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Synthesis of MAX phases Nb$_2$CuC and Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N by A-site replacement reaction in molten salts

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ABSTRACT

New MAX phases Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N and Nb$_2$CuC were synthesized by A-site replacement by reacting Ti$_2$AlN and Nb$_2$AlC, respectively, with CuCl$_2$ or CuI molten salt. X-ray diffraction, scanning electron microscopy, and atomically resolved scanning transmission electron microscopy showed complete A-site replacement in Nb$_2$AlC, which lead to the formation of Nb$_2$CuC. However, the replacement of Al in Ti$_2$AlN phase was only close to complete at Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N. Density-functional theory calculations corroborated the structural stability of Nb$_2$CuC and Ti$_2$CuN phases. Moreover, the calculated cleavage energy in these Cu-containing MAX phases are weaker than in their Al-containing counterparts.

IMPACT STATEMENT

The preparation of MAX phases Nb$_2$CuC and Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N were realized by A-site replacement in Ti$_2$AlN and Nb$_2$AlN, respectively.

Introduction

The MAX phases constitute a family of ternary compounds with a hexagonal structure (space group $P_{6_3}/mmc$, 194) and a molecular formula of $M_{n+1}AX_n$, where M is an early transition metal, A mainly comes from groups 13–16, X is carbon and/or nitrogen, and $n = 1 - 3$ [1,2]. The MAX phases have potential applications in high-temperature electrodes, components with resistance to friction and wear, structural material in nuclear fuel cladding, and as a precursor material for two-dimensional MXene [2–4]. By now, more than 80 members of ternary MAX compositions have been discovered [5]. Recent studies have also demonstrated that the A-site element in MAX phases can be a late-transition metal (e.g. Au, Ir, Zn, Fe and Cu) [6–13]. Transition metals have distinct properties different from other A-group elements due to their large $d$ electron orbits. If late-transition metal elements can be introduced into the A layer of the MAX phase through a replacement reaction, there would be further prospects for tailoring the functionality of MAX phases.

In 2017, Ti$_3$AuC$_2$ and Ti$_3$Au$_2$C$_2$ were synthesized by replacing Si with Au in Ti$_3$SiC$_2$, and Ti$_3$IrC$_2$ was identified by replacing Au with Ir in obtained Ti$_3$Au$_2$C$_2$ [7]. Recently, our group reported a series of new Zn-containing MAX phases (Ti$_3$ZnC$_2$, Ti$_2$ZnC, Ti$_2$ZnN, and V$_2$ZnC) obtained by a replacement reaction between MAX phase precursors and ZnCl$_2$ molten salt [10]. In
these phases, Zn atoms occupy the original Al position at the A site in the MAX-phase structure. The key merit of this A-site replacement strategy is the prevention of competitive phases (such as M-Zn alloys) that can have lower Gibbs free energies than these new MAX phases and would thus be thermodynamically favored. In this synthesis methodology, the redox reaction between Al and Zn\(^{2+}\) and simultaneous evaporation of AlCl\(_3\) accounts for the main driving force. Since Cu\(^{2+}\) cations have higher oxidation potential than Zn\(^{2+}\) cations, Cu atoms have also been incorporated into Ti\(_3\)AlC\(_2\), partially occupying the Al in resultant Ti\(_3\)(Al\(_{1/3}\)Cu\(_{2/3}\))C\(_2\) MAX phase through a similar replacement approach [14]. The partial substitution behavior of Cu in Ti\(_3\)(Al\(_{1/3}\)Cu\(_{2/3}\))C\(_2\) was explained according to the Cu–Al binary phase diagram, in which intermediate Cu–Al alloys are in equilibrium with Al metal below the solidus line. When part of the Al is consumed in a redox reaction and driven out in the form of AlCl\(_3\), Cu and residual Al atoms occupy the A layer of as-formed Ti\(_3\)(Al\(_{1/3}\)Cu\(_{2/3}\))C\(_2\). Although binary phase diagrams (Au–Si, Al–Zn, Al–Cu) have been used to describe the substitution/replacement behavior in these new MAX phases, the atom stacking or mutual atomic interaction in two-dimensional single-atomic A layer should be different from that in three-dimensional materials.

In order to expand this replacement strategy to other novel MAX phases, studies are needed on the incorporation of Cu into a range of MAX phases. Here, Nb\(_2\)CuC and Ti\(_2\)(Al\(_{0.1}\)Cu\(_{0.9}\))N were synthesized by Cu substitution for Al in Nb\(_2\)AlC and Ti\(_2\)AlN phases by reaction with CuI and CuCl\(_2\) molten salts.

