Dynamical properties of $CaIrO_3$ under high pressure from *ab initio* calculations

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$CaIrO_3$ crystallizes in the orthorhombic Cmcm at normal conditions. This compound is attracting important interest as a low-pressure isostructural analog of the predicted postperovskite high pressure phase of $MgSiO_3$. Here we perform an ab initio density functional calculations of the structural and dynamical properties under hydrostatic pressure for the Cmcm and the Pbnm phase of of $CaIrO_3$.

Our studies have been performed in the framework of DFT with echange correlation taken in generalized gradient approximation (GGA) with the PBEsol prescription. We use the pseudopotential method with ultrasoft PAW pseudopotentials with an energy cutoff of 520 eV. Such a large cutoff was required to achieve highly converged results within the projector augmented wave (PAW) scheme. The PAW method takes into account the full nodal character of all the electron charge density distribution in the core region. We use a dense grid of k-special points for integrations along the Brillouin zone (BZ) in order to assure highly converged results.

Lattice dynamics calculations of phonon modes were performed at the zone centre (Γ point) of the BZ. The calculations provided information about the frequency, symmetry and polarization vector of the vibrational modes in each structure. We use direct force-constant approach (or supercell method). Diagonalization of the dynamical matrix provides both the frequencies of the normal modes and their polarization vectors. It allows us to identify the irreducible representations and the character of phonon modes at the Γ point. We will report the Raman and IR actives modes, the pressure derivarives, the phonon dispersion, the phonon density of states and the projected DOS.

Vertical distribution of iodine in pore water collected from Japan Sea sediments: Origin of iodine-rich fluid associated with methane hydrate

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In our previous studies, we have analyzed iodine in many geochemical samples systematically and found that nearly 70% of iodine in the Earth's crust is estimated to exist in marine sediments (Muramatsu and Wedepohl 1998). We also studied occurrences of iodine rich brine associated with methane seepage in different areas surrounding Japan (Muramatsu *et al*. 2001, 2007).

In this study we have analyzed halogens and some other elements in pore water samples collected from Japan Sea sediments of methane hydrate areas. Sediment cores were recovered from the Umitaka Spur and the Joetsu Knoll region, eastern margin of the Japan Sea, during the cruises of Umitaka-Maru in 2009 and R/V Marion Dufresne in 2010 (MD179). The depth of the sediments collected were down to about 40m below sea floor. Concentrations of iodine, bromine and some other elements were analyzed by ICP-MS and those of chloride and sulfate were by ion-chromatography.

Analytical results showed that iodine concentration in pore water increased markedly with depth. The slope of the increase was rather constant. The highest concentration found in the Umitaka Spur was 0.4 mM (about 50ppm) which is nearly 1000 times higher than the seawater concentration. No marked increases of iodine were found in the samples collected from control areas without methane seepage.

We also determined $^{129}I/^{127}I$ ratios by AMS in pore water samples at defferent depth. As a result, the $^{129}I/^{127}I$ ratios tended to be lower in the deeper layers. The lowest ratio was about 0.13×10^{-12}, which was older than 50 Ma. This age is before the opening event of Japan Sea. Considering the age of iodine obtained and the depth profile of the iodine concentrations, iodine and possibly methane are originated from deeper layers and transported with aqueous fluids into the surface layers.

This study was supported by MH21 Research Consortium Japan