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Research Article

Deintercalation of Al from MoAlB by molten salt etching to achieve a Mo_2AlB_2 compound and 2D MoB nanosheets

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Abstract: Two-dimensional (2D) MoB metal borides (MoB MBene) have attracted much attention due to their fascinating properties and functional applications. So far, work on the synthesis of 2D MoB nanosheets by acid or alkaline etching of MoAlB has not been very successful. It has been proposed that the 2D MoB MBene may be fabricated by chemical etching of a Mo_2AlB_2 precursor, but further investigations were not performed possibly due to the difficult preparation of the metastable Mo_2AlB_2 compound at high temperatures by solid-state reactions. Here, we report on the successful synthesis of the Mo_2AlB_2 compound and 2D MoB nanosheets by the deintercalation of Al from MoAlB through a $ZnCl_2$ molten salt etching approach at relatively low temperatures. The influence of etching temperature, etching time, and starting mixtures on the formation of desirable phases have been investigated. A pure Mo_2AlB_2 compound was synthesized at temperatures below 600 ℃, while the 2D MoB MBene nanosheets were obtained at 700 ℃ through the molten salt etching of MoAlB. In addition, the present work further confirms that the MoB MBene can be prepared by etching the as-synthesized Mo_2AlB_2 precursor in LiF–HCl solution. Our work demonstrates that the molten salt etching is an effective method to prepare 2D MoB MBene.

Keywords: two-dimensional (2D) materials; Mo_2AlB_2; MoB metal borides (MoB MBene); molten salt etching; microstructure

1 Introduction

Two-dimensional (2D) transition metal carbides and nitrides, so-called MXenes, have unique physical, electronic, and chemical properties due to their atomically laminated structures [1]. The 2D MXenes with surface terminations (typically –O, –OH, –F, and/or –Cl) are generally synthesized from their corresponding MAX (M is an early transition metal, A is an A-group element, X indicates C, N, or B) precursors with a hexagonal crystal structure by etching a “A” layer with acid solutions, alkali solutions, and molten salts [2–9]. The 2D nanostructure and rich functional terminations make MXenes more promising than their MAX precursors in diverse applications including electrochemical energy storage, catalysis,

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microwave absorption, and infrared stealth [10–13]. Among these etching agents, HF, LiF–HCl, HNO_3, and NaOH acid and alkali solutions are hazardous and environmentally harmful. By contrast, Lewis acidic molten salt is relatively safe and environmentally friendly, and is preferred for MXene synthesis today [5,7,14–16].

Inspired by the successful synthesis of MXenes, considerable efforts have been devoted to the fabrication of 2D nanosheets of transition metal borides, so-called MBenes, from MAB (M = transition metal, A = aluminum, and B = boron) phases. The MAB phases have similar nano-layered structures and attractive properties to the MAX phases, but they have an orthorhombic crystal structure containing stacked M–B blocks interleaved with either monolayer or bilayers of Al [17–20].

According to the crystal structure of 2D MBenes, they are grouped into orthorhombic MBenes and hexagonal MBenes prepared from orthorhombic MAB and hexagonal MAX (X is boron) precursors, respectively, with different synthesis methods [21]. It should be noted that these 2D MBenes can be terminated with or without surface functional groups. The pristine MBenes without surface groups are metallic systems, which endow them with intrinsic electrical conductivity and high adsorption of ions. When terminated by the surface groups, MBenes change from metallic to semimetallic or semiconductive, which is analogue to MXenes [21]. So far, only four kinds of MBenes including three orthorhombic types of CrB, MoB, and TiB and a hexagonal type of $Mo_{4/3}B_2$ have been achieved from Cr_2AlB_2, MoAlB, Ti_2InB_2, and $(Mo_{2/3}Y_{1/3})_2AlB_2$ precursors, respectively, through low-temperature etching and high-temperature dealloying methods [22–27]. Among four MBenes, only 2D $Mo_{4/3}B_2$ MBene is terminated with the –F surface group. The as-synthesized 2D MBenes demonstrate attractive properties even superior to MXenes. For example, Xiong *et al*. [25] reported that MoB MBene as anode materials in LiBs exhibits better electrochemical performance than MXenes. Guo *et al*. [28] reported that MoB MBene exhibits great catalytic activity for hydrogen evolution reactions, indicating its promising application as electrocatalyst for the hydrogen evolution. In addition, MoB MBene has potential applications in the H_2 production, similar to Mo_2C MXene, which acts as visible-light photocatalyst for the H_2 production partially due to the more activity of the Mo element [29,30].

2D MoB MBene was generally synthesized from MoAlB through different chemical etching methods, which are always used for the synthesis of most MXenes. However, work on the synthesis of 2D MoB MBene from MoAlB through the above methods has not been very successful so far. Experimental results demonstrated that 2D MoB MBene could not be directly synthesized by etching MoAlB in HF or LiF–HCl acid solution because these solution corrode M–B slabs and Al layers simultaneously. For example, Gupta and Fuka [31] treated MoAlB with the LiF–HCl solution, and obtained $Mo_{0.67}Al_{0.33}BO_{0.19}F_{0.02}$ particulates with interconnected pores. To overcome the above drawback, Kota *et al*. [32] adopted a dealloying strategy to prepare MBene by heat-treatment of MoAlB at 1500 ℃ for 1 h under vacuum, but they found that MoAlB almost transformed into tetragonal MoB particles rather than MBene. The alkali solution etching route was also used to prepare MoB nanosheets from MoAlB. Alameda *et al*. [24] studied the etching behavior of Al from a MoAlB single crystal in NaOH solution. The stepwise removal of Al atoms from MoAlB induced the formation of metastable Mo–Al–B intergrowth phases such as $Mo_6Al_5B_6$, $Mo_4Al_3B_4$, $Mo_3Al_2B_3$, and Mo_2AlB_2. They found that two MoB nanosheets are partially delaminated from the etched Al region of Mo_2AlB_2, and suggested that the MoB MBene cannot be obtained by direct etching MoAlB, but may be achieved by etching Mo_2AlB_2 in alkali solution.

