

Advances in Molten Salt Synthesis of Non-oxide Materials

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The properties of non-oxide materials are continuously revealed, and their applications in the fields of ceramics, energy, and catalysis are increasingly extensive. Regardless of the traditional binary materials or the MAX phases, the preparation methods, which are environmentally friendly, efficient, economical, and easy to scale-up, have always been the focus of attention. Molten salt synthesis has demonstrated unparalleled advantages in achieving non-oxide materials. In addition, with the development of the process in molten salt synthesis, it also shows great potential in scale-up production. In this review, the recent progress of molten salt synthesis in the preparation of binary non-oxide and MAX phase is reviewed, as well as some novel processes. The reaction mechanisms and the influence of synthetic conditions for certain materials are discussed in detail. The paper is finalized with the discussion of the application prospect and future research trends of molten salt synthesis in non-oxide materials.

1. Introduction

Non-oxides generally included carbides, nitrides, borides, and silicides, which are applied in diverse fields (chemical, mechanical, metallurgical, aerospace, military energy, etc.) due to a series of excellent properties such as high melting point, excellent temperature resistance, thermal shock resistance, and low expansion coefficient.^[1–4] MAX phases, as emerging ternary non-oxides, have layered crystal structure, which combines the high loss tolerance of metal and the high-temperature resistance of ceramics. MAX phases are believed to be able to bridge the gap between metal and ceramic materials and develop rapidly in recent years.^[5–8] In addition, MAX phases are precursor materials for preparing MXenes. Thus, the high-quality, low-cost, and large-scale synthesis of MAX phases is also crucial to the synthesis of MXene materials.

The traditional preparation methods of binary non-oxide materials mainly include the sintering method, sol-gel method, vapor

deposition method, and solvothermal synthesis method.^[4,9–11] Sintering is also an important synthesis method of the MAX phases. However, this method usually requires high temperatures, which leads to high energy consumption. Molten salt synthesis is a method of synthesizing single or polycrystalline powder by using molten salt as reaction media. Compared with solid-phase reaction for which the rate is usually severely limited by the slow diffusion of the reactants, molten salt synthesis reduces the reaction temperature because it allows faster mass transfer through convection and diffusion in the liquid phase. Besides, many inorganics such as metals and oxides are insoluble and stable in conventional molecular solvents. However, molten salt is an ionic liquid existing at high temperatures. Metallic, ionic, or covalent bonds may be destabilized in the presence of a

strong polarizing force, which can be provided by molten salts, resulting in chemical reactions. The main preparation procedure of molten salt synthesis is shown in **Figure 1**.

The salt used in molten salt synthesis can be a single salt or a mixture of several salts, which generally do not react with the reactants, but act as a solvent providing a liquid environment. The target products undergo two processes of nucleation and growth in molten salt. Generally, the reaction mechanisms are considered as "template mode" or "dissolution-precipitation mode" (Figure 1)^[12–15] according to the different dissolution and diffusion of reactants in molten salt. The principle of template synthesis mechanism is that the solubility of reactants in molten salt is greatly different, so the reactants with large solubility dissolve and diffuse to the reactants with small solubility, and then, the target product is generated with it as template, so the target product morphology will be similar to that of the reactants with small solubility. The dissolution-precipitation mode is that both reactants have a certain solubility in the molten salt, and the difference is not large. Thus, the reactants are mixed in the atomic or molecular state and reacted to obtain the nano-level target product. With the progress of molten salt synthesis, different reaction mechanisms have also been proposed, including the disproportionation reaction synthesis mechanism of multivalent metal elements in molten salt, and the oxidation displacement reaction between different metal elements.^[16–19]

Molten salt synthesis is an important method for the preparation of inorganic materials, which has been greatly developed due to a series of unique advantages. At present, molten salt synthesis has been widely used in the preparation of oxide materials,^[20,21] including binary oxides: Ti_4O_7 ,^[22] Mn_2O_3 ,^[23] and SnO_2 ,^[24] perovskite: CaZrO_3 ,^[14] and BaTiO_3 ,^[25] composite oxides: MgAl_2O_4 ,^[13,26] LaAlO_3 ,^[15] $\text{Lu}_2\text{Ti}_2\text{O}_9$,^[27] and $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_2\text{CoO}_{12}$,^[28] and battery materials: LiCoO_2 ,^[29] $(\text{La}, \text{Sr})\text{FeO}_3$,^[30] $\text{LaMnO}_{3-\delta}$,^[31] etc. At the same time,

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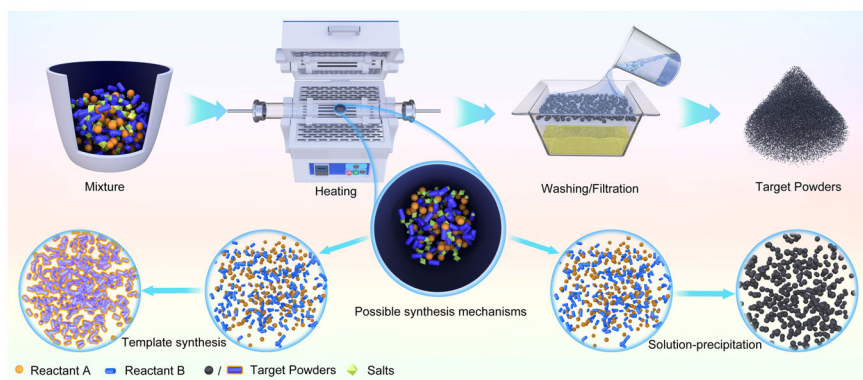


Figure 1. Preparation procedure of molten salt synthesis and schematic of synthesis modes.

molten salt synthesis of non-oxide materials has also been greatly developed. For the synthesis of non-oxide materials, oxygen in the salt must be thoroughly removed before use; otherwise, the product will easily be mixed with oxide impurities. It is noteworthy that it is impossible to remove the condensate salt by water if the target products are sensitive to water. However, the molten salt synthesis method still has great advantages compared with traditional methods.^[32]

- 1 Significantly lower reaction temperature.
- 2 Products with controllable morphology, size, and structure.
- 3 Easy to obtain homogenized powders.
- 4 The process has great potential for industrial application.

With the continuous development of molten salt synthesis, a mushrooming number of non-oxide materials are prepared by it. The interaction between molten salt and reactants is further researched and discovered, the process of molten salt synthesis is constantly improved, and its definition is also continuously broadened. The salt selection principles of molten salt synthesis are introduced in detail in this article. Then, the application of molten salt synthesis in the preparation of non-oxide materials and the process innovation in recent years are described systematically.

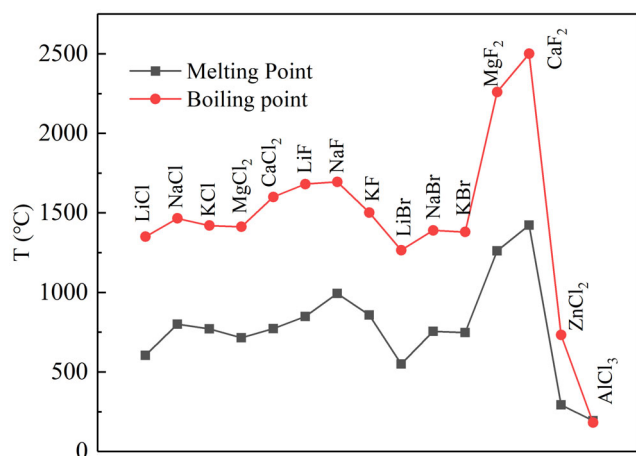


Figure 2. Melting points and boiling points of often-used halide salts at standard atmospheric pressure (data from reference^[33]).

