International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2018): 7.426

Review on Characterization of Nano Sized MXenes for Energy Storage Devices

Imran Khan

Department of Physics, Gandhi Faiz-E-Aam College Shahjahanpur, MJP Rohilkhand University Bareilly 242001, India

Abstract: ***Complex layered structures occur in a wide range of ceramic materials. The so called 'MAX phases' is an exciting playground for property tuning and understanding of process-structure-property relationships. They stand out because of the large variations in chemistry and hence design opportunities within the same materials family. $M_{n+1}AX_n$ (MAX) phases are nano-laminated compounds based on a transition metal (M), a group an element (A), and carbon or/and nitrogen (X), which exhibit a unique combination of ceramic and metallic properties. A new family of 2D materials has emerged, consisting of transition metal carbides, nitrides and carbonitrides, known as MXenes which are electrically conductive in nature. One of the many potential applications for 2D Ti_3C_2 is in electrical energy storage devices, such as batteries, Li-ion capacitors and super-capacitors. The vast majority of MXenes known till date have been produced by selectively etching Al from Al containing MAX phases. During the etching process, the MXene surface acquires terminating functional groups, which is why they are commonly designated as $M_{n+1}XnTx$, where Tx represents surface terminating groups such as -O, -OH, and/or –F.***

Keywords: Nano Materials, MXenes, Conductivity, Dielectrics and Metals.

1. Introduction

Complex layered structures occur in a wide range of ceramic materials. The so- called 'MAX phases' are an exciting playground for property tuning and understanding of process-structure-property relationships. They stand out because of the large variations in chemistry and hence design opportunities within the same materials family. The history of the MAX phases began in the 1960s, when Hans Nowotny's group in Vienna discovered [1] more than 100 new carbides and nitrides. $M_{n+1}AX_n$ (MAX) phases are nano-laminated compounds based on a transition metal (M), a group-A element (A), and carbon or/and nitrogen (X), which exhibit a unique combination of ceramic and metallic properties. A new family of 2D materials has emerged, consisting of transition metal carbides, nitrides, and carbonitrides, also known as MXenes. The vast majority of MXenes known to date have been produced by selectively etching Al from Al containing MAX phases.[2] During the etching process, the MXene surface acquires terminating functional groups, which is why they are commonly designated as $M_{n+1}X_nT_x$, where Tx represents surface terminating groups such as -O, -OH, and/or –F [3-4].

Two-dimensional (2D) solids, the thinnest materials available to us offer unique properties and a potential path to device miniaturization. The most famous example is graphene, which is an atomically thin layer of carbon atoms bonded together in-plane with sp2 bonds. Recently, an entirely new family of 2D solids transition metal carbides (Ti_2C, Ti_3C_2, Nb_4C_3, etc.) and carbonitrides was discovered by Drexel University scientists [5, 6]. Selective etching of the A-group element from a MAX phase results in formation of 2D Mn+1Xn solids, labeled "MXene". 18 different carbides and carbonitrides have been reported to date [7-9]. Structure and properties of numerous MXenes have been predicted by the density functional theory, showing that MXenes can be metallic or semiconducting, depending on their surface termination. Their elastic constants along the basal plane are predicted to be higher than that of the binary carbides. Oxygen or OH terminated MXenes are hydrophilic, but electrically conductive. Hydrazine, urea and other polar organic molecules can intercalate MXenes leading to an increase of the *c* lattice parameter of MXenes [7]. When dimethyl-sulfoxide was intercalated into Ti_3C_2, a stable colloidal solution of single- and few-layer flakes was produced. One of the many potential applications for 2D Ti_3C_2 is in electrical energy storage devices, such as batteries, Li-ion capacitors and super capacitors [3-5]. Ti_3C_2 paper electrodes, produced by vacuum assisted filtration of an aqueous dispersion of delaminated Ti_3C_2, show a higher capacity than graphite anodes and also can be charged/discharged at significantly higher rates. They also demonstrate very high intercalation capacitance (up to 900 F/cm^3) in aqueous electrolytes [8]. More among them were the so called 'H phases' and their relatives Ti_3SiC_2 and Ti_3GeC_2. These phases remained largely unexploited until the mid 1990s, when Barsoum and El-Raghy [11] synthesized relatively phase-pure samples of Ti_3SiC_2 and revealed a material with a remarkable combination of metallic and ceramic properties: it is a good electrical and thermal conductor, machinable, and resistant to thermal shock and oxidation. They later discovered Ti_4AlN_3, making it clear that these phases are a large family described by the general formula '$M_{n+1}AX_n$ phases' (*n* =1, 2, or 3) or 'MAX phases' [12-13]. This structure endows the MAX phases with unique chemical, physical, electrical, and mechanical properties stemming from their layered structure and the mixed metallic-covalent nature of the strong M–X bonds together with M–A bonds that are relatively weak. Because of this unusual property combination, the MAX phases show promise for a wide range of uses in high temperature structural applications, protective coatings, sensors, electrical contacts, micro-electro-mechanical systems, and many more. In 2011, it was demonstrated that the A layers can be selectively etched from the MAX phases [14], to form a new type of 2D material, named MXene to emphasize the relation to the MAX phases and the parallel with graphene. MXenes have rapidly become established as