Mo_2AlB_2 is an MAB phase and has an orthorhombic crystal structure containing stacked M–B blocks interleaved with a monolayer of Al. However, it is a metastable compound and difficult to synthesize at high temperatures with the conventional solid-state synthesis method. In contrast, the topochemical synthesis is an efficient approach to preparing Mo_2AlB_2 by the deintercalation of half Al atoms from MoAlB. For example, Kim *et al*. [33] treated MoAlB with the LiF–HCl solution for more than 48 h, and obtained a pure Mo_2AlB_2 phase. Alameda *et al*. [34] reported a multi-step pathway to synthesize Mo_2AlB_2. They etched MoAlB with NaOH for more than 24 h to form $MoAl_{1-x}B$, and then heat-treated $MoAl_{1-x}B$ at 600 ℃ for 4.5 h to get Mo_2AlB_2, but together with an aluminum oxide on the particle surface. Up to now, work on the synthesis of MoB MBene from Mo_2AlB_2 has not been reported. Whether 2D MoB nanosheets can be fabricated from the Mo_2AlB_2 precursor by chemical etching methods is still unclear.

Based on the above discussions, it can be found that the acid and alkali solutions are generally used to prepare 2D MoB MBene. However, the acid and alkali solutions are not preferred due to their waste disposal problems and environmentally harmful pollution. In addition, the long period also limits the large-scale synthesis of the desired product. By contrast, MXenes have been successfully obtained in a short period of time by Lewis acidic molten salt method [7]. Lewis acidic molten salt method is a safe, effective, and environmentally friendly method to prepare 2D MXenes. However, no studies have focused on the synthesis of 2D MBenes through Lewis acidic etching of MAB phases so far.

In the present work, Mo_2AlB_2 and 2D MoB MBene were synthesized by the stepwise deintercalation of Al from MoAlB with $ZnCl_2$ molten salts at relatively low temperatures. The influencing factors on the desirable products have been investigated. The synthesis of the MoB MBene from the Mo_2AlB_2 precursor by the LiF–HCl solution was also performed.

2 Experimental details

2.1 Preparation of MoAlB

MoAlB was synthesized by pressureless sintering of the mixture of Mo, Al and B powders. Mo (300 mesh, 99.5% purity, General Research Institute for Nonferrous Metals (GRINM), China), Al (300 mesh, 99.5% purity, GRINM, China), and B (300 mesh, 99% purity, GRINM, China) powders with a molar ratio of Mo : Al : B = 1 : 1.3 : 1 were mixed for 10 h in a rotary drum type ball-miller (QGM-8, Zibo Qimingxing New Material Incorporated Co., Ltd., China) with a speed of 150 r/min. The mixture was cold-pressed to form samples (ϕ50 mm × 5 mm), and then sintered in a tube furnace (ZT-30-22Y, Shanghai Chenhua Science Technology Co., Ltd., China) at 1200 ℃ for 1 h in an Ar atmosphere. The heating rate was set as 10 ℃/min. After sintering, the tube furnace was cooled to ambient temperature. The prepared samples were pulverized and sieved using a 200-mesh sieve to get MoAlB powders.

2.2 Synthesis of Mo_2AlB_2 and MoB MBene

Mo_2AlB_2 and MoB MBene were prepared by $ZnCl_2$ molten salt etching of MoAlB at designed temperatures. The influence of the etching temperature, the etching time, and the molar ratio of MoAlB : $ZnCl_2$ on the formation of final products were investigated. MoAlB and $ZnCl_2$ were mixed with different molar ratios of MoAlB : $ZnCl_2$ = 1 : 2, 1 : 4, and 1 : 6. $ZnCl_2$ has a melting point of 283 ℃ and a boiling point of 732 ℃. Therefore, the mixtures were placed into alumina crucibles and sintered in a high-temperature furnace in the temperature range of 500–700 ℃ for 1–4 h in Ar. The heating rate was set as 4 ℃/min. After sintering, the furnace was cooled down to room temperature. The sintered mixtures were washed in HCl solution (5 wt%) for 2 h at 30 ℃, and then re-washed with deionized water. Finally, the resultant powders were dried at 50 ℃.

2.3 Etching of Mo_2AlB_2 with LiF–HCl solution

The as-synthesized Mo_2AlB_2 precursor was also etched in the LiF–HCl solution to get the 2D MoB nanosheets. The LiF–HCl solution was prepared by adding 0.41 g of LiF to 20 mL of 6 M HCl and stirring for 10 min at room temperature. 0.5 g of the Mo_2AlB_2 powders were gradually added to the LiF–HCl solution at room temperature for 24 h and at 40 ℃ for 24 and 42 h. After the etching test, the solution was filtered to collect the resultant powders. The powders were washed with deionized water and centrifugated for several cycles until a pH value of 5–7 was achieved. Finally, the resultant powders were dried at 50 ℃.

2.4 Material characterization and simulation

Geometry optimization of the Mo_2AlB_2 crystal structure was calculated using Cambridge Serial Total Energy Package (CASTEP) module. A simulated X-ray diffraction (XRD) pattern was calculated by Reflex module. Both modules belong to the Materials Studio program (Accelrys Inc., USA). Phase composition was identified by an X-ray diffractometer (Ultima-IV, Rigaku, Japan) with Cu Kα radiation operated at 40 kV and 40 mA. Morphologies of the samples were characterized by a field-emission scanning electron microscope (FE-SEM; JSM-7001F, JEOL, Japan) equipped with an energy-dispersive spectrometer (EDS; X-Max, Oxford Instruments, UK) and a transmission electron microscope (TEM; Tecnai G2 F30, FEI, USA) at an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) was performed in an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo, USA) with a monochromic Al Kα X-ray source ($h\nu$ = 1486.6 eV, where h is the Planck constant, and ν is the phonon frequency) to identify the chemical compositions and bonds.