**Experimental details**

**Preparation of Ti\(_2\)AlN and Nb\(_2\)AlC**

As in previous work, TiN/Ti/Al/NaCl/KCl powder mixture with a mole ratio of 1:1:1:4:4, and NbC/Nb/Al powder mixture with the mole ratio of 1:1:1 was sintered in order to synthesize Ti\(_2\)AlN and Nb\(_2\)AlC MAX-phase powders. For more details, refer to the Supplementary Information.

**Preparation of Ti\(_2\)(Al\(_{x}\)Cu\(_{1–x}\))N and Nb\(_2\)CuC**

The Ti\(_2\)AlN powders were mixed with CuCl\(_2\) in stoichiometric molar ratios of 2:3 for Ti\(_2\)(Al\(_{x}\)Cu\(_{1–x}\))N. The Nb\(_2\)AlC and CuI (molar ratio = 1:3) were used as the starting material to synthesize Nb\(_2\)CuC. The material mixtures of Ti\(_2\)(Al\(_{x}\)Cu\(_{1–x}\))N and Nb\(_2\)CuC was heated in a tube furnace to 600°C and 700°C respectively at a rate of 2°C/min for 7 h under the protection of argon, then cooled down to room temperature at a rate of 5°C/min. Ammonium persulfate solution was used to remove the residual Cu in the reaction process. Finally, the product was filtered, washed, and dried at 50°C.

More details are provided in the Supplementary Information.

**Characterization and density-functional theory calculations**

The phase composition of the samples was analyzed by X-ray diffraction (XRD) with Cu-K\(_\alpha\) radiation. The microstructure and chemical composition were obtained in scanning electron microscopy with an energy-dispersive spectrometer (EDS). Atomically resolved structural analysis was also carried out by high-resolution scanning transmission electron microscopy (HRSTEM) capable of high angle annular dark field (HAADF) imaging and EDS.

Density-functional theory (DFT) calculations were performed in the in the CASTEP code [15,16], using the generalized gradient approximation (GGA) as implemented in the Perdew–Burke–Ernzerhof (PBE) functional [17,18]. Phonon calculations were carried out to evaluate the dynamical stability using the finite displacement approach, as implemented in CASTEP [19,20]. The equation \(E = (E_{\text{broken}} - E_{\text{bulk}})/S\) [10] was adopted to calculate the cleavage energy \(E\). In this equation, \(E_{\text{bulk}}\) and \(E_{\text{broken}}\) represent the total energies of bulk MAX and the cleaving structures with a 10 Å vacuum separation in the corresponding M and A atomic layers, while \(S\) is the cross-sectional surface area of the MAX-phase materials.

More details are provided in the Supplementary Information.

**Results and discussion**

The Cu-substituted MAX phase was synthesized by replacement reaction between Ti\(_2\)AlN and CuCl\(_2\) molten salt at 600°C. Figure 1(a) shows an XRD pattern of the resulting material. Compared to Ti\(_2\)AlN, the (103), (104), and (106) peaks are shifted towards lower angles. The (002) peak is almost vanished and the (004) peak enhances, indicating a change in periodic symmetry along the \(c\) axis and corresponding change in structure factor [10]. The EDS measurement (Figure 1(b)) on the resultant particles shows that the main elements are Ti, Al, Cu and N. Moreover, elemental mapping indicates that Ti, Cu, Al, and N are uniformly distributed in their respective atomic layers of the MAX structure (See Figure S1). Since the content of Al in the final product was low, we calculated the lattice parameters to study the effect of Cu incorporation assuming
Figure 1. (a) XRD patterns of the Ti$_2$AlN and the Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N obtained from the reaction of Ti$_2$AlN and CuCl$_2$. (b) SEM image of the Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N powder and (c) corresponding EDS spectrum. (d) High-resolution (HR)-STEM image of Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N showing atomic positions along [11\bar{2}0] direction. (e) Elemental mapping in STEM-EDS mode and (f) corresponding line-scanning of Ti-K$\alpha$ (red), Cu-K$\alpha$ (green) and Al-K$\alpha$ (blue) signals, respectively.

The result of Rietveld refinement (see Figure S2) shows that $a = 3.037$ Å and $c = 13.532$ Å in the Cu-incorporated MAX phase as compared with $a = 2.999$ Å and $c = 13.650$ Å of Ti$_2$AlN [21], indicating in-plane expansion with corresponding reduction in the $c$ axis after replacement. Figure 1(c) also shows that the morphology of the resulting particles is similar to that of the parent Ti$_2$AlN particles in size and shape (shown in Figure S3).

Figure 1(d–f) show STEM images of the resulting phase. The atomic positions perpendicular to the [11\bar{2}0] zone axis is shown in Figure 1(d). The Ti$_2$N sub-layers preserve the zig-zag pattern separated by A atomic layers. The brightness of dots depends on the atomic mass (intensity $\sim Z^2$), which means that the heavier Cu atoms have replaced Al in the A layers (Figure 1(d)). The Cu layers are brighter than the Ti layers because of their difference in atomic mass. A lattice-resolved EDS mapping and line scan reveal the atomic positions in the crystal structure (Figure 1(e,f)). Cu is predominant in the final product and has the same atomic positions as Al (Figure 1(f)). STEM-EDS results show that the relative atomic ratio of (Al:Cu) is about 1:9. Therefore, all the above characterization results indicates that the Cu-incorporated MAX phase has a chemical formula of Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N.

