Experiment title: Intermediate range-order in ZnCl$_2$	Experiment number: HD-146
Beamline: ID27	**Date of experiment:** from: 18/07/2007 to: 25/07/2007	**Date of report:** 29/08/2007
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Report:

Any investigation of the high pressure and temperature properties of materials will naturally commence with a reevaluation of the pressure and temperature domains of the stable structures. Previous proposals for the high pressure forms of ZnCl$_2$ have included CdI$_2$, distorted-WTe$_2$ and various distortions of other AX$_2$ phases; yet, no convincing unit-cell indexing or Rietveld refinement has been published along with reliable p, T domains with information on reversibility or relative stability. This difficult situation is compounded by the high hygroscopic nature of ZnCl$_2$, which leads to the formation of partially hydrated structures that may or may not be truly stable forms of ZnCl$_2$ at high p, T. Considerable effort has been made to characterize these various structures prepared by wet chemistry and by varying water contents (e.g. Yakel and Brynestad, 1978; Brynestad and Yakel, 1978; Brehler, 1961; Oswald and Jaggi, 1960; Winkler and Brehler, 1959). We find that some of these are indeed truly stable phases at high p, T and have been largely overlooked as such. Of the phases that we have fully characterized, the only new structures are those of CdI$_2$:4H- and CdCl$_2$-type ZnCl$_2$, the remainder have been prepared previously at ambient conditions.

During the beamtime available for HD-146, we have explored p, T space between ambient and 4 GPa at temperatures exceeding melting at around 1000ºC (at 4 GPa). All the experiments have been conducted with an initial glassy form of ZnCl$_2$ (g-ZnCl$_2$) as the route to production of the glass contributes to the overall chemistry with the lowest water content. On pressurizing and heating initially g-ZnCl$_2$, we have encountered several distinct crystalline structures, all previously dubiously assigned or unassigned. These include: red-HgI$_2$-type (low P, high T), several CdI$_2$- polytypes (high P, moderate T), CdCl$_2$-type (highest P, highest T), known monoclinic and orthorhombic forms (low P, high T) and structures similar to both CdI$_2$ and CdCl$_2$, possibly including mixed polytypes (moderate P, low T). Most transitions have been reversed with each other and the melt; however, both the monoclinic P2$_1$/n form and the HgI$_2$ can be recovered metastably to ambient conditions. The transitions between CdI$_2$ polytypes are not expected to be reversible as the same transition sequence in SnS$_2$ is not. The general topology of the current phase diagram and spectroscopic results of e.g. Polsky et al (2000) are confirmed, though comparison with x-ray data (XAFS and diffraction) fair less well, due mainly to the similarity of the related structures. The revised phase diagram should reflect an increase in complexity with phases expected to be a result of partial hydration actually being stable (e.g. P2$_1$/n form) and those previously assigned to CdI$_2$ (e.g. Sakai et al, 1985) not actually being CdI$_2$, though CdI$_2$ is present

elsewhere in the phase diagram. No high pressure phases similar to those tentatively reported by Brazhkin et al (2007) were encountered, though the pressure here is slightly lower than those reported. Given the range of structures observed, an obvious argument may be that our sample charge was being progressively hydrated, yet we have observed the orthorhombic (stable at ambient) structure at several points during our reconnaissance. This form is known to exist only in water-free samples, Brynestad and Yakel (1978). Due to unforeseen loss of beam (>2 days), our phase diagram remains preliminary; with several transitions yet to be reversed; namely, orthorhombic to $P2_1/n$ and melt; $P2_1/n$ and HgI_2 to orthorhombic, but we doubt that the latter transitions would be observable due to extended metastability of both the HgI_2 and monoclinic forms.