3 Results

3.1 Preparation of Mo_2AlB_2 by molten salt etching of MoAlB

Figure 1 shows the crystal structures of Mo_2AlB_2 and MoAlB. Mo_2AlB_2 is comprised of Mo–B slabs interleaved with an Al monolayer (Fig. 1(a)), which is obviously different from Al bilayers in MoAlB (Fig. 1(b)). On the basis of the crystal structures, it is proposed that the deintercalation of an Al layer between the two adjacent Mo–B slabs enables MoAlB to convert into Mo_2AlB_2 with a decrease in the cell volume from 137.7676 to 111.7278 Å^3. The simulated structural parameters and atomic positions of Mo_2AlB_2 are summarized in Table 1, which are consistent with those reported in Refs. [18,35]. The calculated values of d-spacings, 2θ, and intensities for (hkl) reflections of Mo_2AlB_2 are listed in Table S1 in the Electronic Supplementary Material (ESM).

To confirm the above proposition, a molten salt etching approach was adopted to achieve the Mo_2AlB_2 phase by the deintercalation of the Al layers from MoAlB. The mixture of MoAlB/2ZnCl$_2$ (molar ratio) was firstly treated at temperatures of 500–700 ℃ for 2 h. Figure 2(a) presents the XRD patterns for the resultant products, together with that of MoAlB for comparison. It can be found that the temperature has a profound influence on the formation of the resultant phases. After etching at 500 ℃ for 2 h, diffraction peaks corresponding to Mo_2AlB_2 are predominant, but some peaks belonging to MoAlB dramatically decrease in intensity, indicating that most MoAlB has been

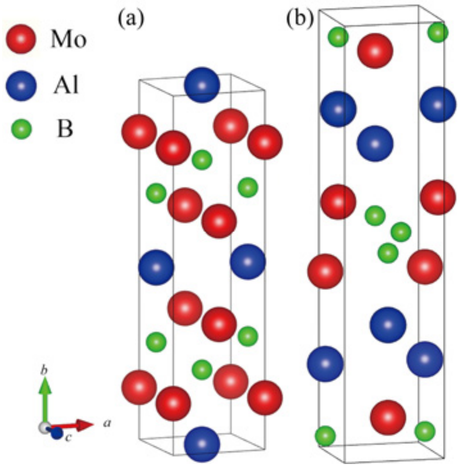

Fig. 1 Crystal structures of (a) Mo_2AlB_2 and (b) MoAlB.

Table 1 Simulated structural parameters for Mo_2AlB_2 and MoAlB

		Mo_2AlB_2	MoAlB
Crystal system		Orthorhombic	Orthorhombic
Space group		*Cmmm* (65)	*Cmcm* (63)
Formula unit		2	4
Lattice parameter (Å)	*a*	3.0747	3.1987
	b	11.4619	13.9218
	c	3.1703	3.0937
Cell volume (Å^3)		111.7278	137.7676
Density (g/cm^3)		7.15	6.45
Atomic position	Mo	(0, 0.1429, 0)	(0, 0.4105, 0.2500)
	Al	(0, 0.5000, 0.5000)	(0, 0.1985, 0.2500)
	B	(0, 0.2923, 0.5000)	(0, 0.0338,0.2500)

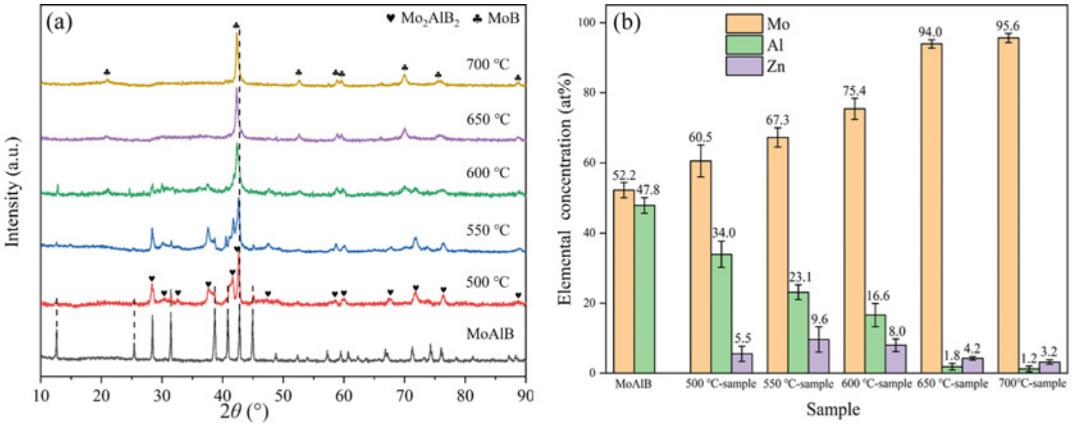

Fig. 2 (a) XRD patterns of resultant products after treatment of MoAlB/2ZnCl$_2$ (molar ratio) at different temperatures for 2 h, together with XRD pattern of MoAlB for comparison. (b) Energy-dispersive spectroscopy (EDS) results showing contents of Mo, Al, and Zn in MoAlB and resultant products.

transformed into Mo_2AlB_2 upon etching in the $ZnCl_2$ molten salt at 500 ℃. The broad peaks of Mo_2AlB_2 suggest that the formed Mo_2AlB_2 phase may have a nanosized structure or contain high density of stacking faults induced by the deintercalation of Al from MoAlB. Reference [24] reports that the high density of the stacking faults was observed in transformed Mo_2AlB_2 after topochemical etching of partial Al from MoAlB. After etching at 550 ℃ for 2 h, Mo_2AlB_2 is the predominant phase with minor MoAlB. This result suggests that Mo_2AlB_2 can be obtained by etching MoAlB in the $ZnCl_2$ molten salt with a molar ratio of MoAlB : $ZnCl_2$ = 1 : 2.

