

SYNTHESIS AND STUDYING THE STRUCTURAL FEATURES OF $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) AND TERNARY CARBIDE $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$

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Abstract

This study focuses on the synthesis and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$, a prominent member of the MXene family known for its unique structural properties. MXene was synthesized using the selective etching of aluminum from Ti_3AlC_2 with different syngony, via hydrofluoric acid treatment. The resulting MXene was systematically analyzed using various techniques; including X-ray diffraction (XRD) and scanning electron microscopy (SEM) were studied. The influence of the structural characteristics of the initial raw material on the morphology and structural features of the synthesized MXene phases was shown. It was revealed that MAX with cubic syngony does not form a 2D structure, while MAX with hexagonal syngony produces a 2D structure with a layer thickness of 35 nm.

INTRODUCTION

Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) were discovered in 2011 [1]. Since the original discovery, more than 20 different compositions have been synthesized by the selective etching of MAX phase and other precursors and many more theoretically predicted. They offer a variety of different properties, making the family promising candidates in a wide range of applications, such as energy storage, electromagnetic interference shielding, water purification, electrocatalysis, and medicine [2]. These solution-processable materials have the potential to be highly scalable, deposited by spin, spray, or dip coating, painted or printed, or fabricated in a variety of ways [3].

MXenes reported to date are synthesized by wet-chemical etching in hydrofluoric acid (HF) or HF-containing or HF-forming etchants [4-6], which add surface functionalities such as -O, -F, or -OH, represented by T_x in this formula as $\text{M}_{n+1}\text{X}_n\text{T}_x$. Etching is required because of strong chemical bonds between A and M elements in MAX phases that make mechanical exfoliation hardly possible. To date, more than 20 members of the MXene family have been synthesized, and dozens more are predicted, making it one of the fastest growing 2D material families [4]. Additionally, the MXene family comes in three atomic structures, ranging from M_2X to M_3X_2 and M_4X_3 , yielding tunability and opportunity to discover and mold materials based on necessary demands [4,7,8]. In contrast to most other 2D materials, including graphene, MXenes possess hydrophilic surfaces [4] and high metallic conductivities (~ 6000 - 8000 S/cm), [9,10] showing promising performance in energy storage devices, [11-14] water desalination [15] catalysis [16], electromagnetic interference shielding [17], transparent, conducting thin films [9,18] and many other applications. Due to this promise, the amount of research on MXenes has been increasing, and methods of synthesis and processing are expanding quickly. The fast evolution of the material can also be noticed in the wide range of synthesis and processing protocols that determine the yield of delamination, as well as the quality of the 2D flakes produced.

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The aim of this work was to study their structural characteristics of Ternary carbide $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ and Ti_3AlC_2 MXenes obtained by different etching conditions from the Ti_3AlC_2 using X-ray diffraction analysis and scanning electron microscopy

MATERIALS AND METHODS

We report here the long term cyclability performance of two $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes synthesized by different etching conditions from the Ti_3AlC_2 parental compound (MAX in the following): the $\text{Ti}_3\text{C}_2\text{T}_x$ obtained in 30% HF for 5 h and the $\text{Ti}_3\text{C}_2\text{T}_x$ obtained in 10% HF for 18 h.

Choice of Etchants and Intercalants. Hydrofluoric acid (HF, 48 wt %) was purchased from Shandong Fan Tai Fine Chemical Biotechnology Co., Ltd. (China). For the etching, there are two different concentrations with different durations were used, all sufficient to synthesize $\text{Ti}_3\text{C}_2\text{T}_x$.

For $\text{Ti}_3\text{C}_2\text{T}_x$, the choice of a synthesis method directly influences the resulting properties in terms of surface terminations, size and quality of the flakes.

Ternary carbide $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ prepared by high energy ball milling under argon atmosphere was purchased from Shandong Fan Tai Fine Chemical Biotechnology Co., Ltd.(China)

Morphological studies of the sample surface were carried out using a JSM-IT 210 scanning electron microscope (Jeol, Japan). During the measurement, an accelerating voltage (EHT - Extra High Tension) of 15.00 kV was applied, the working distance (WD-working distance) was 10.8 mm. The images were obtained in different scales using InTouch Scope software.