2. Selection Principle of Salts

As a reaction medium that provides a liquid environment, salt plays a key role during the reaction.^[32] The composition of the molten salt has a major impact on the purity, morphology, size, and structure of the target products. The choice of salt should generally follow these principles:^[20,26]

- 1 The salt should have a low melting point and a high boiling point so that the operating temperature window will be wider. An eutectic mixed salt is often used to lower the melting point of salts. **Figure 2** shows the halide salts commonly used in molten salt synthesis and their melting and boiling points at standard atmospheric pressure.
- 2 Solubility: Reactants and the target products will be dissolved into the molten salt in the form of atoms or ions. If the solubility of the reactant is larger than that of the target product, the reaction will be conducive to the target direction, and the reaction process will be faster and more thorough. In addition, the solubility of the target product in the molten salt is small, which is also beneficial to avoid the molten salt entering the product as an impurity and improve the purity of the target product.
- 3 Molten salts' viscosity should be as little as possible. The viscosity of molten salt has a major influence on the transmission of solute and energy. Generally, little viscosity is more conducive to the diffusion of solute and energy transmission, which can increase the reaction rate and shorten the reaction time. The values of molten salts' viscosity can be obtained from manual.^[34–37]
- 4 Molten salt should have high chemical stability. A wide electrochemical window is usually required to avoid decomposition of electrolyte when the molten salt is used in electrochemical synthesis.^[38–40] Similarly, the molten salt should not form a stable impurity phase in a wide temperature range, especially not react with the target product in the process of molten salt synthesis. The structure and properties of the target product should be not affected by molten salt. Metal halides and oxide salt systems are commonly used in molten salt synthesis. Anaerobic conditions are usually required for the preparation of non-oxide materials. Hence, halide salts are preferred to prepare non-oxide materials. Compared with oxide salts, halide salts generally have more stable chemical properties and do not decompose at high temperatures. It is worth noting that sometimes molten salts not only serve as solvents but also participate in reactions as reactants.^[19] Meanwhile, the chemical stability of the salt is another matter.
- 5 Salt should be easily soluble in a liquid solvent and will not contaminate the target product. In the final stage of molten salt synthesis, the solidified salt needs to be dissolved with a solvent and then filtered to obtain the target product. Solvents can be water, alcohol, acid, and alkali solutions.
- 6 Vapor pressure: In general, the greater the vapor pressure of salt is, the more volatile it is. If the reaction is carried out in the atmosphere, the loss of salt will be rapid, which will cause a

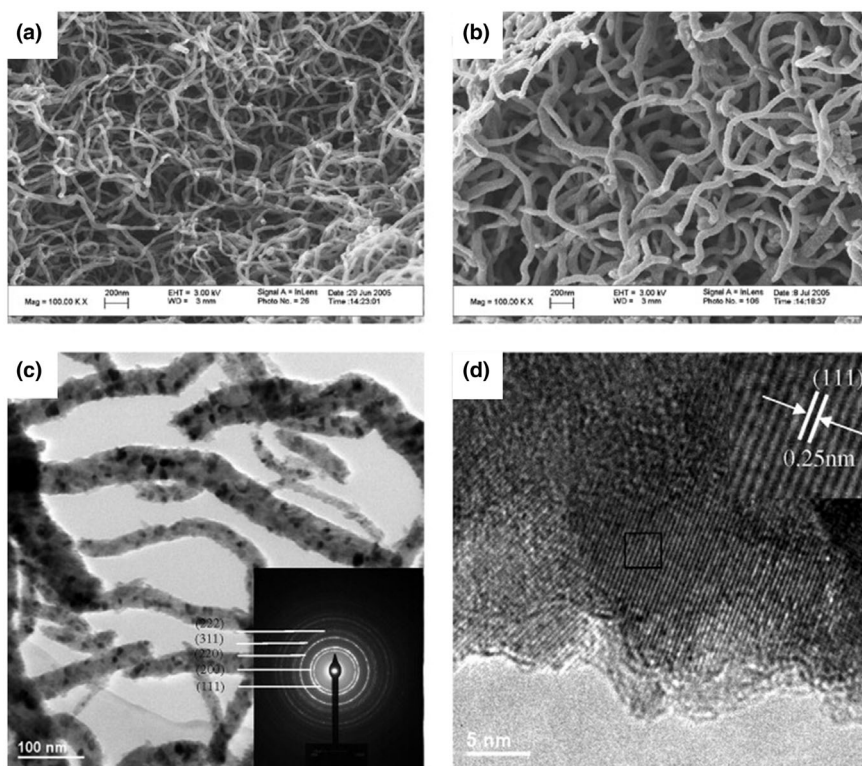


Figure 3. a) SEM images of raw materials (carbon nanotubes); b) fibrillar reaction products; and c, d) TEM images of the curved fibrillar products derived from titanium after the reaction in molten salts; the inset in c) is an SAED pattern (indexed to cubic TiC) from the fibers shown in c); the inset in d) is the magnified image from the box in d) showing that the lattice fringes have a spacing consistent with the {111} plane of the cubic TiC.^[41] Copyright 2009, Elsevier.

variety of effects: waste of salt, increase in cost, and pollution of the environment. The structure, morphology, and size of the target products will also be affected due to the rapid reduction of molten salt.

- 7 Density, corrosivity, and cost. The density of molten salt is related to the delamination between different melts, the distribution of products, and many kinetic phenomena. The density of molten salt usually decreases with the increase in temperature. Corrosion of molten salt is a factor closely related to the service life of equipment. Fluoride salts are more corrosive than chloride salts. So, the durability of the equipment should be considered when selecting molten salt. The cost of salt is an important factor in the selection of molten salt, especially for industrial-scale production. The price of lithium salt, which is more suitable for the preparation of high-value products, is higher than that of sodium salt and potassium salt. NaCl and KCl are usually the first choice of molten salt synthesis. In addition, the reuse and recycling of salt is also an important factor that restricts the cost.

3. Binary Non-Oxides

Binary non-oxide materials mainly include carbides, nitrides, borides, silicides, and sulfides, which are often combined with metals or

nonmetals in the form of covalent or solid solution. Molten salt synthesis is widely used in material preparation.

3.1. Carbides

Carbides account for a large proportion in non-oxide materials and are usually formed by combining carbon with elements possessing smaller or similar electronegativity (except hydrogen). The metal source for the preparation of metal carbides can be a simple substance or its metal oxide, while the carbon source can be graphite, amorphous carbon, multi-walled carbon nanotubes (MWCNTs), or some organic hydrocarbons such as acetylene. Carbon not only is the raw material but also acted as a template during the synthesis process due to its smaller solubility in molten salt compared with the metals. Therefore, the size and morphology of the target products were closely related to the carbon source. Based on this principle, metal carbides with controllable morphology and size can be prepared by selecting carbon sources with corresponding morphology and size. Li et al.^[41] prepared carbide nanofibers under the protection of argon at 950–960 °C for 5 h by the reaction of multi-walled carbon nanotubes (MWCNTs) with various transition metals using LiCl-KCl-KF melt as reaction medium (Figure 3). The target product has a similar size and morphology to those of the MWCNT

precursors. Transition metals can be V, Nb, Ta, Ti, Zr, and Hf. The research shows a general route to the production of carbide nanofibers, and the temperature can be reduced by 400–700 °C compared with the traditional carbothermal reduction method. Similarly, Yang et al.^[18] prepared TiC nanoparticles, nanorods, and nanosheets by molten salt synthesis in molten NaCl-KCl at 850–900 °C based on the template mechanism. In the process, Ti powders were used as metal source, and acetylene black, MWCNTs, and graphite were used as carbon source and template, respectively.