After etching at 600 ℃, the peaks belonging to a new phase of MoB become dominant, and several weak peaks of Mo_2AlB_2 still appear (Fig. 2(a)), suggesting that Mo_2AlB_2 gradually transforms to MoB under such conditions. This result further confirms that Mo_2AlB_2 is a precursor for the mass production of MoB MBene. No new phases except for MoB can be found with increasing temperature from 650 to 700 ℃. The volume fractions of MoAlB, Mo_2AlB_2, and MoB phases are roughly calculated according to the XRD data, and listed in Table S2 in the ESM. After molten salt etching at above 650 ℃, a single phase of MoB is achieved.

To confirm elemental concentrations in MoAlB and the resultant products (denoted as 500 ℃-, 550 ℃-, 600 ℃-, 650 ℃-, and 700 ℃-samples), the abovementioned powders were embedded in resin, and then polished for EDS line analyses along cross-sectional surfaces of the powders. The EDS results are compared in Fig. 2(b). The B is not considered because its content cannot be accurately determined by the EDS. With increasing etching temperature, the Mo content exhibits an increasing tendency, while the Al content shows a decreasing tendency in the as-synthesized samples. The content of Al decreases from 47.8 at% for MoAlB to 23 at% for the 550 ℃-sample. The atomic ratio of Mo : Al(Zn) is about 2.05 : 1, corresponding to Mo_2AlB_2. This result indicates that half of Al atoms should be etched from the Al double layers of MoAlB, resulting in the Al single layer of Mo_2AlB_2. It should be noted that the Al content dramatically decreases to 1.8 at% in the 650 ℃-sample, indicating the formed MoB phase with minor Al. Zn was detected in all of the resultant products. The 550 ℃-sample has a high concentration of Zn, about 9.6 at% (Fig. 2(b)). The above results indicate that the Zn cations from the $ZnCl_2$ molten salt replace Al atoms and occupy their sites in MoAlB, forming a Mo(Al,Zn)B or $Mo_2(Al,Zn)B_2$ solid solution. As the Zn element enters the A-site, lattice parameters vary somewhat due to the difference between the Al and Zn atomic radii, as seen in Table S3 in the ESM. Li *et al.* [5] also reported that Zn-containing MAX phases (Ti_3ZnC_2 and Ti_2ZnC) can be obtained by the replacement reaction between $ZnCl_2$ and MAX precursors for a certain period, and Cl-terminated MXenes ($Ti_3C_2Cl_2$ and Ti_2CCl_2) are finally achieved by further etching the above-mentioned MAX precursors in the $ZnCl_2$ molten salt. The Al depletion, if severe, results in the formation of the MoB MBene, together with the decrease of the Zn content. For example, the MoB samples obtained at 650 and 700 ℃ contain only 4.2 and 3.2 at% Zn, respectively (Fig. 2(b)).

According to the XRD and EDS analyses, Mo_2AlB_2 is stable below 550 ℃. This result is in good agreement with the result reported in Ref. [34] that Mo_2AlB_2 is more unstable at 600 ℃. To investigate the influence of the ratio of MoAlB : $ZnCl_2$ on the

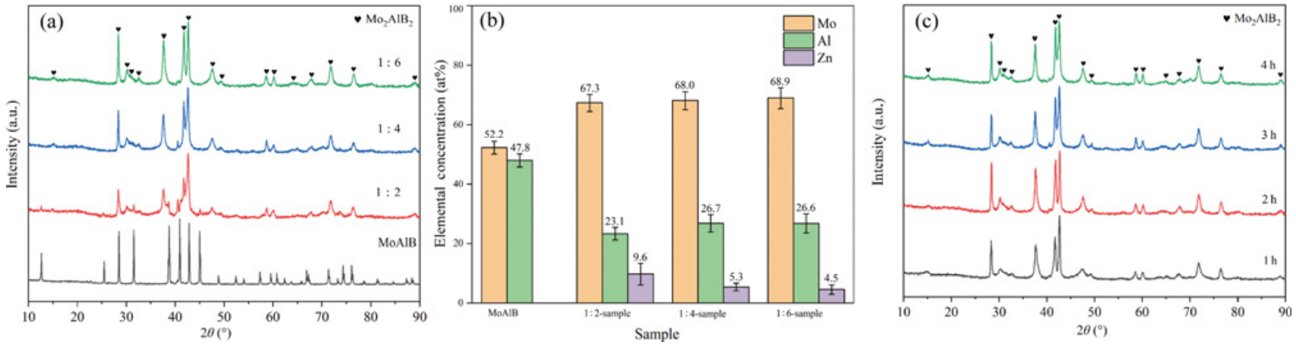

Fig. 3 (a) XRD patterns of MoAlB and resultant products after treatment of MoAlB/$ZnCl_2$ with different molar ratios at 550 ℃ for 2 h. (b) Corresponding contents of Mo, Al, and Zn (at%) in MoAlB and resultant products confirmed by EDS. (c) XRD patterns of resultant products after treatment of MoAlB/6$ZnCl_2$ (molar ratio) at 550 ℃ for different time.

formation of Mo_2AlB_2, the mixtures of MoAlB and $ZnCl_2$ with molar ratios of 1 : 2, 1 : 4, and 1 : 6 were heat-treated at 550 ℃ for 2 h. The XRD results are presented in Fig. 3(a). It can be found that high purity of Mo_2AlB_2 is achieved after treatment of the MoAlB/6$ZnCl_2$ mixture at 550 ℃ for 2 h. The EDS line analyses demonstrate that the atomic ratio of Mo : Al(Zn) in the etched samples changes from 1 : 1 for MoAlB to 2 : 1 for Mo_2AlB_2 (Fig. 3(b)). Meanwhile, the ratio of Mo : Al remains unchanged, further confirming that the formed Mo_2AlB_2 is stable at 550 ℃.

