Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Experimental Section

1. Materials and reagents

Nb_4AlC_3 MAX phase was synthesized in China from commercially available powders: Nb (99.5%, ≤ 44μm; Beijing Xinrongyuan Science and Tech. Co., Ltd, China), Al (99.9%, ≤ 74 μm; General Research Institute for Nonferrous Metals, Beijing, China) and C (99%, ≤ 94μm; Qingdao Tianhe Graphite Co., Ltd, China). Hydrofluoric Acid (HF), 48-51 % in water, was purchased from Acros. Silicon for x-ray diffraction standards (-325 mesh, 99.5%) was purchased from Alfa Aesar.

2. Synthesis of Nb_4AlC_3

Fully-dense and predominantly single-phase Nb_4AlC_3 polycrystalline samples were prepared by in-situ hot pressing of commercial powders. The raw materials were mixed in a molar ratio of Nb:Al:C of 4:1.1:2.7 by ball milling for 24 h in a polyethene jar filled with argon (Ar). The mixed powders were placed in a graphite mould that was pre-sprayed with a layer of BN and compacted with a load corresponding to a stress of 3 MPa. The compacted body was then heated at a rate of 20°C/min up to 1700 °C and held for 1 h under a load corresponding to a pressure of 30 MPa in flowing Ar, then cooled to room temperature. The resulting billet was 98.2 % dense and predominantly single phase Nb_4AlC_3 (some NbC existed as a phase impurity) as determined by X-ray diffraction (XRD) (Fig. S1). Fine powders were prepared by crushing the Nb_4AlC_3 in a crusher (QE-100 pulveriser, Yili Tools Co., China) followed by sieving through a 400-mesh sieve.

3. Synthesis of $Nb_4C_3T_x$

Nb_4AlC_3 powder (< 38 μm particle size) was immersed in 48-51 % aqueous HF for 96 h at ambient temperature with stirring (magnetic Teflon stir bar) in the ratio of 1 g MAX powder : 10 mL HF solution, followed by cycles of washing with distilled water, centrifuge sedimentation (5 minutes at 3500 rpm each cycle), and decanting, until a pH ~ 5 was reached. At that point, the sediment was mixed in ethanol and allowed to dry by evaporation. Yield: 77% by mass.

4. Characterizations and Measurements

For X-ray diffraction (XRD), all samples were mixed in an agate mortar and pestle with 10 wt. % crystalline silicon as an internal standard, and were then cold-pressed to a pressure of 1 GPa in a 1-inch steel die. For MXenes, this procedure is used to orient the 2-dimensional flakes, magnifying the diffraction signal. A Rigaku SmartLab diffractometer (Rigaku Corporation, Tokyo, Japan) was used to measure XRD patterns (Cu K_α radiation source). MAX and MXene samples were scanned at a step size of 0.02° and 0.04° and collection time of 0.5 s per step, respectively.

Transmission Electron Microscopy (TEM) was performed on a JEOL JEM 2100 microscope. Scanning Electron Microscopy (SEM) was performed on a Zeiss Supra 50VP; Energy-Dispersive Spectroscopy (EDS) was performed with this instrument (Oxford EDS, with INCA software). EDS scans were obtained at low magnification (100-200 x) at random points in the sample; three points per sample (two samples each for MAX and MXene) were used to obtain averages to calculate rough elemental ratios. EDS was performed on bulk sintered Nb_4AlC_3 MAX and cold-pressed $Nb_4C_3T_x$ MXene discs. Elemental standards were as follows: C: $CaCO_3$; Al: Al_2O_3; O: SiO_2; F: MgF_2; Nb: Nb metal. XPP matrix correction (Pouchou and Pichoir (1988)) was used for element quantitative analysis.

Resistivity measurements were performed with a 4-point probe, ResTest v1, Jandel Engineering Ltd., Bedfordshire, UK. Measured resistivity was automatically multiplied by the proper thickness correction factor by the Jandel software, and the resulting values were then multiplied by a correction factor of 0.9748 to account for the sample geometry (discs with diameter of 25.4 mm). The geometric correction factor was provided in the manual included with the 4-point probe.