Carbon materials generally have poor wettability to liquid metals, as well as poor antioxidants and hydrophilic properties, which will limit their applications in high-temperature ceramics, refractories, and composites.^[42–46] Preparation of carbide coating on the surface of carbon materials by molten salt synthesis is a common surface modification method, and it has been extensively studied.^[47,48] By adjusting heating temperature and duration, different metal carbide coatings with controllable thickness can be obtained through molten salt synthesis.^[42,49–52]

Nonmetal carbide is a kind of covalent bond compound with high melting point and high hardness. SiC is one of the typical representatives and is the most widely used ceramic material. In the molten salt, silicon can be ionized into cations and delocalized electrons, and the cations are diffused to the surface of C source and react with it to form SiC coating or to form SiC particles with diverse morphologies.^[53–57] Compared with the traditional gas–solid

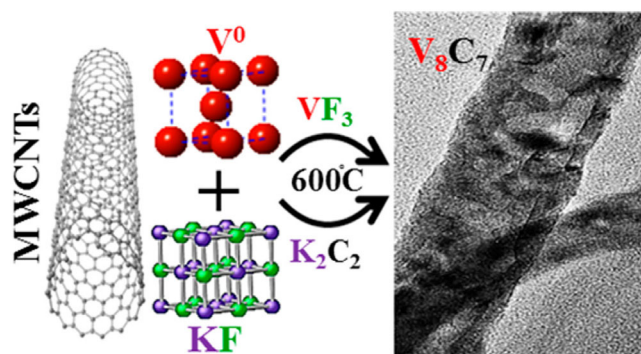


Figure 4. Schematic illustration of the formation mechanism of nanostructured metal carbides by salt-flux synthesis.^[64] Copyright 2015, American Chemical Society.

synthesis method, the reaction time synthesized by the molten salt method is reduced from tens of hours to several hours, and the temperature is reduced by 200–250 °C.

The preparation of porous carbon materials by molten salt, which acts as reaction medium, and porogen agent has been researched, and the materials are used in the fields of poisonous and harmful gas adsorption and water purification.^[58–60] Generally, carbonaceous organic material is used as carbon source. The porous carbonaceous polymer resin is obtained by decomposition of chemical functional groups from the framework at a relatively low temperature.^[61,62] Yu et al.^[63] prepared nitrogen-doped porous carbons with high hydrogen sulfide adsorption capacity by molten salt synthesis, using melamine as nitrogen source, D-glucose as carbon source, and LiCl-KCl as porogen. The product possesses tunable specific surface area and nitrogen content by changing the weight ratio of carbon source to nitrogen source and synthesis temperature. The adsorptive performance of H₂S is superior to that of non-doped porous carbon.

The interaction between molten salt and reactants has a great impact on the formation of intermediate and target products. Schmuecker et al.^[64] studied the influence of fluoride ion on synthesis of carbides. The schematic of formation mechanism is shown in **Figure 4**, and the reaction process can be represented by reactions 1–4:

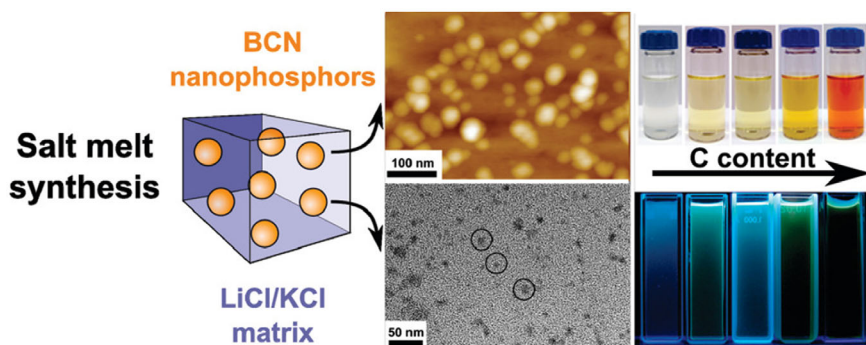
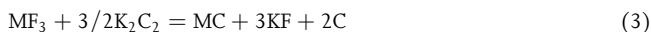


Figure 5. Boron carbon nitride nanostructures from LiCl-KCl melts: tunable water-soluble phosphors.^[72] Copyright 2011, American Chemical Society.



the total reaction:



where M represents V, Ta, and Ti.

In the process, the formation of intermediates (K₂C₂ and MF₃) is a necessary condition for the preparation of the target products, and the presence of intermediates in the beginning of the reaction can further lower the temperature of product synthesis. This also provides theoretical support for some salts containing potassium and fluorine ions to promote the formation of carbides.

In molten salts, most transition metal ions may undergo disproportionation reaction to form new valence states as they are polyvalent elements. It is thermodynamically favored to prepare carbides using metal ions as metal source compared with metal element. The synthesis mechanism can be simply summarized as reaction 5.



where M represents transition metal, and x and y represent different valence states.

Intermediate metal ions react with carbon to form carbides and higher metal ions. Intermediate metal ions are usually metastable and can be prepared by the reaction of metal elements with corresponding higher ions. NbC^[17] and TiC^[18] have been synthesized based on aforementioned formation mechanism. The carbides could be obtained by simply increasing the amount of raw materials and molten salt, which leads to the conclusion that the reproducibility and stability of this method are not sensitive to the sample scale of starting materials and the method can be used to synthesize NbC powder in large scale.

3.2. Nitrides

Nitrides are widely used in cutting materials, high-temperature structural materials, catalytic materials, and light-emitting materials.^[65–69]

Nitrogen is often used as nitrogen source for preparing nitrides, especially binary nitrides. Transition metal oxides, reactive metals, and nitrogen are usually used as feedstocks to synthesize metal nitrides. Molten salts can promote the diffusion of reactants and increase their contact area. VN,^[70] ZrN,^[71] and TiN^[46] nanopowders have been prepared by molten salt using corresponding metal oxides as raw materials.

Boron nitride is one of the most common and widely used nonmetallic nitrides. Lei et al.^[72] developed a simple molten salt synthesis to fabricate layered h-BN nanosheets with a thickness of less

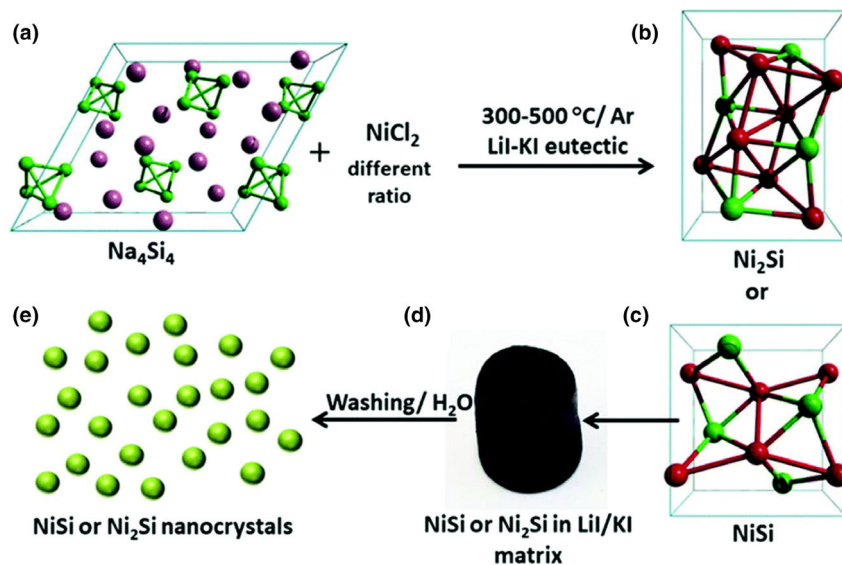


Figure 6. a) Reaction of the ionic Zintl solid Na₄Si₄ with different ratios of NiCl₂ in molten LiI-KI eutectic mixture (pink spheres = Na⁺, green tetrahedra = [Si₄]^{4−}). b, c) Phase-selective synthesis of NiSi and Ni₂Si (red sphere = Ni, green sphere = Si). d, e) NiSi or Ni₂Si embedded in LiI-KI matrix after reaction, and subsequent washing in acidic water to obtain the nanocrystals.^[75] Copyright 2020, Royal Society of Chemistry.

