Title - ***Physical properties and transport mechanisms in natural crystalline phases under high pressure and temperature environments: A first-principles approach***

Index Number: ***162/16/Phys./25***

Abstract

The present thesis explores the physical and chemical behaviour of naturally occurring atomic and molecular crystalline solids in the interior of the earth and other extra-terrestrial planets. Understanding their physical and chemical properties under extreme thermodynamic conditions, e.g., ultra-high pressures and/or temperatures is of vital significance, especially to interpret the phase stability, elastic properties, chemical compositions of planetary materials as well as their microscale transport properties, e.g., diffusion. This study adopts two major computational approaches: electronic structure calculations in the framework of Density functional theory (DFT) and ab-initio molecular dynamics (AIMD) simulations, to elucidate the role of the underlying atomic scale mechanisms in governing the macrophysical behaviour relevant to planetary processes and natural materials development.

A direction of this thesis work focuses on two important nesosilicates: zircon [$ZrSiO_4$] and titanite [$CaTiSiO_5$] present in Earth's crust and mantle. Tetragonal zircon is known as the most potential mineral phase to host heavy elements (U, Th, Pu) in their crystal structures, and this mineral phase is an outstanding material for nuclear waste immobilization and U-Zr-Pb geochronology. Zircon structured coffinite [$USiO_4$] and thorite [$ThSiO_4$] are detected to form solid solutions. Using DFT simulations this thesis provides a comprehensive analysis of the pressure induced zircon- to reidite-type phase transition of $U_{1-x}Th_xSiO_4$ (x = 0 to 1 in steps of 0.25) solid solution. The phase transition pressure (P_T) is shown to vary nonlinearly with increasing Th content in the solid solution and attain a minimum value of 6.82 GPa for x = 0.5. The calculated maximum compressibility of zircon type $U_{0.5}Th_{0.5}SiO_4$ supports this finding, implying that the phase becomes most pressure sensitive (i.e., soft) at this specific U/Th ratio. The thesis also presents a novel approach to the analysis of the polyhedral distortions of triangular dodecahedra (snub-disphenoids). Two parameters (δ and σ^2) have been defined to quantify the longitudinal and angular distortions of highly irregular U/ThO_8-triangular dodecahedra. The distortion analysis indicates that the difference in angular distortions (σ_U^2 and σ_{Th}^2) between the zircon- and reidite-type phases ($\Delta\sigma^2$) becomes minimum when U and Th occur equally in the solid solution. The concurrence of P_T and $\Delta\sigma^2$ minima indicates that the polyhedral distortion plays a critical role in dictating the zircon- to reidite-type transition. The distortions parameters, δ and σ^2 are independent of the elements occupying the snub-disphenoid space. Also, they are defined without any attribute to external parameters. This study hypothesizes that the parameters: δ and σ^2 can be used to calculate the distortion of similar AB_8-type snub-disphenoids in other crystalline phases.

The thesis presents a completely new theoretical data set on the mechanical properties of monoclinic titanite phase. The theoretical calculations reveal unusual negative values of the elastic constant: C_{36} for C2/c phase and negative pressure gradients of the shear elastic constants, C_{44}, C_{55} and C_{36} for both titanite phases. This study predicts the necessary condition for an elastic constant to have a negative pressure gradient. Furthermore, a novel atomic scale mechanism for such negative elasticity is reported; the rotational bond kinematics, driven by valence charge accumulation on (001) plane during the lattice deformation which causes structural collapse in a direction orthogonal to the applied shear strain, resulting in the negative elastic behaviour. Dielectric-function analysis predicts an exceptionally strong opacity of the wide band-gap (3.2 eV) titanite in the UV region, indicating this crystalline phase as a shield material for UV radiation. It is also demonstrated from the theoretical calculations that titanite can be used to develop optical devices, such as filters and polarizers.