Based on the above results, the influence of the etching time on the formation of Mo_2AlB_2 was also studied using the MoAlB/6$ZnCl_2$ mixture at 550 ℃. It can be found that only 1 h of etching results in high purity of the Mo_2AlB_2 phase (Fig. 3(c)). Further prolonging the etching time makes the same result.

Figure 4 presents experimental and simulated XRD results (listed in Table S1 in the ESM). Compared with the simulated XRD pattern, the experimental XRD result of Mo_2AlB_2 obtained by treatment of MoAlB/6$ZnCl_2$ at 550 ℃ for 1 h is in good agreement with theoretical prediction, suggesting the high purity of the as-synthesized Mo_2AlB_2.

Figure 5 shows SEM micrographs of MoAlB and Mo_2AlB_2. MoAlB grains have a typical layered morphology (Fig. 5(a)), and the Mo_2AlB_2 crystals have a more obvious layered microstructure. A partially exfoliated feature was also observed in the Mo_2AlB_2 grains due to the molten salt etching (Fig. 5(b)). TEM images of Mo_2AlB_2 are presented in Fig. 6 and Figs. S1 and S2 in the ESM. The high-resolution TEM (HRTEM) image shows that the interlayer spacing of Mo_2AlB_2 is about 0.59 nm (Fig. 6(a)), corresponding to the (020) plane. The inset in Fig. 6(a) is the corresponding fast Fourier transform (FFT) pattern, indicating a crystalline character. Figure 6(b) presents stacking faults in Mo_2AlB_2. The observation explains the reason why the diffraction peaks of Mo_2AlB_2 are

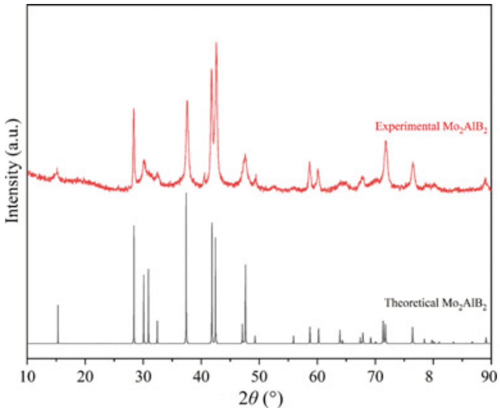

Fig. 4 XRD patterns of simulated and experimental Mo_2AlB_2.

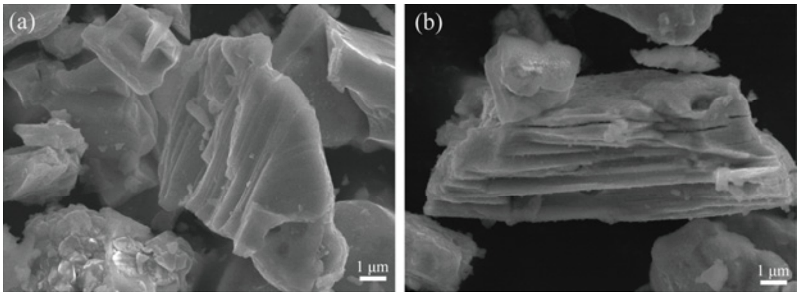

Fig. 5 SEM images of (a) MoAlB and (b) Mo_2AlB_2.

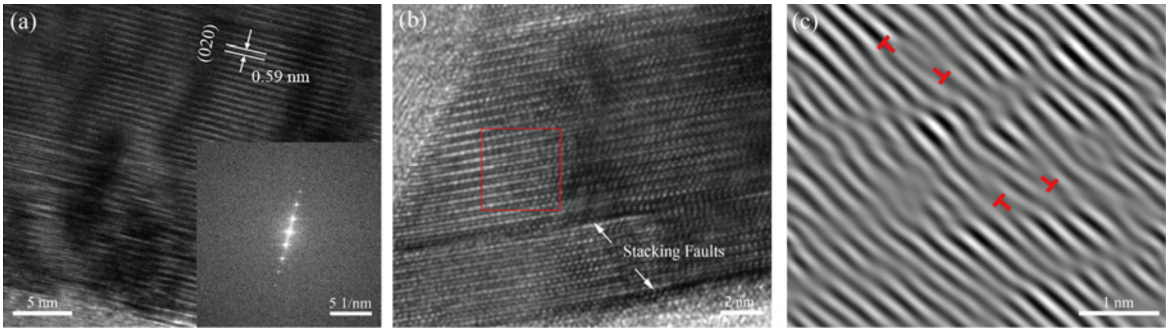

Fig. 6 (a, b) HRTEM images of Mo_2AlB_2; the inset in (a) is corresponding selected area FFT pattern. (c) Corresponding inverse FFT pattern of the area marked with the red rectangle in (b).

broad, as shown in Fig. 1. Figure 6(c) is the inverse FFT pattern, presenting a large number of dislocations. The above defects should form as a result of the deintercalation of Al from MoAlB upon etching in the $ZnCl_2$ molten salt. A series of defect phases including $Mo_3Al_2B_4$, $Mo_3Al_2B_3$, $Mo_4Al_3B_4$, and $Mo_6Al_5B_6$ have also been observed after the deintercalation of the MoAlB precursor [24,36,37]. The selected area electron diffraction (SAED) pattern (Fig. S1 in the ESM) confirms that the Mo_2AlB_2 particle is a single crystal according to a spot pattern, which could be indexed as reflections of an orthorhombic lattice. The ratio of Mo : Al determined by the TEM–EDS analysis is 2 : 0.96, close to the stoichiometric ratio of 2 : 1 for Mo_2AlB_2 (Fig. S2 in the ESM).