than 10 nm, and BCNO nanoparticles using NaBH₄ as B source and CH₄N₂O/CH₅N₃, HCl as C and N source at 700 °C in eutectic LiCl-KCl melt (**Figure 5**). The use of molten salt enhances the kinetics of the reaction between NaBH₄ and CH₄N₂O, or CH₅N₃, HCl. The carbon content can be tuned from 0 to 50 mol% by adjusting the ratio of reactants, so as to precisely control the emission range of the particles from 440 to 528 nm, and the quantum yield reaches 26%. Due to its green synthesis, low toxicity, small size, and stable anti-aggregation properties, the obtained BCNO nanoparticles are promising in diagnostics and optoelectronics.

Molten salt synthesis is also applied in the preparation of nitride materials with controllable structure. Normally, salt does not melt in the process, but plays a key role in the formation of pores and its amount has a great impact on the morphology and performance of the target products. Qian et al.^[73] prepared porous graphite g-C₃N₄ under nitrogen atmosphere at 550 °C using C₃H₆N₆-NaCl fine mixture powders as raw materials. g-C₃N₄ has interconnected three-dimensional porous network and large specific surface area. The mass ratio of C₃H₆N₆ to NaCl has a great influence on the structure and morphology of the product. NaCl-assisted ball milling strategy is considered to be a very feasible method for manufacturing porous structures, which can provide new insights into the direct production of catalysts in practical applications.

A surging number of studies have been made on the preparation of nitrides by molten salt synthesis, and the nitrogen source has also transitioned from nitrogen to nitrogen-containing compounds. It is difficult for N₂ to fully contact the reactants in the molten salt medium. If nitrogen-containing compound is used as nitrogen source, it is liable to be decomposed and lost as the temperature increases. Therefore, the key to the preparation of nitrides by molten salt synthesis is to find a nitrogen source that is inexpensive, is highly reactive, and does not decompose at high temperatures, or to improve the process to ensure

that the nitrogen-containing material in molten salt medium does not lose at high temperature.

3.3. Silicides

The electronegativity of silicon is small, and the covalent bond strength of metal silicide is weaker than that of boride and carbide. Transition metal silicides are refractory intermetallic compounds between transition metal and silicon, which have good conductivity, chemical inertness, and thermal stability, and have important applications in the fields of microelectronics and ceramics. The simple preparation principle of molten salt synthesis is that silicon-containing precursors are reduced to produce the target metal silicides by using molten salts such as solvent, alkali, or alkaline earth metals as reducing agent.^[74]

Kumar et al.^[75] synthesized nanoscaled NiSi/Ni₂Si with Na₄Si₄ as Si source and NiCl₂ as Ni source and solvent (**Figure 6**). LiI-KI eutectic melt was selected as solvent

due to its viscosity comparable to water, wide thermal stability window, and negligible vapor pressure at ~500 °C. The ratio of raw materials of Na₄Si₄ to NiCl₂ has a direct impact on the phase of the product. When the molar ratio of Na₄Si₄ to NiCl₂ is high, NiSi is formed, and when the molar ratio is low, Ni₂Si is formed. The atom diffusion can be enhanced, and reaction rates are increased in the liquid media compared with solid-state processes. The researches on preparation of silicides by molten salt synthesis in recent years are summarized in **Table 1**.

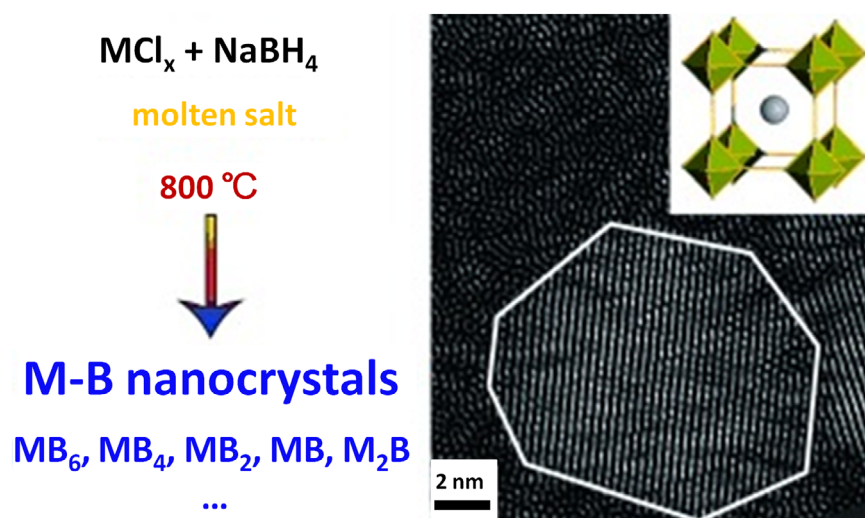
3.4. Borides

The binary compounds formed by boron with metals and nonmetals are generally crystals with high hardness and melting point, which are stable in chemical properties. Traditional synthesis is performed at extremely high temperatures, and only large bulk phases are obtained.^[83,84] Portehault et al.^[85] proposed a general route for the preparation of nanoscaled metal nitrides by molten salt synthesis. This method uses NaBH₄ as boron source and metal chloride salt as the corresponding metal source. Nanoscaled metal boride can be synthesized at a certain temperature in the molten LiCl-KCl salt (**Figure 7**).

In the preparation of boride by molten salt synthesis, elemental B is often used as boron source. Wei et al.^[86] prepared TaB₂ nanoparticles with a flower-like shape in molten NaCl-KCl at 1000 °C using Ta₂O₅ as the tantalum source and elemental B as the boron source. The ratio of salt to reactant has a great effect on the purity and morphology of the target product. Similarly, Wu et al.^[87] synthesized TiB₂ nanoparticles in MgCl₂ medium at 800–900 °C using TiO₂ and B as raw materials. Liu et al.^[88] synthesized Ti_{0.2}Zr_{0.8}B₂ nanoparticles in NaCl-KCl melt at 1050–1100 °C using TiO₂, ZrO₂, and B as raw materials.

