High-pressure structural evolution of the perovskite NH₄MnCl₃

F. Aguado⁴, F. Rodriguez⁵, A.R. Lennie⁶

⁴MALTA-CONSOLIDER Team, DCITIMAC, Universidad de Cantabria, 39005-Santander, Spain
⁵SRS, Daresbury Laboratory, Warrington, WA4 4AD, UK.

aguadof@unican.es

Abstract. The high-pressure evolution of the cubic perovskite NH₄MnCl₃ has been studied in the 0-6 GPa range by angle-dispersive x-ray diffraction. A structural phase transition has been found at low pressure (P_c= 0.4 GPa), in agreement with previous reports. The high-pressure phase has been refined in the tetragonal P4/mbm and orthorhombic Pbnn space groups. In either case, the structure can be described in terms of a tilted perovskite model (one tilt a₀a₀c+ and two tilts a+b-b-, respectively). The average tilting under pressure has been estimated from the lattice parameters. The P-V relation has been fitted by a Murnaghan Equation-of-State with K₀=29(2) GPa and K’₀ = 9(1).

1. Introduction
The behaviour of perovskites under extreme conditions of pressure and temperature has been profusely investigated due to their obvious implications in materials science and geophysics [1]. This interest has raised recently due to the discovery of a high-pressure phase in MgSiO₃ perovskite which could explain the seismic features found above the Earth core-mantle boundary (D’’ layer) [2, 3]. In this sense, halides have been proved to be good analogues for perovskite oxides under high pressure conditions, with the advantage of showing greater compressibilities [4, 5]. Some studies have been performed in order to model the evolution of distorted perovskites under pressure in terms of the BX₆ and AX₁₂ forming polyhedra [6, 7]. However, structural experiments on halide perovskites are still very scarce and the prediction of high-pressure phases deserves this kind of studies in many different systems.

Low temperature studies in some ABX₃ cubic perovskites show distorted structures through octahedral tilting due to the condensation of any of the R₂5 or M₃ modes. NH₄MX₃ (M: Metal ion; X: F, Cl) compounds have been investigated in relation to the role of ammonium in the structural phase transitions (PTs) under temperature and pressure [8, 9]. These PTs are driven by the orientation of NH₄ units (order-disorder), which position is sixfold degenerated in the cubic phase (figure 1) or by mode softening, as in NH₄MnCl₃ [9]. In the AMnCl₃ series, TlMnCl₃ is the only perovskite reported as cubic at ambient conditions. KMnCl₃ is distorted (space group Pnma), whereas Rb and Cs members crystallize in any of the hexagonal perovskite-related structures. Among ammonium halides, NH₄MnF₃ shows a distorted structure upon cooling, which has been defined as tetragonal P4/mmb [10] or orthorhombic Pnma [11]. For NH₄MnCl₃ two low-temperature orthorhombic phases have been previously reported: Pbnn [12] and Cmcm [13]. The former, found below 110K, was refined to a
pseudo-tetragonal structure ($a=b$) involving two different Mn-Cl distances in the MnCl$_6$ octahedra and two different Mn-Cl-Mn octahedron tilting angles ($\phi$). The latter, which is stable in the 258-128K range, implies a more complex structure with three different Mn-Cl values, although just one significant tilting angle is present. The transition temperature was measured at high pressures [9], which provided $P_c = 0.4$ GPa at 293 K. Nevertheless, no structural study at high pressure has been carried out on this compound so far. Consequently, this work studies the structural evolution of NH$_4$MnCl$_3$ with pressure, aiming to determine its high pressure phase among all possible space groups representing tilted perovskites.

2. Experimental

Angle-dispersive XRD experiments under high pressure were conducted at the station 9.5HPT in the SRS facility (Daresbury, UK). The wavelength was fixed at 0.444Å and sample to detector distance, refined through Si-standard calibration, was 340.8 mm. A Merril-Basset diamond anvil cell (DAC) was mounted as high-pressure environment.

Single crystals of NH$_4$MnCl$_3$ were grown from stoichiometric amounts of MnCl$_2$ and NH$_4$Cl by the Bridgman method [14]. All the preparations and cell loading was carried out in a glove box under nitrogen atmosphere to avoid moisture. Powdered samples were mixed with paraffin oil (pressure transmitting media) and loaded in the DAC, together with some ruby chips for pressure calibration.

Diffraction images were collected with a Mar345 image-plate detector and then processed and integrated by the Fit2D software [15]. TOPAS was used for profile refinement (Le Bail fitting) of the characteristic 1D integrated patterns.