X-ray studies were carried out on a Miniflex 600 instrument (Rigaku, Japan) with monochromatized $\text{CuK}\alpha$ -radiation, separated by a nickel filter with a wavelength of $\lambda=1.5418 \text{ \AA}$ at 40 kV and a current of 15 mA. The samples were studied in the form of a powder. The shooting was carried out in the range of angles $2\theta=5^\circ-70^\circ$. The results were processed using the SmartLab Studio II program.

RESULTS AND DISCUSSION

In general, the physical properties of nanomaterials are closely dependent on their atom arrangements and crystal structure stability. Additionally, achieving functionality in practical applications also calls for intricate design of materials at a molecular level (e.g., elemental modification) prior to processing into architectures [19]. Investigation of such properties requires characterization methods with high level of spatial resolution, sensitivity, and nondestructibility, which cannot be offered by the typical electron-microscopy and bench-top chemical characterization methods. In this regard, X-ray-based techniques show high relevance for quite a few reasons.

X-ray structural study of titanium carbide $\text{Ti}_3\text{C}_2\text{T}_x$ synthesized by etching with hydrofluoric acid of various concentrations from aluminum titanium carbide (3D) showed crystalline reflections with maxima at angles of $2\theta=7.12^\circ, 9.21^\circ, 18.47^\circ, 28.06^\circ, 34.11^\circ, 35.30^\circ, 37.50^\circ, 41.69^\circ$ and 60.72° in the considered range of scattering angles. The most intense maximum, observed at the angle $2\theta=18.47^\circ$, refers to the crystallographic reflection (200), while at the angle $2\theta=28.06^\circ$ a new crystalline reflection appears, corresponding in the plane (30-1) (Fig. 1). However, at the same time, for the initial aluminum titanium carbide (3D), crystalline reflections are observed with maxima at angles of $2\theta = 9.48^\circ, 19.04^\circ, 33.91^\circ, 38.64^\circ, 38.87^\circ, 41.60^\circ$ and 60.01° with reflection planes (002), (004), (101), (008), (104), (105) and (110), respectively. X-ray phase analysis of the aluminum titanium carbide (3D) sample showed that it has a hexagonal syngony with lattice parameters $a\approx 3.08 \text{ \AA}$, $b\approx 3.08 \text{ \AA}$, $c\approx 18.62 \text{ \AA}$, $\alpha\approx 90.00^\circ$,

$\beta \approx 90.00^\circ$ and $\gamma \approx 120.00^\circ$. In the diffraction patterns of the multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ powder obtained by selective removal of aluminum at a concentration of 30% hydrofluoric acid, a decrease in the intensity of the crystalline reflex at $2\theta = 9.48^\circ$ corresponding to the (002) plane is observed.