Table 1. Molten salt synthesis of silicides

Silicides	Raw reactants	Salt systems	Synthesis mechanism, temperature and products	Refs
CrSi ₂	CrCl ₃ /Na ₂ SiF ₆ /K	CrCl ₃ -Na ₂ SiF ₆	CrCl ₃ + 2Na ₂ SiF ₆ + 11K → CrSi ₂ + 4NaF + 8KF + 3KCl 650 °C 20–50 nm particles	[76]
VSi ₂	VCl ₄ /Si/Na	MgCl ₂ -NaCl	VCl ₄ + 2Si + 4Na → VSi ₂ + 4NaCl 650 °C 40–60 nm particles	[77]
Mn ₅ Si ₃	MnCl ₂ /Mg ₂ Si	MnCl ₂	5MnCl ₂ + 3Mg ₂ Si → Mn ₅ Si ₃ + 5MgCl ₂ + Mg 650 °C Mn ₅ Si ₃ nanocage and nanotube	[78]
TiSi ₂	SiCl ₄ /TiCl ₄ /Na	-	2SiCl ₄ + TiCl ₄ + 12Na → TiSi ₂ + 12NaCl 650 °C TiSi ₂ 60 nm particles	[79]
Ti ₅ Si ₃	(a) SiCl ₄ /TiCl ₄ /Mg (b) SiCl ₄ /TiCl ₄ /Zn (c) SiCl ₄ /TiCl ₄ /Al SiO ₂ /TiO ₂ /Mg	- LiCl-KCl	(a) 3SiCl ₄ + 5TiCl ₄ + 16Mg → Ti ₅ Si ₃ + 16MgCl ₂ 650 °C Ti ₅ Si ₃ 40 nm particles (b) 3SiCl ₄ + 5TiCl ₄ + 16Zn → Ti ₅ Si ₃ + 16ZnCl ₂ 650 °C Ti ₅ Si ₃ 30 nm particles (c) 9SiCl ₄ + 15TiCl ₄ + 32Al → 3Ti ₅ Si ₃ + 32AlCl ₃ 650 °C Ti ₅ Si ₃ 25 nm particles 3SiO ₂ + 5TiO ₂ + 16Mg → Ti ₅ Si ₃ + 16MgO 700 °C Ti ₅ Si ₃ 25 nm particles	[79] [80]
β-FeSi ₂	Na ₂ SiF ₆ /FeSi/Si	NaCl-NaF	900 °C β-FeSi ₂ bulk	[81]
MoSi ₂	MoO ₃ /Mg/Si	NaCl	MoO ₃ + 3Mg + 2Si → MoSi ₂ + 3MgO MoSi ₂ 5–15 μm particles	[82]
MoSi ₂ -Si ₃ N ₄	Mo/Si/N ₂	NaCl	Mo + 5Si + 2N ₂ → MoSi ₂ + Si ₃ N ₄ MoSi ₂ -Si ₃ N ₄ sub-micron-sized particles	[82]
NiSi/Ni ₂ Si	Na ₄ Si ₄ /NiCl ₂	LiI-KI	Na ₄ Si + 2NiCl ₂ → Ni ₂ Si + 4NaCl 7–16 nm particles	[75]


Figure 7. Process under relatively mild conditions (500–900 °C) provides the general route toward nanocrystals of metal (Ca, Ce, Mo, Nb, Hf, Fe, Mn) borides.^[85] Copyright 2011, Wiley-VCH.

The methods of synthesizing boride powder can be divided into two types from the difference of raw materials: metal chloride and borohydride; and metal or its oxide and boron or its compound and/or reducing agent. There is a problem of uneven mixing of raw materials when these processes are solid-solid reactions. The liquid environment provided by the molten salt can achieve sufficient mixing of raw materials at the molecular or atomic level, which greatly reduces the energy required for the reaction.

3.5. Sulfides

Layered transition metal sulfide is a new two-dimensional semiconductor material that has attracted wide attention in recent years. Due to its special electronic structural characteristics, it exhibits excellent optical and electrical properties, so it is widely used in electronic, optoelectronic, and photonic devices.^[20] In 2016, Zhou et al.^[89] prepared MoS₂ with a three-dimensional honeycomb structure by the salt template-assisted method.

(NH₄)₆Mo₇O₂₄•4H₂O and CH₄N₂S were used as raw materials, which were dissolved in deionized water with NaCl, then frozen at −20 °C for 24 h. Subsequently, the water was removed by freeze-drying. The powder was heated at 750 °C for 2 h under an argon atmosphere. After cooling, deionized water removed NaCl from the product, and MoS₂ with a three-dimensional honeycomb structure can be obtained as shown in **Figure 8**. The product is an excellent lithium ion battery (LIB) anode material. Unprecedented initial coulomb efficiency, large reversible capacity, excellent cycling performance, and enhanced velocity ratio give the three-dimensional honeycomb MoS₂ great potential for commercial applications.

There are few studies on the molten salt synthesis of sulfides, so the research progress of ternary and quaternary sulfide molten salt synthesis methods is introduced together here.

Lancry et al.^[90] prepared Cu₂Mo₆S₈ ternary sulfide in molten KCl-K₂CO₃ salt at 850 °C with MoS₂, CuS, and Mo as raw materials. Benchikhi et al.^[91,92] studied the preparation of nanoscaled sulfides by molten salt synthesis. Precursors were prepared by reaction in ethylene glycol using SC(NH₂)₂, CuCl₂•2H₂O, InCl₃, and NaOH as raw materials, and then, the precursors were mixed with KSCN to synthesize nanoscaled CuInS₂ at 550 °C. Moreover, nanoscaled Cu₂ZnSnS₄ was synthesized at 400 °C using KSCN as sulfur source, and CuCl₂•2H₂O, SnCl₂•5H₂O, and ZnCl₂ as metal source.

4. Ternary Non-Oxides

Molten salt synthesis has also been applied in the preparation of ternary non-oxide materials. The synthesis temperature can also be lower than that of conventional solid-state reaction routes.^[93] MAX phases are important ternary non-oxide material, which has developed rapidly since its discovery due to the excellent properties.

