Chemical reactions between sodium chloride and yttrium under high pressure (Y. Yin, D. Laniel, A. Aslandukov, A. Aslandukova, L. Dubrovinsky, N. Dubrovinskaia/Bayreuth, M. Hanfland/Grenoble)

High pressure is known to affect significantly chemistry and reactivity of materials. Compounds with unusual stoichiometry attract attention because they often demonstrate novel types of chemical bonding and may have interesting properties. Remarkably, many novel high-pressure compounds are unpredictable based on chemical rules valid at ambient conditions. Recent discoveries of numerous unconventional sodium and potassium halides (like Na_3Cl, $NaCl_3$, and KCl_3) at pressures of 20 to 70 GPa indicate that chemical relations in alkali halides systems may be very different from those know from classical chemistry. In particular, usually extremely chemically stable halite, NaCl, may become reactive at high pressure that may result in the synthesis of novel compounds with potentially unusual electronic, optical, and mechanical properties.

In order to test this hypothesis, we loaded a rare earth metal yttrium and dried NaCl powder into a DAC with a pressure chamber of 120 µm in diameter made in a rhenium gasket pre-indented to the thickness of 30 µm. The mixture was compressed to 41 GPa. After double-side laser heating of the sample to ~2000 K with a YAG laser, the samples were characterized using Raman spectroscopy and synchrotron single-crystal X-ray diffraction (SCXRD) measurements at the European Synchrotron Radiation Facility (ESRF). The SCXRD data allowed us to identify a new phase among other reaction products. The structure of the new rhombohedral phase (space group #166, $R\bar{3}m$, a=3.364(2) Å, c=17.72(7) Å in the hexagonal setting; the rhombohedral cell parameters are a=b=c=6.21 Å, α=β=γ=31.46°) was solved and refined to R1=7.5% (Fig. 1). According to the result of SCXRD data analysis, the chemical composition of the phase is Y_2CCl. Theoretical calculations perfectly reproduce the details of the Y_2CCl structure at 40 GPa and demonstrate that the phase is dynamically stable at the synthesis pressure. In the structure of the novel carbidochloride, yttrium atoms form a distorted cubic close packing (*ccp*) (Fig. 1). If one considers Cl and C as equal balls, the alternating close-packed layers of C and Cl also form a distorted *ccp* (Fig. 1). Thus, the structure can be described as of the distorted NaCl (B1) type with carbon and chlorine atoms forming the *ccp*, whose octahedral voids are occupied by Y atoms. The Y-C contacts (~2.30 Å) are significantly shorter than Y-Cl (~2.59 Å), as expected. One of the Y-Y contacts is relatively short (~3.14 Å) that is close to the Y-Y distances in yttrium metal, thus indicating possible metallic character of the material.

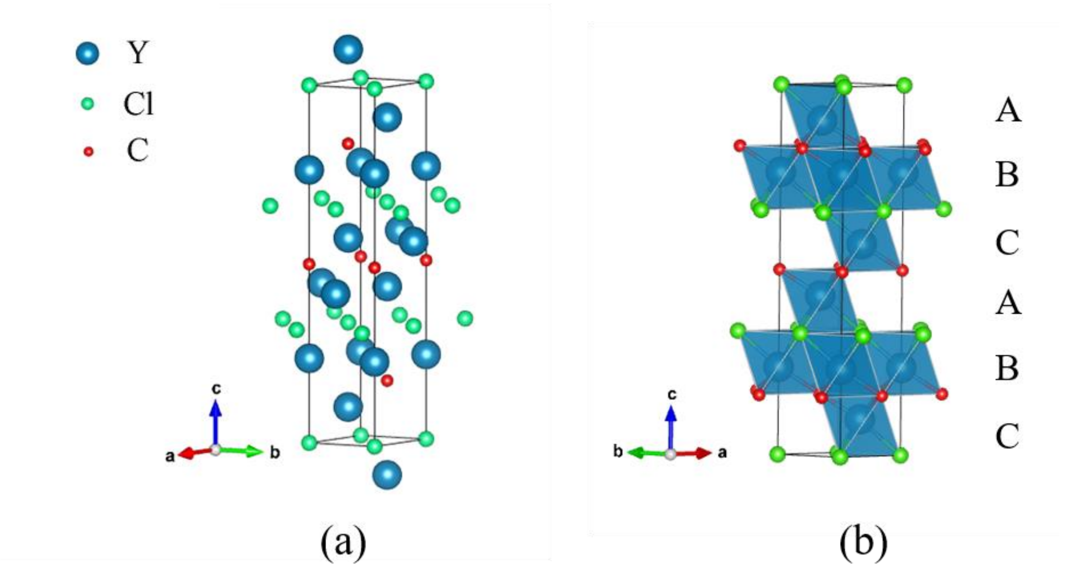

Fig. 1. Crystal structure of Y_2ClC at 41 GPa in the hexagonal setting. (a) Ball model, in which Y, Cl, and C atoms are shown in blue, green, and red colors; (b) polyhedral model built of (YC_3Cl_3) octahedra; A, B, C letters highlight the *ccp* formed by Y atoms themselves; the structure can be viewed as the *ccp* formed by C and Cl atoms together with the Y atoms occupying all of its octahedral voids.

The synthesis of Y_2CCl by a direct reaction of Y and NaCl in a laser-heated DAC suggests that sodium chloride indeed not chemically inert at high pressures and temperatures. That limits alkali halides application as thermal insulation and pressure medium materials in DACs experiments at high temperatures, but opens up great perspectives for the synthesis of novel materials with unusual chemistry.