ESRF	**Experiment title:** Structural characterization of alkali halides with polyhalogen anions using single-crystal X-ray diffraction at high pressure	**Experiment number**: CH-6544
Beamline: ID11	**Date of experiment**: from: 06.04.2023 to: 11.04.2023	**Date of report**: 10.09.2023
Shifts: 15	**Local contact(s)**: Eleanor Lawrence bright	*Received at ESRF:*

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Report:

High pressure (HP) dramatically changes the chemistry of materials. Quantum-chemical calculations predict unusual but stable stoichiometries of alkali halides, such as, for example, $NaCl_3$ and $NaCl_7$, Na_2Cl, Na_3Cl_2 and Na_4Cl_3, Li_nI (n = 2-5), and CsF_m (m = 2-6), and suggest uncommon properties. Despite the numerous predictions, very few of them have been experimentally confirmed. So far, the synthesis of the compounds with the stoichiometries AX_3, A_3X, and AX_5 (A is an alkali metal, X is a halogen) have been reported at high pressures. The list includes, for example, polymorphs of $NaCl_3$ (space groups Pnma and $Pm\bar{3}n$), KCl_3 ($Pm\bar{3}n$ and $P\bar{3}c1$), KBr_3 (Pnma and $P\bar{3}c1$), CsI_3 (Pnma, $P\bar{3}c1$, and $Pm\bar{3}n$), as well as Na_3Cl (P4/mmm) and KBr_5 ($P2_1$) compounds. The majority of them were characterized in a diamond anvil cell (DAC) using powder X-ray diffraction (XRD) and Le Bail analysis, and only the two polymorphs of CsI_3 (Pnma and $P\bar{3}c1$) were studied using single-crystal X-ray diffraction (SCXRD). Although the synergy of powder XRD and ab initio structure predictions is very helpful to obtain a structure solution, the interpretation of some powder XRD remains ambiguous (e.g., those of KBr_3 and KBr_5).

As planned and described in the beamtime proposal, we aimed to study the alkali halide systems which halogen atoms have a great potential to be stablized in polyhalogen anions. Seven diamond anvil cells equipped with 250 or 120 μm culets loaded with LiF, LiCl, LiBr, or a piece of Mg metal together with the halogens source (CF_4, CCl_4, and CBr_4), respectively, were brought to the ID11 beamline. The samples were laser-heated at regular pressure intervals after which they were mapped with the X-ray beam in order to determine if a chemical reaction had occurred. When new diffraction lines different with the starting materials were observed, a single-crystal X-ray diffraction data collection was performed.

Through the investigation of the laser-heated samples, we successfully synthesized a novel magnesium chloride with the composition of Mg_3Cl_7 in the pressure range of 44 to 73 GPa. The compound has an unusual chemical bonding with evidences of covalent-ionic mixing in the structure. This is one more example that HP can stabilize compounds with very different (unusual) chemical bonding characteristics (the Mg-Cl interaction at 1 bar is completely ionic).

The aim of the experiment has been partailly achieved. The publication is under preparation and the ID11 stuff will be included as a co-author.