3. 2 Preparation of 2D MoB MBene by molten salt etching of MoAlB

The XRD and EDS analyses (Fig. 2) show that the Al atoms have been removed from MoAlB at above 600 ℃ in the $ZnCl_2$ molten salt, resulting in the formation of MoB. No other diffraction peaks corresponding to binary borides such as MoB_2, MoB_3, and MoB_4 [38–40] were found in the present study. The XRD pattern of the as-synthesized MoB after etching at 700 ℃ was compared with the standard XRD pattern of MoB (ICDD PDF Card No. 51-0940), as shown in Fig. 7. It was found that the as-synthesized MoB has the strong (112) diffraction peak, indicating that the formed MoB has a sheet structure with a preferred (112) plane. According to the XRD results, the lattice parameters of the as-synthesized MoB MBene are calculated and listed in Table S4 in the ESM, which are similar to those of MoB (ICDD PDF Card No. 51-0940) but different from the reported parameters for 2D MoB MBene (Table S4 in the ESM). In the present study, the high temperature upon molten salt etching possibly induces 2D MoB nanosheets with a high degree of crystalline perfection. Further work on the separation of stacked nanosheets of MoB to achieve a single or few layer of the 2D MoB MBene will be performed.

Figure 8(a) presents an SEM micrograph for the resultant MoB. The as-synthesized MoB has a 2D nanosheet structure, with a thickness ranging from 10 to 100 nm (Fig. 8(b)). This feature illustrates that the Al layers are completely removed from Mo_2AlB_2, resulting in MoB nanosheets or MoB MBene. The morphology of the as-synthesized MoB MBene is similar to that of CrB MBene obtained by the deintercalation of Al from Cr_2AlB_2 with the HCl solution [22].

The as-synthesized MoB MBene was further characterized by the XPS. The overview XPS spectra of MoB MBene (red) and MoAlB precursor (black) are depicted in Fig. 9(a). The signal peaks of Al 2p, B 1s, Mo 3d, and O 1s located at 74, 188, 232, and

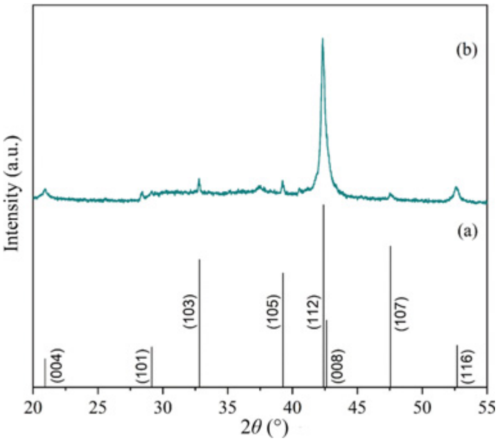

Fig. 7 XRD patterns of (a) MoB (ICDD PDF Card No. 51-0940) and (b) 2D MoB MBene produced at 700 ℃ and further washed by HCl solution.

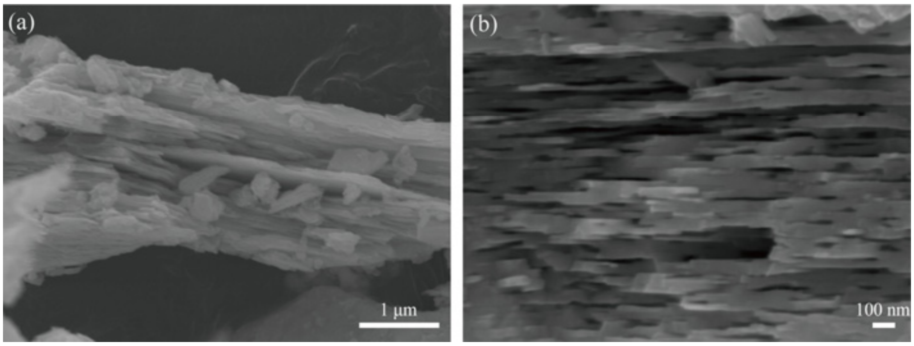

Fig. 8 SEM micrographs of resultant MoB MBene: (a) low-magnification SEM image and (b) high-magnification SEM image.

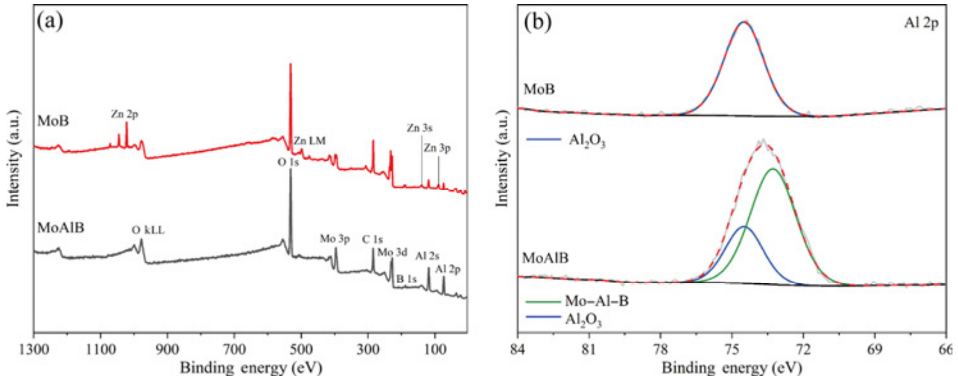

Fig. 9 (a) XPS full spectra of MoAlB precursor (black) and as-synthesized MoB MBene (red). (b) High-resolution XPS spectra with peak fitting of Al 2p.