Brucite [$Mg(OH)_2$] is a hydrogen-rich naturally occurring hydroxide phase, especially encountered abundantly in subduction zones of Earth's plates. The presence of two-dimensional wells between layers of MgO_6-octahedra in $P\bar{3}$-type brucite provides large interstitial space for the hydrogen atoms to diffuse in the lattice

framework. A part of this thesis investigates the hydrogen or proton diffusion in crystalline $P\bar{3}$-type trigonal brucite in the pressure range 10-85 GPa and in the temperature range 1250-2000K using AIMD simulation. The diffusion coefficients of H, mediated by the amorphization of the H-sublattice, show an anomalous variation with pressure along different isotherm. The diffusion of H is observed to attain maxima in the pressure range 73-76 GPa before decreasing in magnitude on further increment of pressure. The present study reveals that proton diffusion is highly anisotropic in brucite, with virtually no proton diffusion occurring along the crystallographic *c*-axis. The protonic conductivities are also evaluated and compared with the geophysical magnetic satellite observations. The conductivity analysis suggests that brucite can occur in appreciable amounts in the lower mantle and mantle transition zone. The finding explains the occurrence of high conductivity zones in deep earth, widely reported in solid earth geophysics.

Another direction of this thesis deals with the major constituents of the ice giants Uranus and Neptune, such as molecular mixtures of methane, water and ammonia. At combined high pressure-high temperature conditions these molecular mixtures can contribute to electrical conductivity of planetary interiors through superionicity, where protons diffuse through stationary heavy atoms in the lattices. Atmospheric abundances of nitrogen and sulphur inferred from microwave absorption experiments are found to be anomalous with reference to the solar ratios, implying the presence of substantial amounts of H_2S in these planets. Using AIMD simulation, a line of the thesis work explores the plastic and superionic natures of the ammonia monosulphide [NH_3:H_2S - 1:1] phases. The calculated phase diagram from AIMD simulations shows that the ambient phase (Space Group-P4/nmm) preferentially melts from the solid state at 500K, where the rest high-pressure phases undergoe plastic deformation (or rotational states), followed by superionic states before the onset of melting at higher temperatures. The simulations also reveal a sharp increase of the melting points from the P4/nmm phase at 500K in ambient condition to Cc phase at 2250K and 20 GPa, which reaches a maximum of 2500K at 40 GPa. For the high-pressure $P2_1/m$ and Abm_2 phase the melting point remains fixed at 2500K and then drops to 2250K for the Cmma phase at 167 GPa. The thermal corrections to pressure for the phases beyond 40 GPa decrease following melting. The melts are thus denser than their solid counterparts at the elevated pressures mentioned above. The steep slope in the melting curve at lower pressure has potential implications for planetary science and points towards the possible existence of solid NH_3-H_2S mixture in the shallow mantle region of Uranus and Neptune. Barring the ambient phase, the phase diagram demarcates a zone of fast hydrogen diffusion, in the presence of stable sulphur and nitrogen sublattice. This fast proton transport results in superionicity in ammonia monosulphide. An analysis of the pair distribution function is presented to identify the formation of short-lived H_2, S_2 molecules and other chemical motifs like H_2NS and HSNH at elevated pressure and temperature, triggered by rapid movement of constituting atoms. The density of states calculation confirms the low-pressure phases as wide band-gap semiconductor (1.0 to 3.5 eV), apart from the Abm_2 and Cmma phase. The band-gap is reduced on increasing temperatures, and the reduction is most prominent for the Cc phase at 20 GPa, 2.86 eV at 500K to 0.8 eV at 2250K.

Overall, this present thesis provides a distinctive description of the effect of elevated pressure and/or temperature as well as of the ultra-active chemical environment on the physical and microscale transport properties of crystalline solids from an atomistic point of view. These key properties are pertinent for the composition of planetary interiors together with an outlook on novel characteristics of materials.

08/12/2022

Signature of the supervisor

NIBIR MANDAL
Professor
Dept. of Geological Sciences
Jadavpur University
Kolkata - 700 032

Sudip Kumar Mondal

Signature of the candidate

08.12.2022