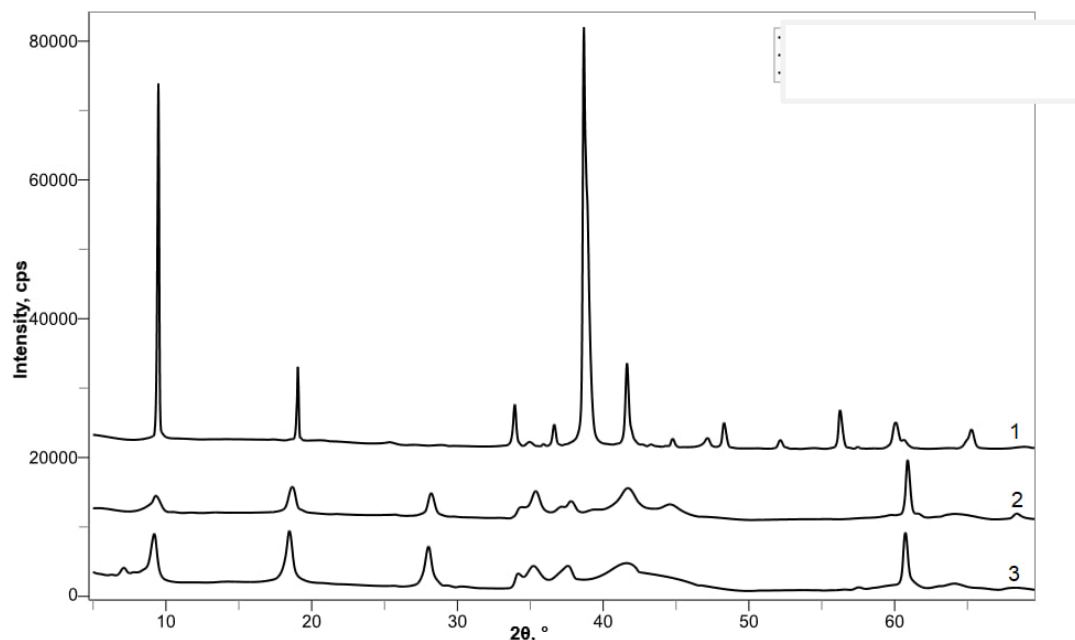


Figure 1. X-ray diffraction pattern of powders: 1) Ti_3AlC_2 , 2) $\text{Ti}_3\text{C}_2\text{T}_x$ (HF 10%), 3) $\text{Ti}_3\text{C}_2\text{T}_x$ (HF 30%)

A shift in the peaks of the basal plane towards small angles to $2\theta = 7.12^\circ$ is also observed, which corresponds to a d-spacing of 12.39 Å. This is due to the fact that during the etching process, intercalation of ions (H^+ , F^-) and water molecules occurs between the MXene layers, which requires longer and higher-temperature vacuum drying for the complete removal of intercalated water molecules from the powder.

At the same time, during the etching process, the crystallite sizes calculated by the Debye-Scherrer method from the broadening of the crystalline reflexes decrease. The crystallite sizes of the MAX phase were decreased from 58 nm to 28 nm after etching.

Thus, the structure of titanium carbide $\text{Ti}_3\text{C}_2\text{T}_x$ synthesized by selective removal of aluminum at a concentration of 30% hydrofluoric acid was studied. It was revealed that the etching process leads to the formation of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ with an accordion structure with a plate thickness of 35 nm.

X-ray structural study of $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$, etched with hydrofluoric acid of 30% concentrations from Ternary carbide $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ showed crystalline reflections with maxima at angles of $2\theta = 35.91^\circ$, 41.71° and 60.46° in the considered range of scattering angles. The most intense maximum, observed at the angle $2\theta = 41.71^\circ$ refers to the crystallographic reflection (200). At the same time, for the initial aluminum titanium carbide $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ crystalline reflections are observed and no changes were observed in the all maxima at angles with reflection planes (111), (200), (220) respectively. X-ray phase analysis of the both $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ and $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ after 30-HF samples showed that they have a cubic syngony with lattice parameters $a=b=c \approx 4.37 \text{ Å}$, $\alpha=\beta=\gamma=90.00^\circ$.