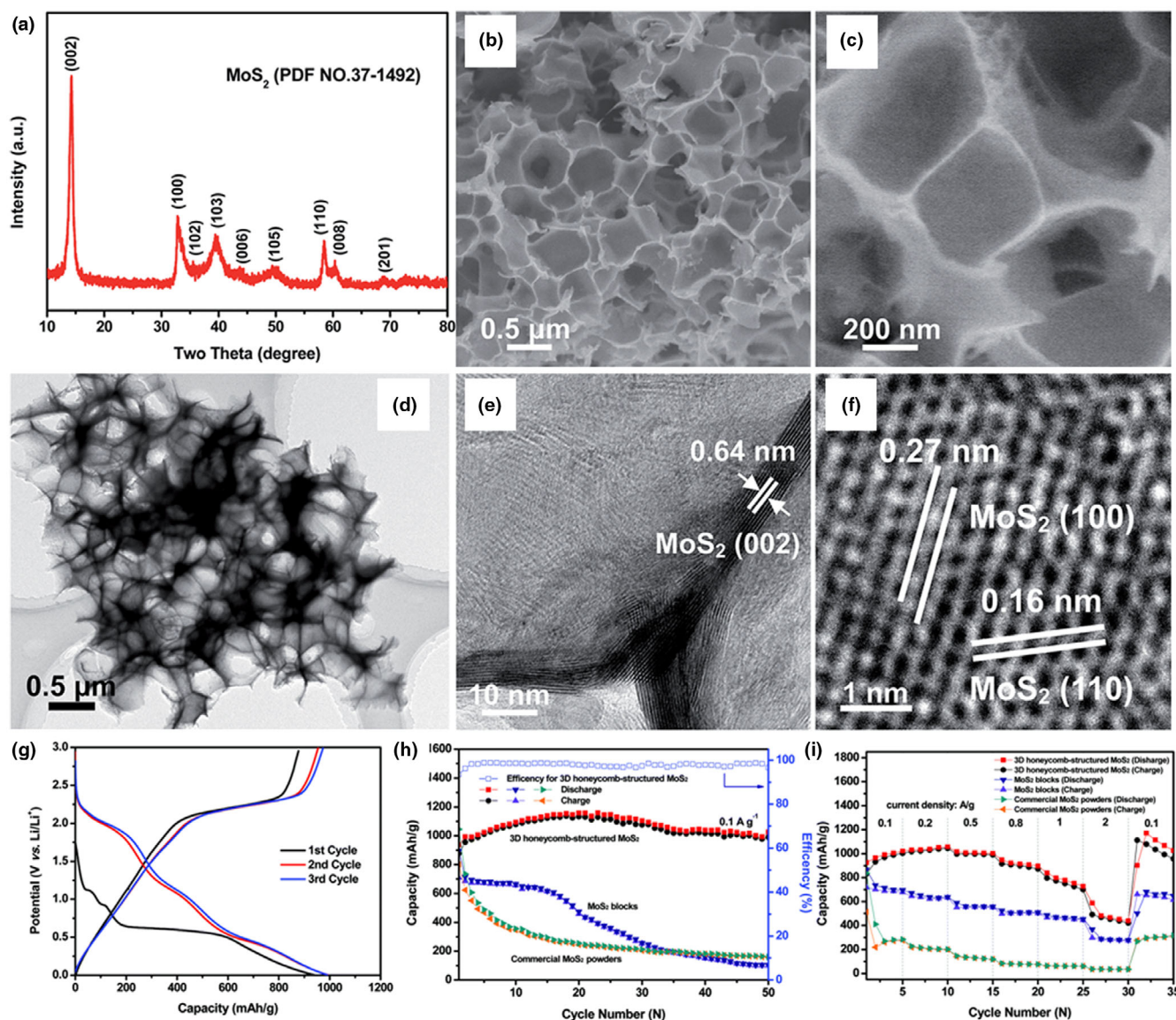


Figure 8. a) XRD pattern; b, c) SEM; and d–f) TEM images of 3D honeycomb-like structured MoS₂; g) galvanostatic discharge/charge profiles of the 3D honeycomb-like structured MoS₂ electrode at a constant current density of 0.1 A g^{−1}; and h) cycle performance and i) rate capability of the electrodes of 3D honeycomb-structured MoS₂, MoS₂ blocks, and commercial MoS₂ powders.^[89] Copyright 2016, Royal Society of Chemistry.

4.1. MAX Phases (X is Carbon)

When carbon-containing MAX phases are prepared by molten salt synthesis, the raw material is usually elemental powder, and the carbon source can also be carbide. In 2008, Tian *et al.*^[94] prepared micron-sized Cr₂AlC powder using metallic Cr powder, metallic Al powder, and graphite powder as raw materials in molten NaCl-KCl salt at 1000 °C under argon atmosphere. The amount of salt has a significant effect on the purity and yield of the target product. In 2015, Xiao *et al.*^[95] prepared nanoscaled Cr₂AlC powder at 1250 °C with KCl as solvent, and metallic Cr powder, metallic Al powder, and carbon black as raw materials. Ti-Al-C is the most researched and widely used series in MAX phases. In 2018, Galvin *et al.*^[96]

prepared micron-scaled Ti₂AlC and Ti₃AlC₂ with different ratios of metallic Ti powder, metallic Al powder, and graphite powder as raw materials in molten NaCl-KCl salt at 1000 and 1300 °C, respectively. Ti₃AlC₂ can also be synthesized from Ti₂AlC-TiC mixture in molten NaCl at 1150 °C under argon atmosphere. This method is more efficient in terms of energy and cost because it lowers the synthesis temperature by 200 °C.^[97]

MAX coating is a better choice to improve the surface properties of some substrates. In 2018, Li *et al.*^[98] synthesized a uniform and smooth TiC/Ti₂AlC coating on the surface of carbon fiber by molten salt synthesis. The raw materials are metallic Ti powder and metallic Al powder, which are evenly mixed with NaCl-KCl and placed on the carbon fiber. The coating with controllable thickness of TiC (inside) and Ti₂AlC

Table 2. Molten salt synthesis of common MAX phases

MAX phases	Raw reactants	Salt systems	Synthesis temperature and products	Refs
Cr ₂ AlC	Cr/Al/graphite powder	NaCl-KCl	900–1200 °C 2–8 μm particles	[94]
	Cr/Al/carbon black	KCl	1000–1250 °C 300 nm particles	[95]
Ti ₂ AlC	Ti/Al/graphite powder	NaCl-KCl	900–1000 °C sub-micron-sized particles	[96]
	TiC/Ti/Al	NaCl-KCl	1100 °C micron-sized particles	[19]
TiC/Ti ₂ AlC	Ti/Al/carbon fiber cloth			[98]
		1 NaCl-KCl	1 1000–1100 °C TiC/Ti ₂ AlC coating	
		2 NaCl-KCl-CaCl ₂	2 1000–1100 °C TiC/Ti ₂ AlC coating which is similar to (a)	
		3 NaCl-KCl-MgCl ₂	3 1000–1100 °C TiC coating	
		4 NaCl-KCl-NaF	4 1000–1100 °C no coating	
Ti ₃ AlC ₂	Ti/Al/graphite powder	NaCl-KCl	1300 °C micron-sized particles	[96]
	Ti/Al/acetylene black	NaCl-KCl	950–1000 °C nanoparticles	[100]
	Ti/Al/acetylene black	NaCl-KCl	950–1000 °C nanoparticles	[101]
	Ti ₂ AlC/TiC	NaCl	1150 °C nanoparticles	[97]
	TiC/Ti/Al	NaCl-KCl	1100 °C micron-sized particles	[19]
Ti ₃ SiC ₂	Ti/Si/C	NaCl	1100–1300 °C micron-sized particles	[102]
V ₂ AlC	V/Al/graphite powder	NaCl	1200–1400 °C micron-sized particles	[103]
	VC/V/Al	NaCl-KCl	1100 °C micron-sized particles	[19]
	V/Al/graphite powder	NaCl-KCl	1100 °C micron-sized particles	[99]
Ti ₂ AlN	TiN/Ti/Al	NaCl-KCl	1100 °C micron-sized particles	[19]
	Ti/AlN	NaCl-KCl	1100 °C micron-sized particles	[99]
Ti ₃ ZnC ₂	Ti ₃ AlC ₂	ZnCl ₂	550 °C micron-sized particles	[19]
Ti ₂ ZnC	Ti ₂ AlC			
Ti ₂ ZnN	Ti ₂ AlN			
V ₂ ZnC	V ₂ AlC			

(outside) can be obtained by reasonably adjusting duration at 1000–1100 °C. TiC/Ti₂AlC coating has a good protective effect on carbon fiber in static air and water vapor below 800 °C.

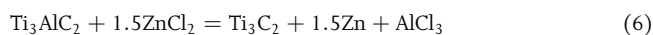
4.2. MAX Phases (X is Nitrogen)

If nitrogen gas is used as nitrogen source to prepare nitrogen-containing MAX, the stoichiometric ratio of the target product is difficult to control, which is different from the preparation of carbon-containing MAX. Therefore, nitride is usually selected as nitrogen source when preparing nitrogen-containing MAX. Li et al.^[19] prepared Ti₂AlN micron scale powder using AlN as nitrogen source and Al source mixed with Ti powder in molten NaCl-KCl salt at 1100 °C. Roy et al.^[99] also obtained Ti₂AlN micron scale powder from TiN, metallic Ti powder, and Al powder as raw materials in molten NaCl-KCl salt at 1100 °C. Table 2 summarizes the MAX phases prepared by molten salt synthesis.