532 eV, respectively, appear in the two spectra. The appearance of Zn signals indicates the existence of Zn^{2+} or the as-formed ZnO in MoB MBene (Fig. S3 in the ESM). The Zn atoms were easily oxidized to ZnO on the surface of the MoB MBene upon etching at temperatures below 700 ℃. ZnO is difficult to discover by XRD due to its low amount, but can be detected by XPS. The appearance of C in the XPS spectra may be due to the absorption of CO_2. Figure 9(b) presents the high-resolution spectra of Al 2p, with bonded states of elements. The Al 2p XPS spectra of MoAlB contain two fitting peaks at 72.7 and 74.4 eV, assigned to Mo–Al–B and Al–O bonds, respectively. The detected Al–O bond is contributed by Al_2O_3. Al_2O_3 was always detected in the Al-containing MAB phases due to the oxidation on the surface. After molten salt etching, no Mo–Al–B peak but only Al–O peak was detected, suggesting the complete removal of Al from MoAlB. Detailed analyses of other elements are shown in Fig. S3 and Table S5 in the ESM. It should be noted that no bonds corresponding to –Cl surface group were detected by the XPS, suggesting the formed 2D MoB MBene without terminations.

3.3 Preparation of 2D MoB MBene by acid etching of Mo_2AlB_2

Although researchers proposed that Mo_2AlB_2 may be the precursor for preparing 2D MoB MBene, no work has been conducted to confirm the above proposition so far. In the present study, we try to etch the Al layers from Mo_2AlB_2 with an acid etchant to prepare MoB MBene. It is well known that MXenes are generally achieved by chemical etching MAX phases with the LiF–HCl acid solution. Therefore, the LiF–HCl acid solution is preferentially chosen to etch the Mo_2AlB_2 precursor.

Mo_2AlB_2 powder was immersed in the LiF–HCl acid solution at room temperature for 24 h and at 40 ℃ for 24 and 42 h. The phase compositions of the etched powder was identified by the XRD, as shown in Fig. 10. After etching at room temperature for 24 h, the XRD patterns of the etched samples are similar to that of Mo_2AlB_2, indicating that Mo_2AlB_2 is still the predominant phase. As the etching temperature was increased to 40 ℃ for 24 h, Mo_2AlB_2 is still the main phase with minor MoB. However, etching at 40 ℃ for 42 h induces two new phases of Li_2MoO_3 and MoB. The former phase is an unwanted impurity, but the latter is a desirable phase. Under such conditions, the MoB phase is predominant. This result confirms that 2D MoB MBene can be successfully obtained by chemical etching the Mo_2AlB_2 precursor with the LiF–HCl solution. It should be noted that there is a residual Mo_2AlB_2 phase after etching in the LiF–HCl solution at 40 ℃ for 42 h, indicating that the etching rate of such solution is very slow. In addition, the acid solution is hazardous. Therefore, the molten salt etching of MoAlB is preferred to achieve 2D MoB MBene.

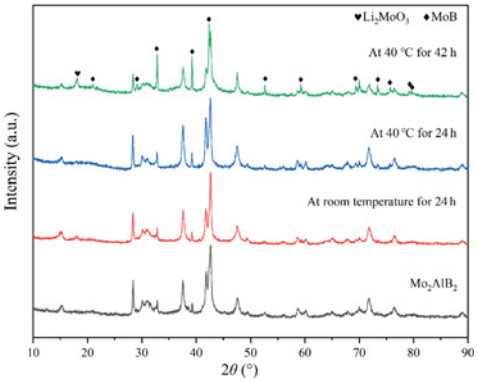

Fig. 10 XRD patterns of Mo_2AlB_2 before (the black line) and after etching in LiF–HCl solution under different conditions.

4 Discussion

The temperature plays a critical role in the phase formation from MoAlB to Mo_2AlB_2 and finally to the MoB MBene in the MoAlB–$ZnCl_2$ reaction system. The schematic for the phase formation is described in Fig. 11(a).

At temperatures below 600 ℃, a reaction between MoAlB and $ZnCl_2$ occurs, as described by Reaction (1):

$$4MoAlB + 3ZnCl_2 = 2Mo_2AlB_2 + 3Zn + 2AlCl_3\uparrow \quad (1)$$

At temperatures above 600 ℃, Reaction (2) occurs between Mo_2AlB_2 and $ZnCl_2$:

$$2Mo_2AlB_2 + 3ZnCl_2 = 4MoB + 3Zn + 2AlCl_3\uparrow \quad (2)$$

The reaction mechanism of MoAlB and $ZnCl_2$ is similar to that of MAX and Lewis acidic salt [6]. In the $ZnCl_2$ molten salt, the coordinately unsaturated Zn^{2+} is a strong acceptor for Cl^- and electrons, and thus acts as Lewis acidity. Owing to the stronger Mo–B bonds and the weaker Mo–Al bonds, the weakly bonded Al atoms in MoAlB are easily converted into Al^{3+} with a redox reaction, as described by Reaction (3):

$$2Al + 3Zn^{2+} = 3Zn + 2Al^{3+} \quad (3)$$

The generated Al^{3+} ions spontaneously bond with Cl^- to form $AlCl_3$. $AlCl_3$ as a gaseous phase rapidly evaporates at the experimental temperatures of 500–700 ℃ due to its boiling point of 180 ℃. The liquid environment enables the reactions to proceed quickly and efficiently.

At temperatures below 600 ℃, the energy is not enough to completely remove all Al atoms from the structure of MoAlB by $ZnCl_2$. Once an Al atom in the Al layer is removed from the lattice site, a new bond forms between Mo and Al in the other layer, as described in Fig. 11(a). With continuous etching, the removal of half of Al atoms in MoAlB with bilayer Al results in the formation of Mo_2AlB_2 with the Al monolayer.