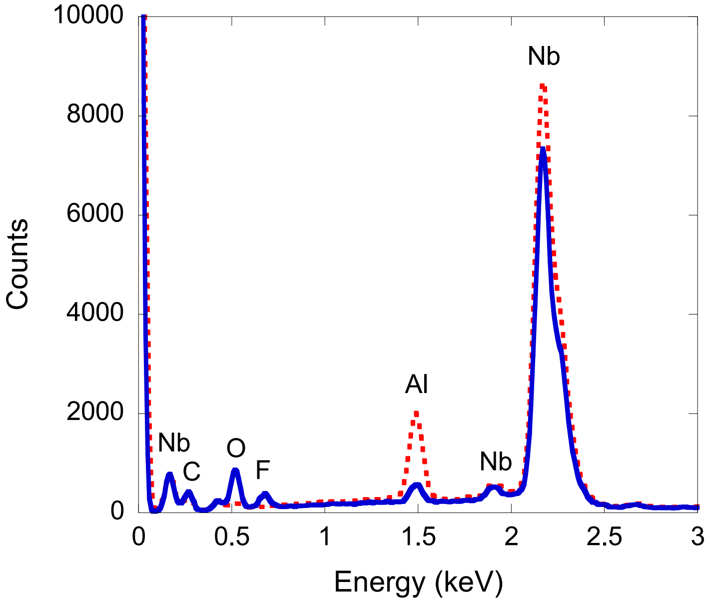

Figure S1: EDS spectra of Nb_4AlC_3 (red, dashed) and $Nb_4C_3T_x$ (after etching, blue, solid).

5. PDF Analysis

Synchrotron X-ray total scattering experiments were conducted at beam line X17A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with an X-ray energy of 67.42 keV ($\lambda = 0.1839$ Å). A large area 2D Perkin Elmer detector (2048 × 2048 pixels and 200 × 200 µm pixel size) was mounted orthogonal to the beam path with a sample-to-detector distance of 205.493 mm. The raw 2D data were azimuthally integrated and converted to 1D intensity versus 2θ using FIT2D.[1] Nickel was also measured as a standard material to calibrate the sample-detector distance.

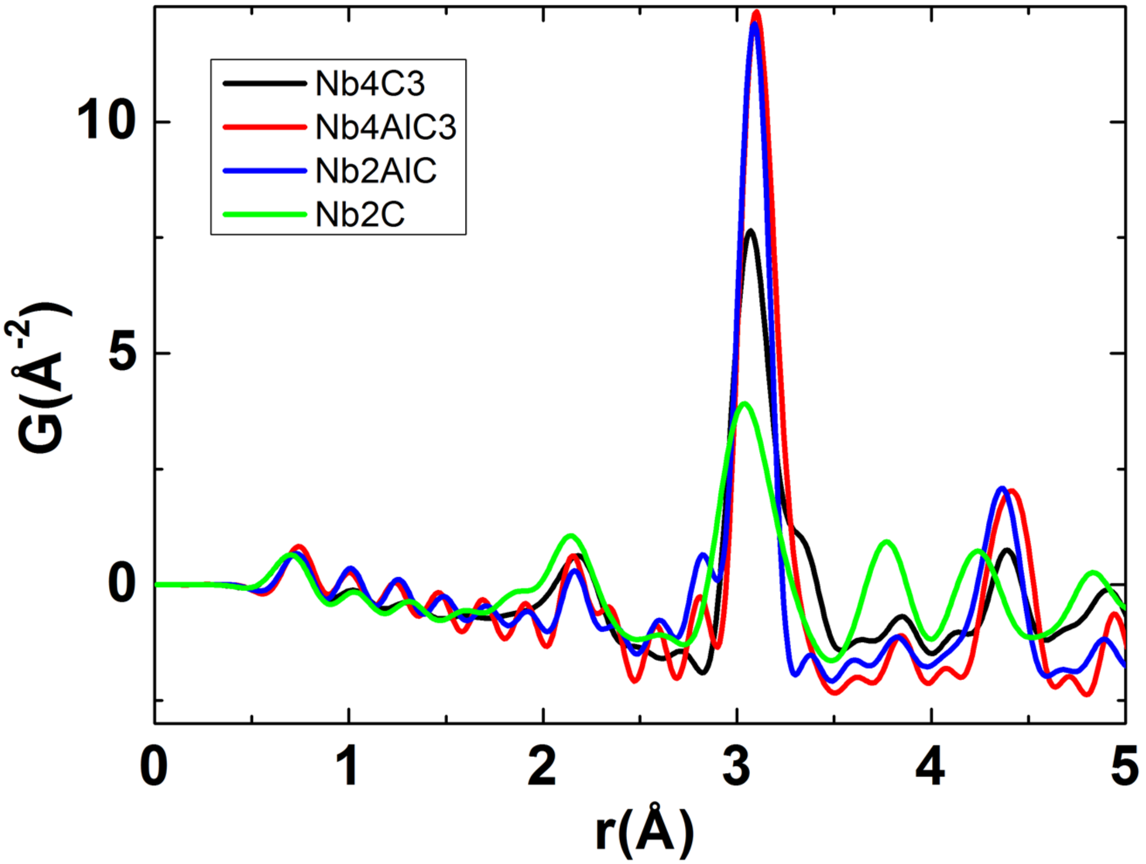

Figure S2. Pair distribution functions shown over a low-*r* region up to 5 Å for Nb_2CT_x and $Nb_4C_3T_x$ MXenes, and their corresponding MAX phases. The shoulder peak at ~3.3 Å is only present in the $Nb_4C_3T_x$ MXene, and not in Nb_4AlC_3, Nb_2AlC, or Nb_2CT_x.

