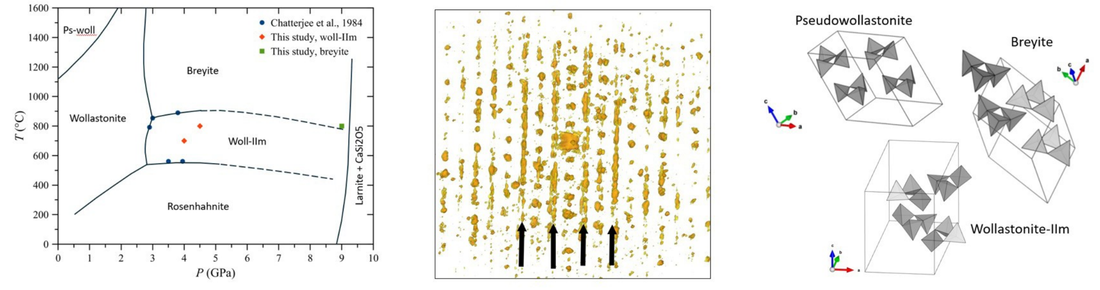
Over the past few years, the $CaSiO_3$ system has been extensively investigated due to its status as one of the most abundant and pure calcium silicates on Earth. Despite its simple chemical composition, this system exhibits interesting structural complexity, featuring a significant number of polymorphs and polytypes across various pressure and temperature conditions [1-2] (Fig. 1.a). In minerals such as wollastonite and parawollastonite, stable at relatively low pressures and temperatures, the silicon tetrahedra are arranged in chains. In contrast, polymorphs stable at higher pressure-temperature conditions, like pseudowollastonite (ps-woll) and breyite, exhibit a 3- fold rings configuration (Fig.1.c). Beside these, a single study reports a potential new polymorph with unknown structure, named woll-IIm [3], further increasing the complexity of the system.

In this study, we conducted multianvil syntheses at different P-T conditions (Fig. 1.a) to stabilize crystals of this polymorph and obtain structural information. By combining 3D electron diffraction and synchrotron single crystal X-ray diffraction techniques, we successfully solved the structure. Woll-IIm phase was first identified as triclinic by 3D electron diffraction in the lower temperature synthesis (4 GPa, 700°C), but only its unit cell could be determined and not its crystal structure, since the crystals were twinned at a nanometric scale and exhibited strong streaking in diffraction (Fig. 1.b). In the high temperature synthesis (4.5 GPa, 800°C) crystal grains suitable for single crystal x-ray diffraction were successfully isolated and their diffraction were indexed thanks to the unit cell determined by 3D ED. Woll-IIm is characterized by 3-fold rings tetrahedra configuration with unit cell parameters a=8.1911(10) Å, b=9.3441(9)Å, c=10.4604(10)Å, α=73.901(8)°, β=89.814(9)°, γ=77.513(9)°, and space group $P\bar{1}$. In-situ single crystal diffraction experiment using diamond anvil cell (DAC) in the pressure interval 0-10 GPa allowed the determination of its bulk modulus K_0=90.7(5)GPa. Additionally, we performed in-situ DAC experiment on previously synthesised pseudowollastonite single crystal in the pressure interval 0-14 GPa. Contrary to what is reported in literature [4], we did not observe any pressure-induced phase transition in this ring-type polymorph.

The results allowed a comparison of the elastic behaviour among the different ring structures in the $CaSiO_3$ system. Woll-IIm is significantly less compressible than pseudowollastonite and breyite, suggesting that slight variations in the orientation of silicon tetrahedra within the structural rings may play a crucial role in determining the material's elastic properties (Fig. 1.c). We also observe that there is no direct and straightforward structural relationship between woll-IIm and breyite, as evidenced by the latter's quenchable nature. This further suggests that the natural occurrence of one of the two ring structures can provide insights into the temperature conditions during its formation.



1.a 1.b 1.c

Figure 1. 1.a, PT woll-IIm stability field according to [3] and this study (picture modified after [3]); 1.b, 3D reconstruction obtained with 3D ED of the reciprocal space of Woll-IIm viewed along a direction slightly tilted off (100). The arrows indicate the planes where the streaking is evident.; 1.c, Different ring-type structures in the $CaSiO_3$ system, showing different silicon tetrahedra orientation within the rings.

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