3. Results and discussion

Figure 2 shows the high-pressure evolution of the XRD pattern in the 0-6 GPa range. Several superlattice reflections and peak splitting, observed above 0.6 GPa, clearly indicate symmetry lowering in agreement with the previously reported phase transition data [9]. Le Bail fitting (profile matching) has been performed for all the diffraction patterns. Three different space groups, representing perovskite distortions through tilting mechanisms, have been checked: 1) $P4/mbm$ with a simple in-phase tilting scheme along the c-axis ($a^0c^0$, following Glazer’s notation [16]) in a $\sqrt{2}a_{pc}\times\sqrt{2}a_{pc}\times a_{pc}$ unit cell; 2) $Pbnm$ ($\sqrt{2}a_{pc}\times\sqrt{2}a_{pc}\times 2a_{pc}$) with tilts in the three axes ($a^b c^b$) and 3) $Cmcm$ ($2a_{pc}\times 2a_{pc}\times 2a_{pc}$) with tilts along two axes ($a^b c^+$), as in the work by Tornero et al. [13]. These three choices belong to the following tilted-perovskite group-subgroup sequence [17]:

$Pm-3m \rightarrow P4/mbm \rightarrow Pbnm$ (or $Cmcm$)

It has been found out that $P4/mbm$ is adequate for patterns at moderate pressures, as is observed in figure 3, where results of Le Bail fitting are shown at ambient pressure, 0.6 and 0.9 GPa in the 7-12
angular range ($2\theta$). The number of Bragg reflections perfectly matches the tetragonal $P4/mbm$ and superlattice peaks associated with additional tilts in the structure are not evident. However, it must be noted that at higher pressures any of the orthorhombic structures provide best figures of merit ($R_p$ or $R_{wp}$), suggesting the orthorhombic symmetry is best suited for the refinement. Consequently, the more general $Pbnm$ space group has been adopted for all the structural refinements. Thus, pseudo-cubic parameters $a_{pc}$, $b_{pc}$ and $c_{pc}$, obtained from the refined lattice parameters, are plotted in figure 4. As pressure increases $a_{pc}$ and $b_{pc}$ split steadily, thus indicating loss of pseudo-tetragonal character with pressure. In any case, the average tilting angle as a function of pressure can be obtained on the assumption that the one-tilt system $a_0d_{c+}c^-$ (as for $P4/mbm$ symmetry) is preserved in the explored pressure range and MnCl$_6$ octahedra are undeformable, through the expression:

$$\varphi = \arccos \left( \frac{a_m}{\sqrt{2c}} \right)$$

where $a_m = (a + b)/2$ for the $Pbnm$ space group and the Mn-Cl length of the regular octahedron is defined by $d_{\text{Mn-Cl}} = c/4$. The results are depicted in figure 4. The tilting angle increases continuously in the explored pressure range, from $0$ ($\varphi = 180$ deg. at ambient conditions) to approximately $16$ deg. The internal deformation of MnCl$_6$ octahedra would partially reduce the calculated angle.

The Murnaghan Equation-of-State for NH$_4$MnCl$_3$ has been used to fit the $V(P)$ relation in NH$_4$MnCl$_3$ (figure 5). There is a volume reduction of approximately $10\%$ in the 0-6 GPa range. The obtained bulk modulus ($K_0$) is slightly higher than others in AMnCl$_3$ perovskites where A is a cation.

The high pressure behaviour of NH$_4$MnCl$_3$ perovskite is similar to that observed in some GdFeO$_3$-type orthorhombic perovskites, the tilting of which increases with pressure [6]. However, it is important to point out that perovskites bearing ammonium could transform in a different way, due to
the hydrogen bond effects. In this respect, full structural Rietveld refinements are desirable in order to determine the internal positions of Cl atoms, which define the internal octahedral distortion and the Mn-Cl-Mn tilting angles. This work is currently in progress.

Acknowledgements

Financial support from the Spanish Ministerio de Ciencia e Innovación (Project No MAT2008-06873-C02-01/MAT) and the MALTA–Consolider Ingenio 2010 (Ref. CSD2007-00045) are acknowledged.

References

[1] Navrotsky A 1989 Perovskite: A Structure of Great Interest to Geophysics and Materials Science (Arizona: American Geophysical Union)
[2] Murakami M, Hirose K, Kawamura K, Sata N and Ohishi Y 2004 Science 304 855
[3] Oganov A R and Ono S 2004 Nature 430 445
[4] Aguado F, Rodriguez F, Hirai S, Walsh J N, Lennie A R and Redfern S A T 2008 High Press. Res. 28, 539
[5] Umemoto K, Wentzcovitch R M, Weidner D J and Parise J B 2006 Geophys. Res. Lett. 33, L15304
[6] Zhao J, Ross N L and Angel R J 2004 Acta Cryst. B 60 263
[7] Martin C D and Parise J B 2008 Earth Planet. Sci. Lett. 265 630
[8] Bartolome J, Palacio F, Calleja JM, Agullo-Rueda F, Tornero J, Cardona M and Migoni R 1986 J. Mol. Struct. 143 75
[9] Aleksandrov K S, Bartolome J, Gorev M V and Flerov I N 2000 Phys. Stat. Sol. B 217 785
[10] Helmholtz R B, Wiegers G A and Bartolome J 1980 J. Phys. C: Solid St. Phys. 13 5081
[11] Rubin J, Palacios E, Bartolome J and Rodriguez-Carvajal J 1995 J. Phys. Cond. Matter 7 563
[12] Shachar G, Makovsky J, Shaked H 1971 Solid State Commun. 9 493
[13] Tornero J D, Cano F H, Fayos J and Martinez-Ripoll M 1978 Ferroelectrics 19 123
[14] Marco de Lucas M C, Rodriguez F, Prieto C, Verdaguer M and Gudel H 1995 J. Phys. Chem. Solids 56 995
[15] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 High Press. Res. 14 235
[16] Glazer A M 1972 Acta Cryst. B 28 3384
[17] Howard C J and Stokes H T 1998 Acta Cryst. B 54 78