The low amount of Al in Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N is noteworthy. In our recent work on Ti$_3$AlC$_2$, only partial substitution of Cu in Ti$_3$(Al$^{1/3}$Cu$^{2/3}$)C$_2$ was achieved. Thus, the same reaction in other MAX phases should be investigated to understand the underlying mechanism.

Figure 2(a) shows XRD patterns of the raw Nb$_2$AlC and the final product obtained through the same replacement methodology in CuI molten salt. Before treatment by ammonium persulfate solution, the characteristic peaks of Cu ($2\theta \approx 43^\circ$, $2\theta \approx 51^\circ$ and $2\theta \approx 75^\circ$) are detected (Figure S4), which indicates the generation of Cu metal during the replacement reaction between Al (derived from Nb$_2$AlC) and CuI. In addition, it can be observed that main the diffraction patterns of the Nb$_2$AlC MAX phase and product after Cu replacement are similar, but the (002) diffraction peak of the Cu-incorporated MAX phase became significantly weaker, as in the case of Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N. On the contrary, the (006) peak became stronger, which means that the Cu...
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Figure 2. (a) XRD patterns of the Nb$_2$AlC and the Nb$_2$CuC obtained from the reaction of Nb$_2$AlC and CuI. (b) Rietveld refinement of XRD of the Nb$_2$CuC.

Table 1. Atomic positions in Nb$_2$CuC determined from the Rietveld refinement.

| Element | $x$   | $y$   | $z$         | Symmetry | Wyckoff symbol |
|---------|-------|-------|-------------|----------|----------------|
| Nb      | 1/3   | 2/3   | 0.59272     | 3m       | 4f             |
| Cu      | 1/3   | 2/3   | 0.25        | −6m$^2$  | 2c             |
| C       | 0     | 0     | 0           | −3m      | 2a             |

Table 1. Atomic positions in Nb$_2$CuC determined from the Rietveld refinement.

substitution in between Nb$_2$C layers changes the stacking of atoms perpendicular to c plane [6,7,11]. To confirm the lattice parameters of the resultant product, Rietveld refinement of the XRD pattern was carried out assuming phase-pure Nb$_2$CuC, as shown in Figure 2(b). The simulated pattern, with a reliability factor $R_{wp}$ of 7.88%, is in good agreement with the experimental data. The previously reported lattice parameters of the Nb$_2$AlC are $a = 3.106$ Å and $c = 13.888$ Å [22], whereas the calculated lattice parameters of Nb$_2$CuC are $a = 3.153$ Å and $c = 13.587$ Å. The atomic positions of Nb$_2$CuC determined from the Rietveld refinement are listed in Table 1.

SEM images of Nb$_2$AlC and Nb$_2$CuC particles are shown in Figure 3(a,b), respectively. The Nb$_2$CuC retains the layered morphology like the raw Nb$_2$AlC. The EDS spectrum of Nb$_2$CuC is shown in Figure 3(c), and all Nb, Cu, and C elements were detected. Only very weak Al signal was present in the EDS spectrum, which is due to small Al(OH)$_3$ attached on Nb$_2$CuC particles (Figure S5). Figure 3(d–f) illustrates the EDS element mapping results of Nb-L$\alpha$, Cu-K$\alpha$ and C-K$\alpha$ signals of the particle shown in Figure 2(b), respectively. The uniform distribution of Nb, Cu, and C in their respective atomic layers indicates that Cu has fully replaced Al in Nb$_2$AlC.

In order to further determine the structure of Nb$_2$CuC, STEM was performed. Figure 4(a,b) show the atomic arrangements with the beam aligned along the [11\overline{2}0] and [\overline{1}100] directions, respectively. As can be observed in both images, one darker layer (the A elements) interleaves two adjoining brighter layers of Nb with larger atomic mass. The presented images are similar to STEM images of other M$_2$AX phases having the characteristic zig-zag stacking of the 211 M$_{n+1}$X$_n$ layers [6,12]. In Figure 4(c), the atomic-resolved EDS element mapping and line scan of Nb-L$\alpha$ and Cu-K$\alpha$ further identified the atom position of Cu, all at A sites, corroborating the synthesis of Nb$_2$CuC MAX phase through a replacement reaction, to form a MAX phase with only Cu on the A site.

