Crystal Structures of Novel i-MAXs Phases Uncovered by STEM

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Z-contrast scanning transmission electron microscopy (STEM) with atomic resolution presents successful alternative technique beyond direct method/Patterson method, to determine crystal structures in direct space without phase problem.1,2 Here, we demonstrate this effective method for novel i-MAX phases as listed below.

MAX phases are a family of laminated ternary carbides and nitrides of hexagonal structure. Including >70 different compounds, MAX phases display a unique combination of metallic and ceramic properties. The general formula can be expressed as Mn+1AXn (n=1-3), where M is a transition metal Ti, Mo, Hf, etc., A is group 13 to 16 element, e.g., Al, Si, and X is C or N.3 Additionally, MAX phases can form quaternary phases by adding the fourth element on the M, A or X site, typically forming solid solutions, e.g., (V0.5Cr0.5)n+1AlCn or out-of-plane chemically ordered phase (o-MAX) Cr2TiAlC2,4 with the same space group of P63/mmc (#194) as the ternary MAXs. To date o-MAX phases only form in 312 and 413 structures, not in 211, possibly due to only one crystallographic site for M, A, and X. Most recently, we have discovered a new family of in-plane chemically ordered quaternary MAX phases (i-MAX) (M2/3M'1/3)2AlC by means of A-HRSTEM.5-7 The microscope used is the Linköping monochromated double-aberration-corrected 60-300 Titan3, operated at 300 kV with SuperX EDX detector. i-MAXs have a carbide sheet MM'CM'M with distinct M' ordering chains within M-dominated layer, which transfers the symmetry of the in-plane ordering carbide sheet from 6-fold to mirror symmetry. i-MAXs can form various crystal structures by stacking the in-plane ordering carbide sheets along c-axis in different ways. Thus, two new crystal structures, one orthorhombic structure of space group Cmcm (#63) and another monoclinic structure of space group C2/c (#15) are formed. After etched off Al and M', another new family of potential energy-related 2D nanomaterials with ordered divacancies, elevated conductivity and supercapacitance is created.

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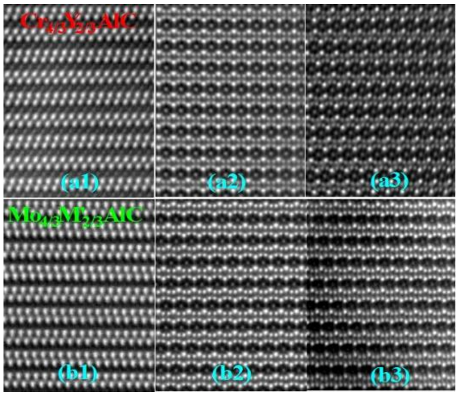

Fig. 1 STEM images of $Cr_{4/3}M'_{2/3}AlC$ with space group of Cmcm (a1-3), and $Mo_{4/3}M'_{2/3}AlC$ with space group of C2/n (b1-3).