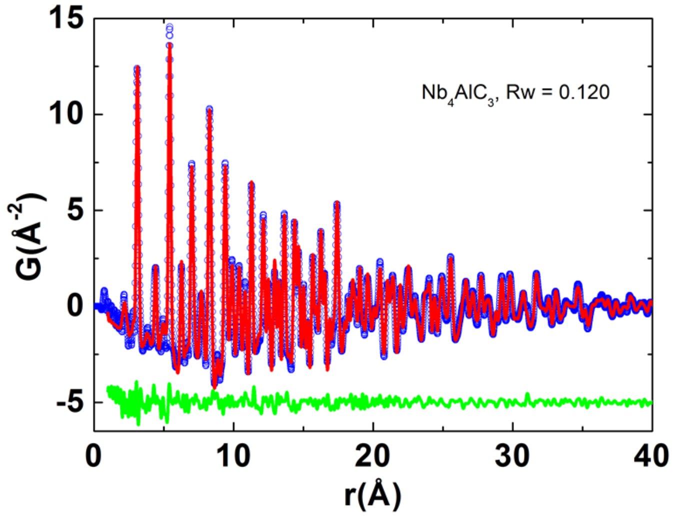

Figure S3. Pair distribution function fit of MAX parent Nb_4AlC_3. Blue circles and red solid line correspond to observed and simulated pair distribution function data, respectively, with green difference curve offset below.

Table S1. Structures of the Nb_4AlC_3 and $Nb_4C_3T_x$. The space group is $P6_3/mmc$. For Nb_4AlC_3 the atoms are on the following special positions: Nb1 at 4f (1/3, 2/3, *z*), Nb2 at 4e (0, 0, *z*), Al at 2c (1/3, 2/3, 1/4), C1 at 2a (0, 0, 0) and C2 at 4f (2/3, 1/3, *z*). For $Nb_4C_3T_x$ MXene, terminating O/F atoms are on (0, 0, *z*) with O/F mole ratio to be 3:1 that was determined from an EDS experiment. Water molecules are introduced to sit between the layers. The total content of water is constrained by the EDS result. As constrained by the space group the water molecules could sit at 2b (0, 0, 1/4), 2c (1/3, 2/3, 1/4), 2d (2/3, 1/3, 1/4), 6h (*x*, 2*x*, 1/4) or 12j (*x*, *y*, 1/4) positions.

	Nb_4AlC_3	**$Nb_4C_3T_x$**
R_w	0.120	0.281
a (Å)	3.1296	3.1331
c (Å)	24.1238	31.0801
z(C)	0.1090	0.0806
z(O/F)	-	0.1865
z(Nb1)	0.0548	0.0444
z(Nb2)	0.1577	0.1221
x(O) (6h)	-	0.0900
x(O) (12j)	-	0.3274
y(O) (12j)	-	0.9195
O_{occ}(2b)	-	0.0108
O_{occ}(2c)	-	0.0027
O_{occ}(2d)	-	0.0008
O_{occ}(6h)	-	0.2261
O_{occ}(12j)	-	0.2679
U_{iso}(O/water) (Å^2)	-	0.0036
U_{iso}(F) (Å^2)	-	0.0132
U_{iso}(O) (Å^2)	-	0.0800
U_{11}(C) (Å^2)	0.0132	0.0208
U_{33}(C) (Å^2)	0.0776	0.0003
U_{11}(Al) (Å^2)	0.0370	-
U_{33}(Al) (Å^2)	0.0140	-
U_{11}(Nb) (Å^2)	0.0043	0.0074
U_{33}(Nb) (Å^2)	0.0023	0.0029
δ_2 (Å^2)	2.5854	4.0401
Q_{damp} (Å^{-1})	0.0456	0.0826
Q_{broad} (Å^{-1})	0.0275	0.0449

References

1. A. P. Hammersley, S. O. Svenson, M. Hanfland and D. Hauserman, *High Press. Res.* 1996, **14**, 235.