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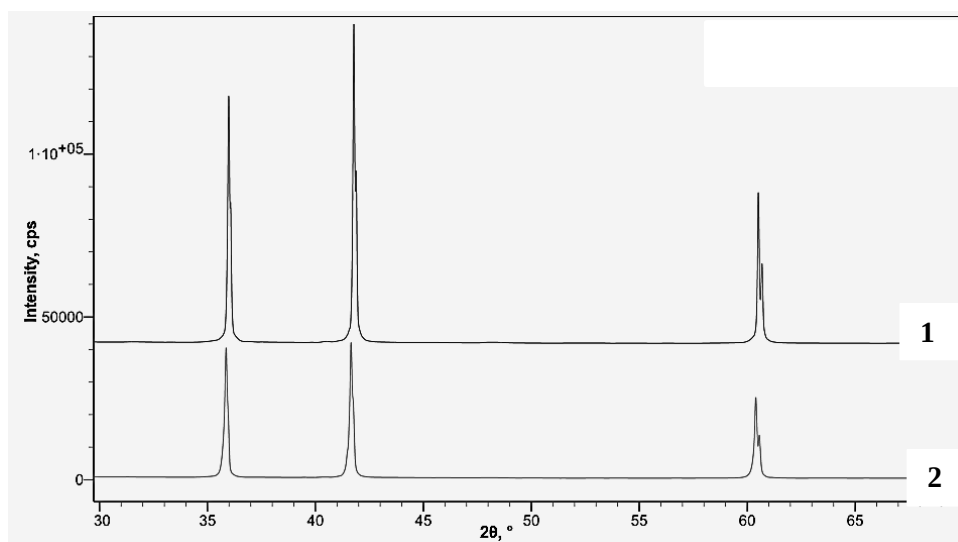


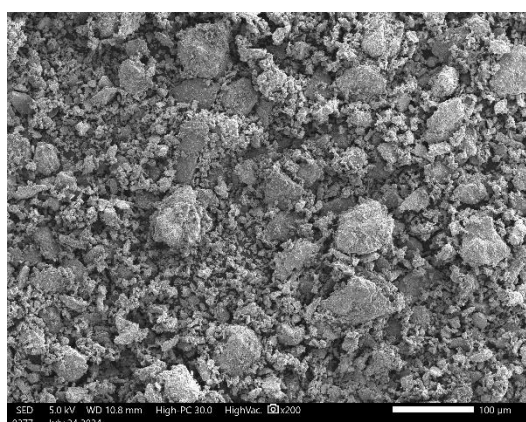
Figure 2. X-ray diffraction pattern of powders: 1) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$, 2) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ after 30-HF

At the same time, during the etching process, the crystallite sizes calculated by the Debye-Scherrer method from the broadening of the crystalline reflexes decrease. The crystallite sizes of the MAX phase were decreased from 90.7 nm to 56.8 nm after etching.

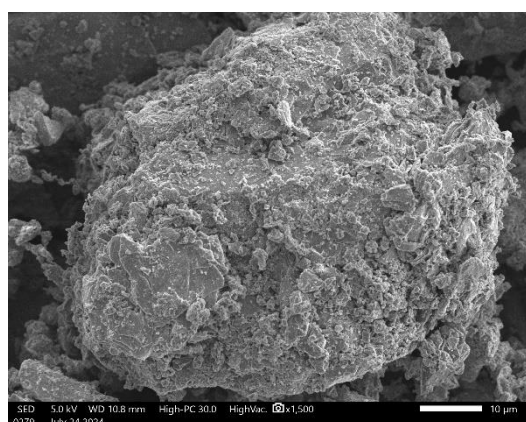
Thus, the structure of Ternary [carbide](#) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ synthesized by selective removal of aluminum at a concentration of 30% hydrofluoric acid was studied. It was revealed that the etching process does not affect to the formation of Ternary [carbide](#) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$.

SEM studies of the MAX phase surface morphology reveal crystals with a layered morphology, with individual crystals appearing as stacked plates or lamellae, and lamellar and flaky morphologies are also observed. These plates are quite large and thin, reflecting the layered nature of the material. The plate sizes range from 200 nm to 10 microns (Fig. 3. a, b).

SEM images of the MXene $\text{Ti}_3\text{C}_2\text{T}_x$ surface show a flaky morphology, with individual $\text{Ti}_3\text{C}_2\text{T}_x$ sheets appearing crumpled and wrinkled. This indicates the layered nature of the material, where the layers are not perfectly flat, but have a rough, uneven surface (Fig. 2. c-g). The size of the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes varies from approximately 35 nm to 2 micrometers across, with some flakes appearing larger and more interconnected. The flake surface shows a pronounced roughness with visible peaks and pits, probably due to surface terminations (T_x) and the exfoliation process.