The first run was conducted via the room temperature pressure-induced crystallization of g-$ZnCl_2$, forming a phase previously improperly described as CdI_2-type, or, when based on spectroscopic data as a mixed $CdI_2/CdCl_2$ phase, figure 1 left panel. It may be that this phase is a polytype or similar structure with stacking defects that incorporate aspects of both type-structures or a mixture of several CdI_2 polytypes (e.g. 2H, 4H, 6H (which is the same size and has many common reflections with $CdCl_2$-type), 12R, 18R, etc), similar to the situation in orange HgI_2. Evidence for hkl-dependent peak broadening is seen clearly; often seen in mixed polytype PbI_2. Upon further increase of pressure, the CdI_2 aspect of the phase becomes clear. Increasing temperature we identify further transformations from CdI_2:2H(2T) to CdI_2:4H polytype (or, C6- to C27-type, identical to the situation in SnS_2 and CdI_2; Guenter and Oswald, 1968; Gierlotka and Palosz (1986); though the transition in SnS_2 has an 18R intermediate; Palosz et al, 1986; Mitchell et al, 1982). In common with other CdI_2-type structures, the 2H-equivalent c/a is equal to ~1.57 for all the CdI_2-like structures seen here. Then, just below melting, the 4H structure recrystallizes as the $CdCl_2$-type structure (at 3.2 GPa and 750 ℃). Thus, the highest pressure-temperature form of $ZnCl_2$ observed is of $CdCl_2$-type .The behaviour of $ZnCl_2$ at high pressure is then dominated by the interplay between variations in the ABAB and ABCABC stacking sequences that differentiate these two endmember type structures, similar to the situation in $FeCl_2$ seen by Vettier & Yelon (1975), for example, at low temperature and at modest pressure.
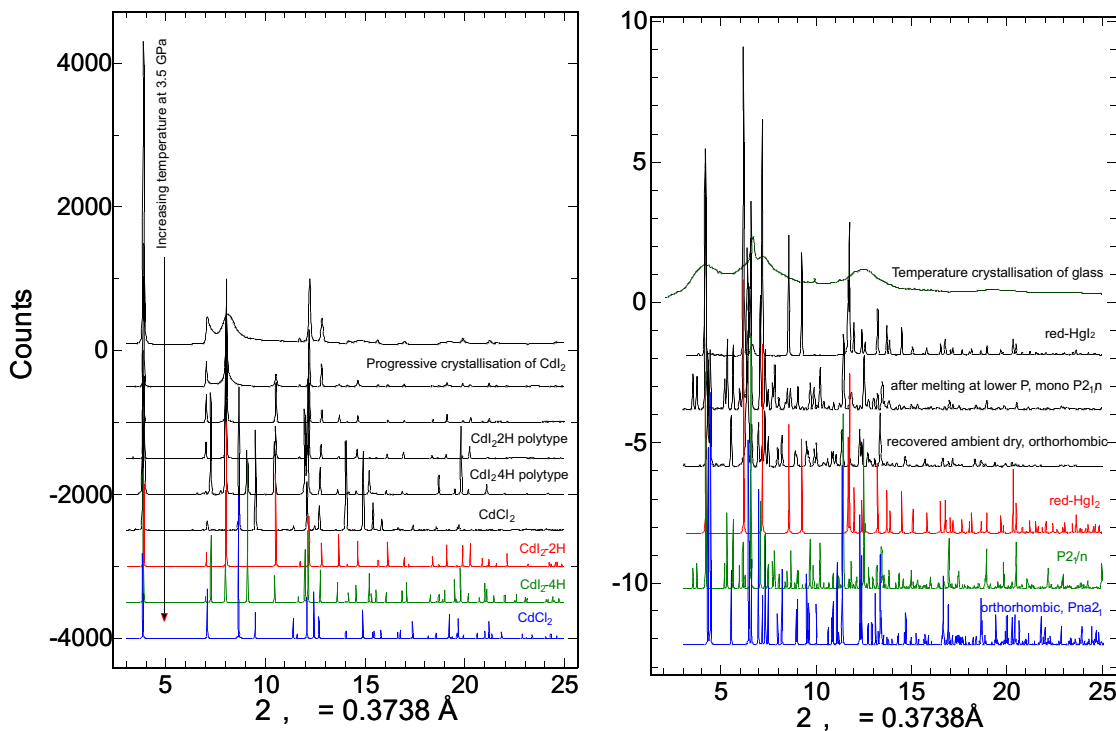

Figure 1. Left, high pressure octahedral phases from pressure-crystallised glass. Right, Low pressure tetrahedral coordinated structures from temperature-crystallised glassy $ZnCl_2$. Obverved data are black and various calculated structures are shown coloured.

A further run linked the low pressure regime with the higher pressure data collection, figure 1 right panel. This time however, the glass was crystallized with temperature under a pressure of ~ 1 GPa, forming the red-HgI_2 type structure. Pressure was then increased to form the 'mixed' phase and reversed. From this point the temperature was then increased, indicating direct melting from HgI_2-type. This structure was condensed and we proceeded by reducing the temperature to follow the melting curve to lower pressures. The next phase to form from the melt was the monoclinic $P2_1/n$ structure and then the orthorhombic stable-at-ambient dry form

of $ZnCl_2$ with space group $Pna2_1$. Several intermediate data were collected to reverse the various transitions between these phases and the melt and to check for metastability. The main difference between these lower pressure phases and the high-pressure phases above is that the local coordination changes from tetrahedrally bound Zn-Cl to six-fold octahedral Zn-Cl layer structures. Therefore, it is entirely possible that above the triple point at 2.5 GPa and 600 °C there lies a region where this change is followed in the liquid. Given the unclear nature of the 'mixed' crystalline structure it is unlikely that any change in local liquid structure mirrors this 4- to 6-fold coordination increase in a 1st order fashion, even when the transition is sufficiently energetic to give rise to devitrification of glassy $ZnCl_2$ at room temperature. In terms of structural sequences, there is no other AX_2 material that has this whole suite of structures over such a modest pressure and temperature range, though individual elements of this sequence are present in many other systems; e.g. HgI_2, $FeCl_2$, SnS_2, PbI_2, etc. The most important point to come from this study is perhaps that the highest pressure and temperature structure is not that of CdI_2 but $CdCl_2$ and difficulties in structural work will be compounded by the prevalance of polytypism. The different stacking sequences in these CdI_2 polytypes do have different elastic strain energies due to slightly ($\Delta c/c \sim 10^{-4}$) different layer repeats and can have (surprisingly) different densities and defect concentrations, e.g. Palosz et al (1990). These will therefore be affected by p, T conditions (see e.g. Palosz and Salje, 1989). Despite that Sakai et al (1985)'s observed phase has been wrongly assigned to CdI_2-type - it is the 'mixed' phase rather than either of the CdI_2 forms seen here - much calculation and many theoretical studies have been conducted with the assumption that only C6 CdI_2 –type, i.e. 2H, is seen as the high pressure form of $ZnCl_2$, we have identified at least five distinct high pressure structures in addition to the 'mixed' phase and the orthorhombic form at ambient conditions.

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