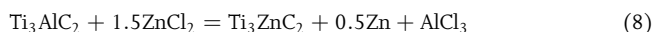
4.3. Novel MAX Phases

In MAX phases, A is traditionally from main groups 13–16. However, it is difficult to synthesize when A-site is late transition metal element, such as Fe, Zn, and Ni. For late transition metals, M-A intermetallic compound is generally more stable than the corresponding MAX

phases at high temperature, which means that it is difficult to obtain the target MAX phases through thermodynamic equilibrium process. The novel MAX phases obtained through replacement reaction have been reported by some researchers such as Ti₃SiC₂^[104,105] and Ti₃SnC₂.^[106] In 2019, Li et al.^[19] introduced a method for preparing novel MAX phases by replacement reaction using molten salt as medium and reactant, and the principle is shown in Figure 9. The raw materials are the traditional MAX phases (Ti₃AlC₂, Ti₂AlC, Ti₂AlN, and V₂AlC). ZnCl₂ is used as solvent and Zn source, and the reaction is performed at 550 °C. When the molar ratio of the MAX raw material to ZnCl₂ is 1:1.5, novel MAX phases (Ti₃ZnC₂, Ti₂ZnC, Ti₂ZnN, and V₂ZnC) are obtained. The reaction can be expressed by reactions 6–8 (taking Ti₃AlC₂ as an example).



the total reaction:



ZnCl₂ is Lewis acid in the molten state.^[107,108] Then, it can be ionized into Zn²⁺ and ZnCl₄^{2−}. Coordinately unsaturated Zn²⁺ is a strong acceptor of electrons and Cl[−]. Al in Ti₃AlC₂ can be easily oxidized to Al³⁺ in the acidic environment. Zn bonds with unsaturated Ti₃C₂ to

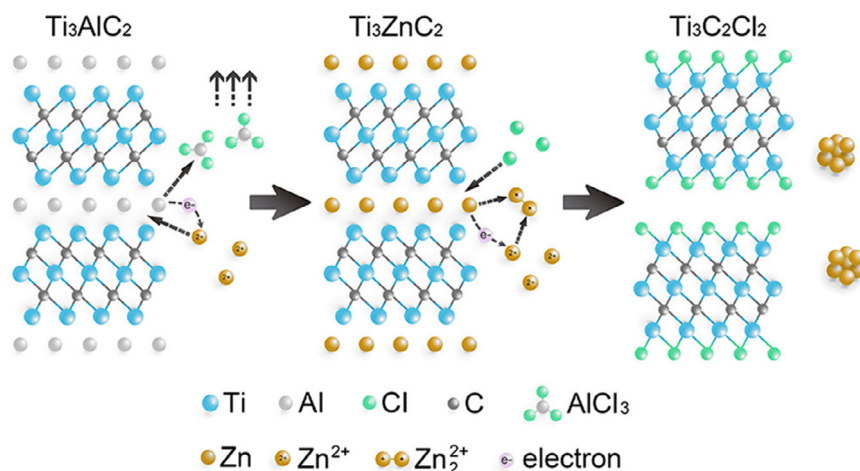
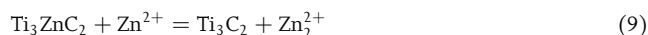
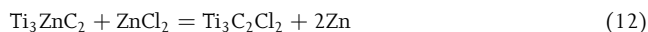


Figure 9. Schematic diagram of element replacement approach by reaction with Lewis acidic molten salts to synthesize nanolaminated MAX phases.^[19] Copyright 2019, American Chemical Society.

form Ti_3ZnC_2 . When the amount of ZnCl_2 is further increased to 1:6, the two-dimensional Cl^- -terminated MXene $\text{Ti}_3\text{C}_2\text{Cl}_2$ is obtained. The reaction can be expressed by reactions 9–12.



the total reaction:



Zn can react with Zn^{2+} to form a low-valence zinc ion Zn_2^{2+} . Therefore, the weakly bonded Zn atoms in Ti_3ZnC_2 can be easily extracted from the two-dimensional A-site plane and dissolved in the ZnCl_2 molten salt. At the same time, Cl^- spontaneously inserts into the A-site plane to form $\text{Ti}_3\text{C}_2\text{Cl}_2$. The exclusively Cl^- -terminated MXenes were obtained for the first time by molten salt synthesis, and the etching effect of Lewis acid in molten salt provides a green and feasible way to prepare MXenes through an HF-free chemical approach.

5. Novel Process

Novel processes can often shorten the manufacturing process, improve product quality, and reduce production cost. The development of molten salt synthesis method has a history of 50 years. With the demand of environmental-friendliness, and high-quality and industrial-scale powder preparation, the process of molten salt synthesis is also continuously improved.

5.1. Molten Salt Shielding Synthesis (MS^3)

In the preparation of non-oxide materials, especially oxidation-prone materials, non-oxide salt systems are usually selected as the

solvent to prevent the oxidation of the target product; meanwhile, the process is carried out under the protection of vacuum or inert gas. This undoubtedly raises energy requirements, increases equipment costs, and limits the industrial-scale application of molten salt synthesis to a certain extent. Molten salts can shield the reactants from the air if they are immersed in molten salts. In the synthesis of some materials, the phenomenon that molten salt can protect the target product from oxidation has been recorded.^[109] In 2019, Dash et al.^[110,111] proposed a process of directly synthesizing oxidation-prone materials in air, which is termed as molten salt shielding synthesis (MS^3). **Figure 10** shows the main flow of the process. After the raw materials are mixed and compacted, a dense layer of salt is encapsulated on the surface of the sample. The salt used

for encapsulation can be KBr or other salts with high ductility at room temperature. Subsequently, the sample is heated in the atmosphere in a crucible containing KBr. The heating can be divided into two stages: salt pre-melting and salt post-melting. In the pre-melting stage, the air-impermeable salt shell protects the sample from oxidation, and after the melting of the salt shell, the salt in the crucible has melted, and the sample will be immersed in the molten salt to protect it from oxidation. That is, the salt shell insulates air at low temperatures, while the molten salt insulates air at high temperatures. The oxygen content of Ti_3SiC_2 synthesized by MS^3 is found to be 1.53 wt%, which can be comparable to that of the commercially available Ti_3SiC_2 (1.25 wt%), and its purity is higher than that of commercial compound. The oxygen content of the target product depends on the oxygen content of the initial powder and the salt used for sintering. MS^3 is a general method for the synthesis of non-oxidized binary compounds, non-oxidized ternary compounds, and elemental metals with controllable structure. This process does not require any expensive equipment such as vacuum furnaces, spark plasma sintering furnaces, hot isostatic pressure, or atmosphere-controlled furnaces requiring continuous flow of argon or any inert gas to prevent oxidation. The synthesis temperature can be lowered by 100 °C with MS^3 compared with traditional solid-state reaction. This process can be scaled up to an industrial scale by simply making the process continuous or increasing the batch size. A batch size of 500 g Ti_3SiC_2 powder has been synthesized successfully.

Roy et al.^[99] improved the MS^3 process to prepare V_2AlC and Ti_2AlN . Instead of using salt to encapsulate the sample, eutectic mixed salt with low melting point is selected. The salt has melted or started to melt before the raw material starts to oxidize, which can prevent oxidation at low temperature. Two MAX phases, V_2AlC and Ti_2AlN , were synthesized by this process in eutectic NaCl-KCl mixed salt. The oxygen content in V_2AlC was 1.1 wt%, which proved that the molten salt mixture had sufficient shielding effect on the metal precursor during synthesis. The synthesis temperature can be reduced by 200–400 °C compared with the traditional method. It can be seen that this process is more economical and suitable for large-scale industrial production.

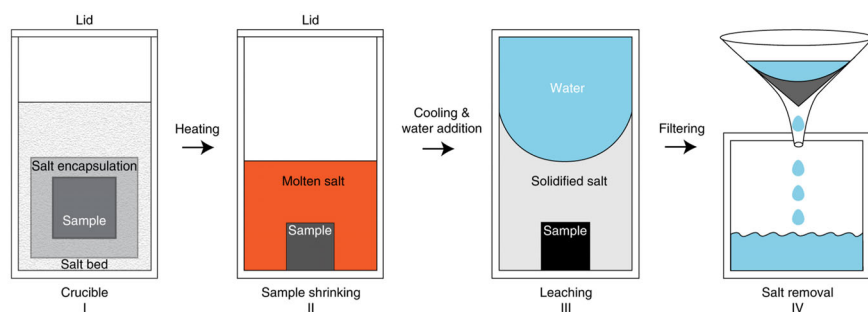


Figure 10. Stepwise schematic of the MS³ process.^[110] Copyright 2019, Springer Nature.

