

Phase transitions in minerals induced by pressure and studied by experimental charge densities - feasibility studies

Almost all (ca. 99.7%) out of 1.5mln known crystal structures have been determined by applying a 100-year old spherical Independent Atom Model (IAM) in the refinement of X-ray data. This also includes almost all minerals (ca. 5500). There are only a few thousands of crystal structures refined by aspherical approaches such as quantitative Multipole Refinement (MR) of electron density or Hirshfeld Atom Refinement (HAR) based on quantum chemically derived aspherical atomic densities. This includes ca. 35 minerals refined within last 50 years by multipole refinement. We have just refined experimental electron density for single crystal of grossular under pressure and up to our knowledge this is the very first successful refinement of quantitative electron density in minerals under pressure using multipole refinement. In the past, we have also refined experimental electron density for fluorite at ambient conditions. These results and a new design of Diamond Anvil Cell with wider opening angle (up to 120° allowing for up to 50GPa pressure) opens completely new field of mineralogical studies.

So the aim of this project is to apply MR in pioneering combination of experimental charge densities with high pressure and variable temperature studies of minerals and processes they undergo. We plan to perform feasibility studies of phase transitions in model minerals induced either by applying pressure or temperature (or both stimuli). We want to select minerals which undergo phase transitions below 50GPa, diffract well enough at high diffraction angles (this is a must for experimental charge densities), and for which - at least for some of them – phase transitions have already been studied at the structural level by using routine DAC and routine IAM X-ray structural studies. We will practically demonstrate how far deeper insight can be gained by applying multipole refinement of experimental electron densities in minerals comparing to routine structural studies. This includes the following:

- (a) far better (more precise and more accurate) geometrical (bond lengths and valence angles) and thermal (ADPs) parameters of atoms in minerals,
- (b) possibility of tracing flow of charge (charge transfer) among ions in the crystal lattices of minerals under variable pressure or temperature,
- (c) reliable experimental topology of charge distributions and charge and volumes of ions forming crystal lattices of different phases of minerals – this will allow for more reliable theoretical modelling of ionic crystals - and point and integrated electron density parameters at critical points of electron density distributions and at other key points of the mineral structures studied (for example deviations from sphericity of ions in crystal lattices of minerals)
- (d) reliable estimates of energy of electrostatic interactions, electrostatic potential (ESP) and its parameters in minerals, electric field gradient and, in general, all one electron properties of atom which can be correlated with different mineralogical and physicochemical properties of minerals,
- (e) we also want to explain the nature of changes of the most important interactions which determine phase transitions particularly at the level of changes of details of electron density and analyse the most important factors influencing phase transitions).

The phase transitions in the following minerals will be studied (of course only when different phases of these minerals diffract well enough at high diffraction angles): **Kyanite** [from Brazil and from the Kola Peninsula, Russia, Al_2SiO_5 , Triclinic, P-1], **Diopside** [Bazenowskoje, Russia, $\text{CaMgSi}_2\text{O}_6$, Monoclinic, C2/c], **Enstatite** [Kraubath, Austria, $\text{Mg}_2\text{Si}_2\text{O}_6$, Orthorhombic, Pbc], **Pyrope** [Czechia and Italian Alps, $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$, Cubic, Ia3d], **Olivin**, **Forsterite** [from Vesuvius volcano and Norway Mg_2SiO_4], **Wollastonite** [(from Garby Izerskie, Poland, $\text{Ca}_3\text{Si}_3\text{O}_9$ Triclinic, P-1], **Brucite** [from N'chwanging II Mine, RSA, $\text{Mg}(\text{OH})_2$, Trigonal, P-3m], **Quartz** (α and β) [SiO_2], **Boracite** [$\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$, Orthorhombic, Pca2₁], **Diamond** and **Graphite** and other interesting minerals and new phases undergoing phase transitions.

Ability to describe structural modifications with increasing pressure and/or temperature should be of interest for geophysicists describing the way seismic waves pass through the Earth's mantle and those working on mantle gravity models. Changing structures under pressure might also affect the way in which trace elements are incorporated into mantle minerals and, importantly, how they are released during partial melting of the mantle. By combining experimental charge densities with pressure and temperature, we can model different mineralogical processes taking place at the upper mantle, transition zone and quite a great part of the lower mantle, determine the role of accessory hydrous silicates in deep global volatile cycling, study pressure-temperature stability for Dense Hydrous Aluminium Iron Magnesium Silicates, study new yet unknown mineral phases and minerals. A century after the Braggs, mineralogy deserves a new opening based on aspherical models of electron density and we will do this within this project.