It has been reported that cations of Lewis acidic salt can intercalate into the A-sites in the MAX phases, resulting in the formation of novel MAX phases. For example, in the Ti_3AlC_2–$ZnCl_2$ system, Al from Ti_3AlC_2 was oxidized to Al^{3+} and evaporated as $AlCl_3$, and the Zn cations from $ZnCl_2$ diffused into empty Al-sites to form Ti_3ZnC_2 (Fig. 11(b)) [5]. However, no MoZnB or Mo_2ZnB_2 was found during the treatment of the mixtur of MoAlB and $ZnCl_2$. This may be ascribed to the following two aspects: First, the bonding

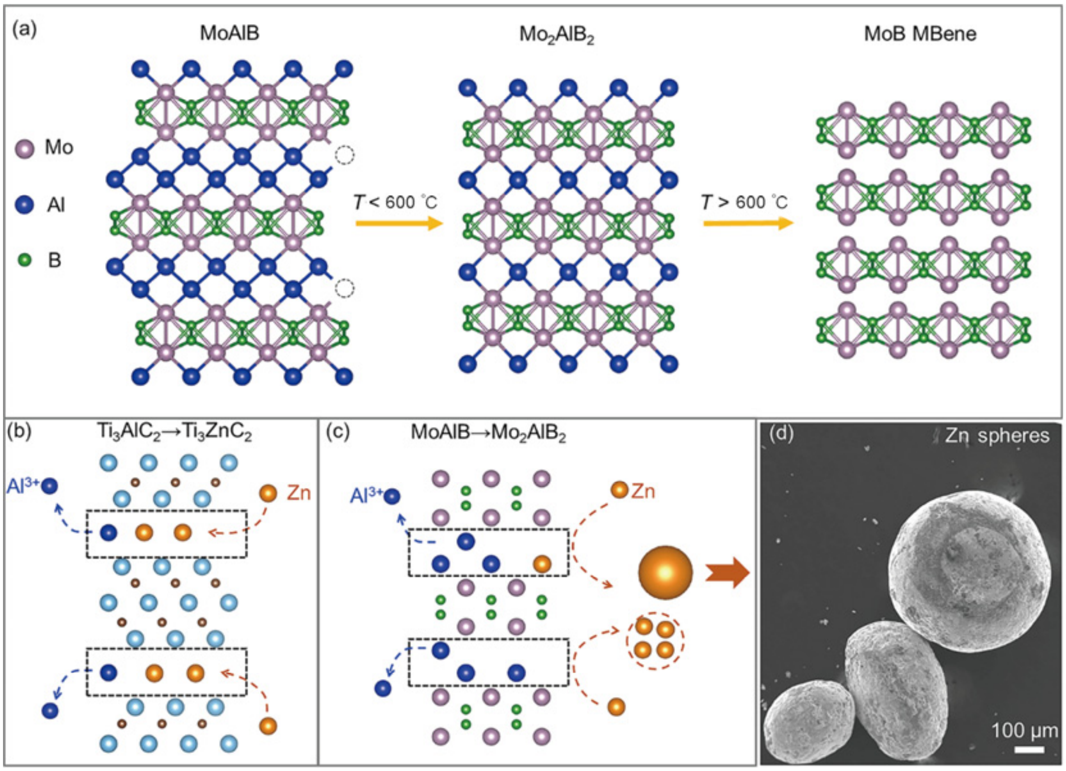

Fig. 11 (a) Schematic of Mo_2AlB_2 and MoB MBene formation mechanisms in $ZnCl_2$ molten salt, (b) formation of Ti_3ZnC_2 from Ti_3AlC_2 in $ZnCl_2$ molten salt, (c) formation of Mo_2AlB_2 from MoAlB, and (d) SEM image of Zn spheres formed in molten salt.

energy of Mo–Al influences the diffusing behavior of atoms in the Al-sites of MoAlB. Mo–Al in MoAlB has higher bonding energy than Ti–Al in Ti_3AlC_2, and therefore breaking the Mo–Al bond needs more energy. The Al atom is removed from its normal site in MoAlB, leaving a vacancy (the left image in Fig. 11(a)). The breaking bond of Mo will contact with another breaking bond of Al to form a new Mo–Al bond. After the removal of half of Al atoms from the MoAlB structure, the reconstruction of the Mo–Al bonds leads to the formation of Mo_2AlB_2 with monolayer Al. The lattice spacing between the Mo–B slabs in Mo_2AlB_2 shrinks, as compared with that between MoAlB. The spacing shrinkage makes the deintercalation of Al by the Zn cations relatively difficult below 600 ℃. This may explain why Mo_2AlB_2 forms at temperatures below 600 ℃. In addition, based on the XRD and EDS results, the appearance of Zn in the Mo_2AlB_2 phase suggests that a few Al vacancies may be occupied by the Zn cations (Fig. 11(c)). However, most of the Zn atoms prefer to cluster in the liquid condition, and then nucleate and grow into Zn spherical particles, as depicted in Fig. 11(d). The Zn particles can be removed by HCl solution from the reaction system to obtain pure Mo_2AlB_2 and MoB MBene.

As the temperature is increased to 600 ℃, the energy is enough to trigger the deintercalation of Al from Mo_2AlB_2 by $ZnCl_2$ molten salt etching. Once all Al atoms are removed, the structure of Mo–B slabs is rearranged to form 2D MoB MBene (the right image in Fig. 11(a)). However, these nanosheets are more likely to agglomerate at high temperatures, forming a stacking flake structure, as shown in Fig. 8.

5 Conclusions

A Mo_2AlB_2 phase and 2D MoB MBene were obtained by stepwise deintercalation of Al from MoAlB with the $ZnCl_2$ molten salt etching method. The influence of the etching temperature, the etching time, and the molar ratio of MoAlB : $ZnCl_2$ on the formation of the final products have been investigated. The pure Mo_2AlB_2 phase was obtained at temperatures lower than 600 ℃, and 2D MoB MBene was achieved at temperatures lower than 700 ℃. In addition, 2D MoB MBene was also prepared by etching Mo_2AlB_2 as the precursor with the LiF–HCl solution. Compared with acid etching, the molten salt method is preferred to synthesize 2D MoB MBene because it is a safe and more efficient approach.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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