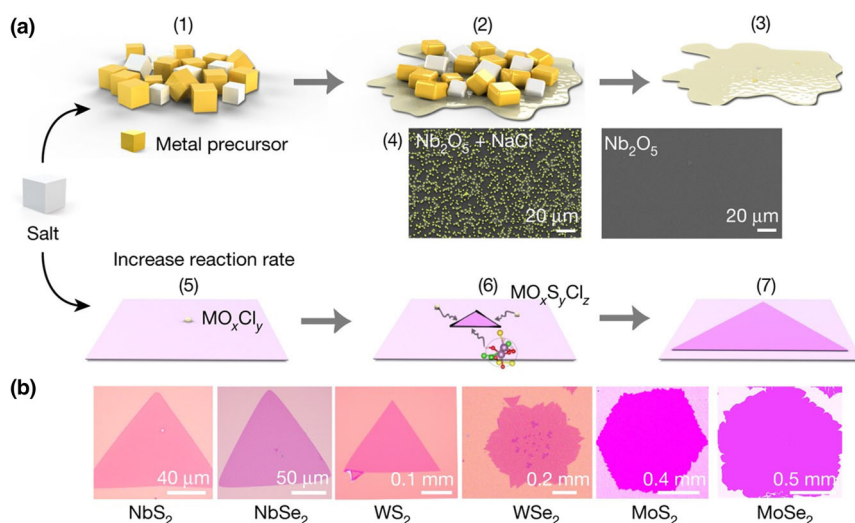
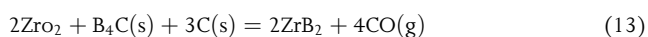


Figure 11. a) Schematic diagram of reaction mechanism during molten salt-assisted CVD growth. 1–3) The proposed process of the added salt decreasing the melting point of the precursors; 4) SEM images of the Nb nucleus with (left) and without (right) added salt; and 5–7) the growth process of the 2D atomic layer, with intermediate products. b) Different single-crystalline monolayers prepared by the salt-assisted CVD method.^[118] Copyright 2018, Springer Nature.

5.2. Combination of Molten Salt Synthesis and Other Methods

During the preparation of some materials, molten salt synthesis can be used in combination with other methods. For instance, molten salt synthesis is used in parallel with combustion or self-propagating methods, or in series as a subsequent step in mechanical alloying. The combination of multiple methods can often play a better effect through the reasonable control of process parameters. Microwave synthesis is a material synthesis method that has been extensively researched. Microwaves have the characteristics of preferentially heating reactants with high microwave absorption rates.^[112,113] The combined use of microwave synthesis and molten salt synthesis has also been studied in recent years.

Liu et al.^[114] prepared ZrB₂ nanoscaled powders from reactants of ZrO₂, B₄C, and amorphous carbon using a novel molten salt and microwave co-assisted carbothermal reduction (MSM-CTR) method. The solvent of the reaction is molten NaCl-KCl, and the reaction can be represented by reaction 13.

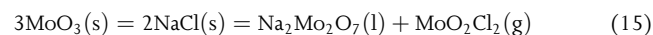


The results show that pure ZrB₂ can be obtained by microwave heating at 1200 °C for 20 min. Compared with the traditional

heating mode, the metal-reducing agent Mg is not required to be added, and the duration can be shortened from 3 h to 20 min at the same temperature.^[115] The obtained ZrB₂ powder is composed of good single-crystal nanorods with a diameter of 40–80 nm. MSM-CTR is a simple and effective method for preparing high-quality ZrB₂ powder. Bi et al.^[116] also prepared silicon carbide-coated graphite composite powders from reactants of graphite flakes and silicon powders in molten NaCl-NaF at 1150 °C by microwave-assisted molten salt synthesis. The formation temperature of silicon carbide coating was reduced to about 150 °C compared with conventional molten salt synthesis.

In addition, salts are always used in chemical vapor deposition (CVD) processes, especially in the synthesis of 2D non-oxide materials. CVD is considered to be an effective method to fabricate 2D materials on a large scale. However, the high melting point of the metal precursors and the thermodynamic instability of the metastable phase are the limiting factors for the synthesis of a large number of 2D materials. Molten salt-assisted CVD synthesis has been proved to be an effective method to address these issues. The salts in the CVD process usually can lower the melting point of precursors, raise their vapor pressure, form high active intermediate products, decrease activation energy, or increase overall reaction rate.^[117] Zhou et al.^[118]

reported that 47 kinds of 2D transition metal chalcogenides can be prepared by adding salt in the CVD process. Figure 11 shows the schematic reaction mechanism and some optical images of the resulting products. Mixing precursors with NaCl can form molten solution and then generate intermediate products, and hence can reduce the melting point of the reactants and raise the vapor pressure. The reaction equations are as follows.



MoO₂Cl₂ can be obtained by the reaction of MoO₃ and NaCl, and it is easy to evaporate. The equations are confirmed by X-ray diffraction and thermogravimetric analysis.^[119] Intermediate metal oxychlorides allow chemical reactions with chalcogenides to form transition metal chalcogenide nucleation and layers by lowering the energetic barrier and increasing the growth rate. Many literatures have reported the synthesis of 2D non-oxide materials assisted by

molten salt, and described the function of salt in decreasing melting points and formation of intermediate products, decreasing energy barrier, and increasing growth rate.^[120–123]

6. Conclusions and Future Perspectives

Preparation of binary carbides, nitrides, borides, silicides, and sulfides by molten salt synthesis is described in detail. Compared with the traditional sintering method, molten salt synthesis can significantly reduce the synthesis temperature and shows unparalleled advantages in the preparation of nanoscaled particles with controllable structure, morphology, and size. Molten salt synthesis has also been applied to the two-dimensional MXenes and MAX phases, which have developed rapidly in recent years. The application of the MS³ method promotes the industrialization of the preparation of non-oxide materials by the molten salt method. Among various material synthesis methods, molten salt synthesis not only has a broad development prospect due to environmental-friendliness, high efficiency, and economy, but also faces some challenges.

Most of the reactant powders in molten salt synthesis are simple substances due to their greater solubility and tendency to react with C and N in molten salts compared with oxides. However, some oxides are precursors in the preparation of metals. Therefore, if the raw materials of molten salt synthesis are oxides, the whole process can be shortened and the production cost can be further reduced. The solubility of oxide in molten salt is very small, and its dissolution behavior still needs to be further studied. If the solubility of oxides in molten salt can be maximized by regulating the molten salt composition, the molten salt synthesis will become more controllable.

Materials prepared by the molten salt synthesis continue to expand, the synthesis mechanism is further studied, and its definition is also being broadened. In some synthetic processes, molten salts are no longer just solvents that provide a liquid-phase environment, but also participate in the reaction as reactants, which is more common in high-valent metal salts or acidic salts. The interaction mechanism between molten salt and reactants still needs to be continuously researched. There may be multiple intermediate reactions in the whole process, so the target products can be better controlled through further study of the interaction mechanism of molten salt and reactants.

Molten salt synthesis is a highly adaptable method that can be used in combination with many methods, including traditional combustion, mechanical alloying, microwave preparation, and chemical vapor deposition. With the continuous improvement in the molten salt synthesis process, the preparation of non-oxide materials under the atmospheric condition has been studied and demonstrated good industrial application potential. The shortening of the preparation process, the reduction in the equipment capability, and the environmental-friendliness of the method will make it play an important role in the industrial production of powder preparation.

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Conflict of Interest

The authors declare that there is no conflict of interest associated with this study.

Keywords

MAX phases, molten salt, nanostructure, synthesis

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