The structures of Ti$_2$AlN, Ti$_2$CuN, Nb$_2$AlC, and Nb$_2$CuC MAX phases were calculated by DFT calculations. The lattice parameters, elastic constants and cleavage energies of Ti/Nb and Al/Cu atomic layer in the MAX phases are listed in Table 2. The calculated lattice parameters of Ti$_2$CuN and Nb$_2$CuC show reduced $c$ values compared to Ti$_2$AlN and Nb$_2$AlC, respectively, consistent with our experimental results. However, the experimental $a$ value of Ti$_2$(Al$_{0.1}$Cu$_{0.9}$)N conflicts with the calculated $a$ value, which may be due to the fact that A layers are not completely replaced. The elastic constant $C_{44}$ and shear modulus G of Cu-containing MAX are significantly higher than that of precursor MAX. The phonon dispersion relations are plotted in Figure S6. The vibrational frequencies have no imaginary component, showing that all these MAX phases are dynamically stable. The variation of cleavage energy in the M-Al and M-Cu atomic layers suggests weaker bonding between M and Cu atoms.

The incorporation of transition elements (Zn, Cu) into A site of the MAX phase has been discussed in our previous reports where chloride salts were used [10,14]. Here, we used an alternative molten salt CuI, which has a melting point of 600°C. At 700°C, CuI is molten and ions of
Cu$^+$ and I$^-$ can contact solid reactants [23]. As a strong electron acceptor or Lewis acid [24,25] in molten salt, Cu$^+$ oxidizes Al a drive it out from Nb$_2$AlC. The Al$^{3+}$ cation is then coordinated with Cl$^-$ to form AlCl$_3$ which evaporates (boiling point $\sim$ 360°C). However, the occupancy of copper in the final products is not simply determined by the phase diagram. In the Au–Si and Al–Zn binary phase diagrams, two end members of metal components are separated below the solidus line, which provided a predictable guideline for synthesis of new MAX phases, such as Ti$_3$AuC$_2$ and M$_{n+1}$ZnX$_n$ (M = Ti or V; X = C or N, n = 1 or 2) [7,10]. In contrast, based on the Cu–Al binary phase diagram, it does not appear possible to obtain a single-phase Cu end member from the Al-rich side, since equilibrium intermediate Al–Cu alloys should form, which is why Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ was formed in earlier work [14]. Previous reports also indicated this alloying behavior of Cu into MAX phase [26,27]. However, the present work indicates that this reasoning based on phase-diagram-guidelines is incomplete since an end
member with only Cu on A sites (Nb₂CuC) and one with very high Cu content (Ti₂(Al₀.₁Cu₀.₉)N) were formed. The atomic arrangement in bulk materials, accurately predicted in phase diagrams, will change in a confined space due to the different crystal field strength exerted by other components. In the nanolaminated MAX-phase crystal structure, A atoms have relatively weak bonding with the nearest M atoms and negligible bonding with the next A layer. When an A’ atom (here Cu) occupies the original A-atom position, the crystal field exerted by M atoms modifies the arrangement of A’ in A atomic sites, which may explain why full replacement of A atoms can be achieved in the present work despite the thermodynamic tendency to form a Cu–Al mixture.

**Conclusion**

In summary, the new MAX phases of Ti₂(Al₀.₁Cu₀.₉)N and Nb₂CuC were synthesized by A-site replacement reaction in molten salt. Complete or partial occupancy of Cu at the original Al site in the final MAX phases was demonstrated through atomically resolved scanning transmission electron microscopy. Density-functional theory calculations corroborated the structural stability of these new MAX phases and predicted their elastic properties and low cleavage energy of M–A bonding.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**References**

[1] Barsoum MW. The MX₃+1AXₙ phases: a new class of solids. Prog Solid St Chem. 2000;28:201–281.
[2] Sun ZM. Progress in research and development on MAX phases: a family of layered ternary compounds. Int Mater Rev. 2011;56:143–166.
[3] Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional nanocrystals produced by exfoliation of Ti₃AlC₂. Adv Mater. 2011;23:4248–4253.
[23] Shirakawa Y, Saito M, Tamaki S, et al. Structures of molten CuCl, CuBr and CuI. J Phys Soc Jpn. 1991;60:2678–2683.

[24] Jensen WB. The Lewis acid-base definitions: a status report. Chem Rev. 1978;78:1–22.

[25] Liu D, Zhong C. Characterization of Lewis acid sites in metal-organic frameworks using density functional theory. J Phys Chem Lett. 2010;1:97–101.

[26] Dezellus O, Gardiola B, Andrieux J, et al. Experimental evidence of copper insertion in a crystallographic structure of Ti3SiC2 MAX phase. Scr Mater. 2015;104:17–20.

[27] Nechiche M, Gauthier-Brunet V, Mauchamp V, et al. Synthesis and characterization of a new (Ti1-ε,Cuε)3 (Al,Cu)C2 MAX phase solid solution. J Eur Ceram Soc. 2017;37:459–466.