Direct observation of pressure induced charge density redistribution at ions in zeolite, hsianghualite

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Modern approaches of X-ray diffraction allow for detailed quantitative studies of electron density in crystals of minerals. They can be combined with high pressure studies [1] as we demonstrate in this work for model zeolite mineral hsianqhualite, $Ca_3Li_2(Be_3Si_3O_{12})F_2$.

At the level of electron density analysis first order configurational components in crystal structure description (Fig. 1a) were replaced by Bader's atomic basins [2] which quantitatively characterise electron density of particular ions in mineral structures as well as precisely defined space, they occupy (Fig 1b). Their anisotropic and highly non-spherical shape reflects interatomic interactions and is sensitive to applied pressure. According to our studies the charge of ions in the crystal lattice differs from the formal, integer values and when external pressure is applied a redistribution of charge among ions takes place. This redistribution changes the size and shape, mostly at the edges of ionic basins in nonbonding fragments (Fig. 1c, d).

Negative compressibility of the F ion was observed. It was caused by the flow of electrons increasing the total negative charge and, consequently, increasing the volume of F ion at 1.9 GPa pressure (Fig 1d). Also, inside of atomic basins of atoms electron density redistributes notably due to pressure.

The quantitative characterization of minerals under high pressure at the subatomic level of electron density, rise possibilities to better understand the nature of mineralogical process, phase transitions and formation of new phases and to study plastic deformations of minerals using diamond anvil cells.

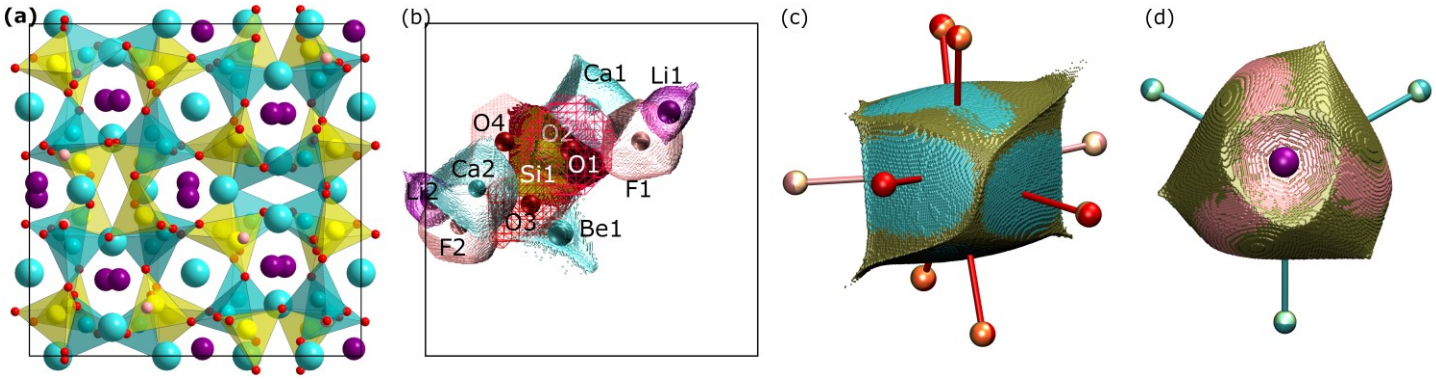

Figure 1. The unit cell contents of hsianghualite crystal structure (a); the assymetric part of the unit cell with atomic basin representation (b); Projection of atomic basins at 1.9GPa in tan colour onto atomic basins of the same atom at ambient conditions for Ca (c) and F (d).

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