a



b

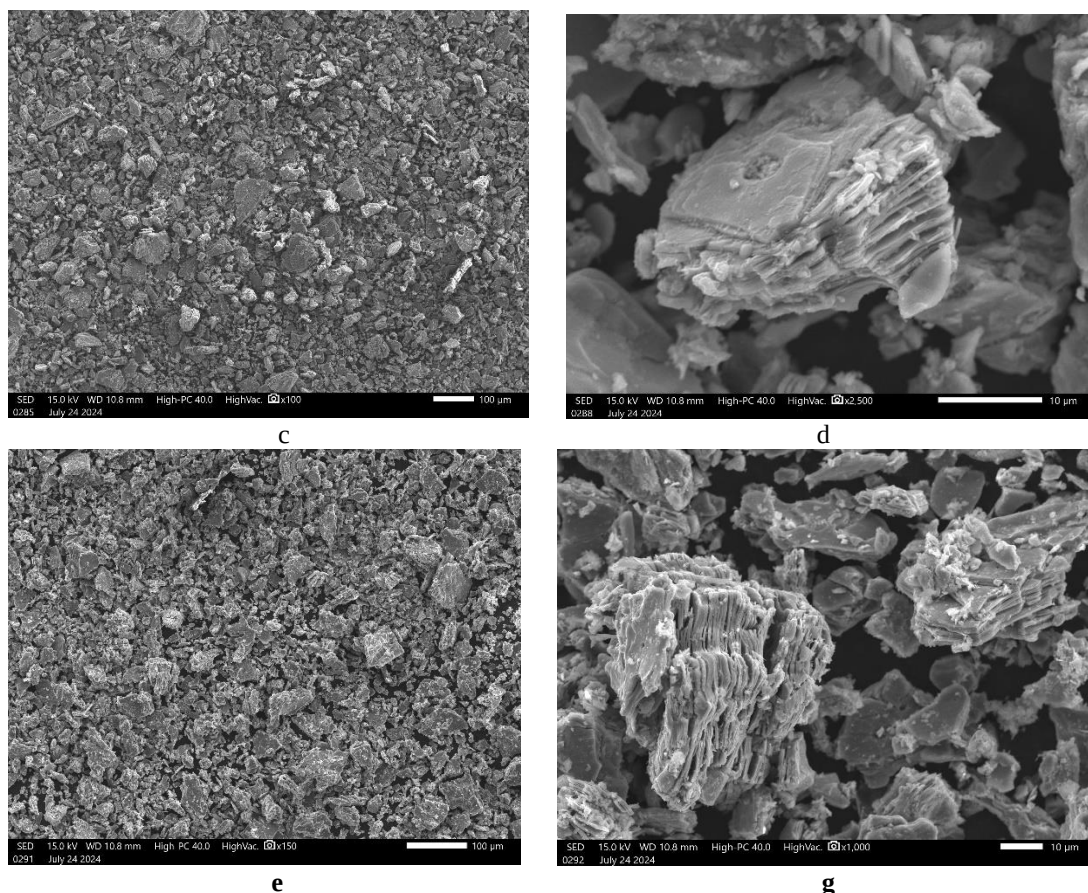
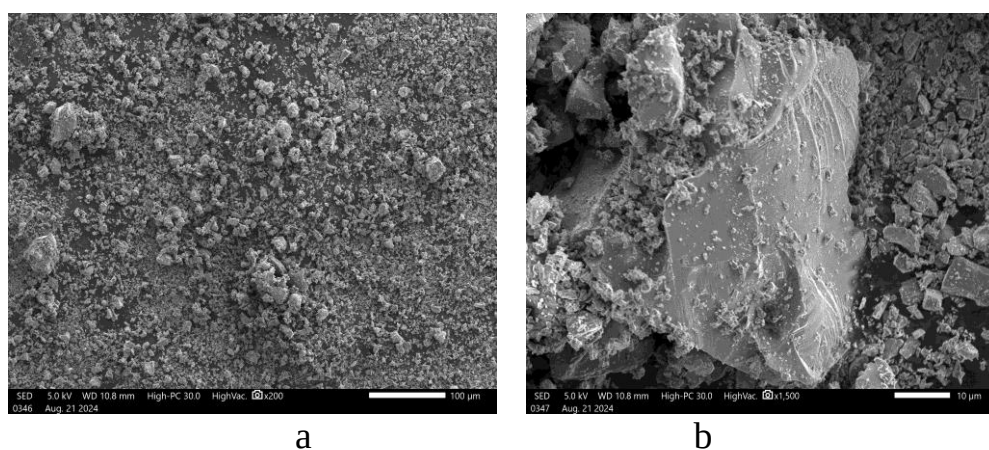


Figure 3. SEM images of MAX and MXene powders. a) Ti_3AlC_2 (100mkm), b) Ti_3AlC_2 (10 mkm), c) $\text{Ti}_3\text{C}_2\text{T}_x$ 10-HF(100 mkm), d) $\text{Ti}_3\text{C}_2\text{T}_x$ 10-HF (10 mkm), e) $\text{Ti}_3\text{C}_2\text{T}_x$ 30-HF (100 mkm), g) $\text{Ti}_3\text{C}_2\text{T}_x$ 30-HF (100 mkm).

Depending on the concentration of the acid used for etching, different morphologies are observed. An accordion morphology is observed for powders etched with 30-HF (d) and partly with 10-HF (g).

SEM studies of $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ samples before and after etching with hydrofluoric acid showed that particles of various shapes and sizes from 500 nm to 10 microns are observed before etching (Fig.4. a-b-c), and after etching the number of small particles becomes smaller, but at the same time Large particles exhibit bulges of various shapes and structures. Bulge sizes vary from 1 micron to 5 microns (Fig. 4d).



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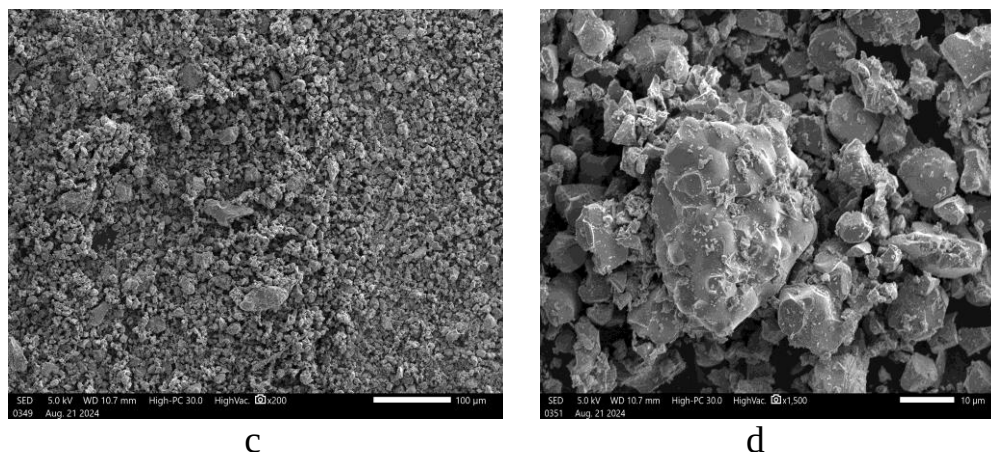


Figure 4. SEM images of $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ and $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ after 30-HF powders. a) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ (100 mkm), b) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ (10 mkm), c) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ after 30-HF (100 mkm), d) $\text{Ti}_{0.9}\text{Al}_{0.1}\text{C}$ after 30-HF (10 mkm)

CONCLUSION

Thus, MXene was obtained from the MAX phase by selective etching with hydrofluoric acid of various concentrations. It was revealed that with increasing concentration of hydrofluoric acid, layered MXene is formed in the form of an accordion. It has been shown that the thickness of the layers varies from 35 nm to micron size. When etching a MAX phase with a cubic system, a decrease in crystal size is observed, but a layered structure does not form.

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