a novel class of 2D materials with remarkable possibilities for composition variations and property tuning.

The electrical and mechanical properties measured for the first representatives of MXenes are promising. Our challenge is to develop improved methods for the synthesis of 2-D carbides, nitrides, oxycarbides, carbofluorides and other compounds in bulk and as thin films (e.g., molecular beam epitaxy, chemical vapor deposition, electrochemical or chemical exfoliation of MAX phases, synthesis from graphene, etc.). Another challenge is to predict and experimentally measure the properties of 2-D ceramics. A final challenge is to integrate the 2-D ceramics into glass, ceramic, and other matrices, and to develop 3-D structures utilizing 2-D building blocks for a variety of applications.

2. Experimental Procedure

First of all we shall synthesize the MXenes by using vapor deposition, sintering and thin film synthesis technique. On the other hand we have taken the transition metal carbides (like Ti_2C, Ti_3C_2, Nb_4C_3, etc. from (Alfa Aesar, A Johnson Matthey Company USA and Sigma- Aldrich). Grinding and mixing of micro and nano powder separately carried out in a mortar for 30 minutes to achieve homogeneity. Pellets (diameter~1.00cm and thickness for Micro~0.08 cm and for Nano~.03cm) of these powders were made by the hydraulic press by uniformly applying the pressure of 100 MPa, which results in fully isotropic material properties. The micro powder pellets were sintered at high temperature for 2 hrs to achieve strength and pellets of nano powder were not sintered just to avoid grain growth and agglomeration. SEM will be used to study the morphology and the microstructure of these samples. XRD will also be used to verify the crystallinity and the structure of these as grown nanostructures. Finally, we shall study the structural and electrical transport properties of these nanostructures. The sample holder for these measurements will also be specially designed. To explain the transport mechanism we shall measure I-V characteristics at different temperature.

(a) Sample preparation
Thin films of different thickness will be prepared by using pulsed laser deposition (PLD) technique, onto glass and silicon wafer substrates at different temperature on a base pressure of 10^{-8} Torr. The substrates were thoroughly cleaned in a detergent solution and then in a chromic acid and finally, cleaned using trichloroethylene. Double distilled water was used throughout in different stages of cleaning. To avoid the fractionation of the alloy during evaporation and, thereby, to ensure the correct average composition of the films formed, a high deposition rate was used to prepare the studied films. The thickness of the films was measured by using a quartz crystal monitor.

(b) Structural study and microscopic measurements
To understand the behavior of a crystal we have to study the structural properties of materials. So XRD will be used to verify the crystallinity and the structure of these as grown nanostructures. The data of in the crystalline state will be fitted using FULLPROF code for Rietveld refinement. The detailed microscopic studies will be carried out using Scanning Electron Microscope (SEM).

(c) Electrical transport measurements
Investigations on the temperature dependence of conductivity, the effect of impurities on activation energy, the effect of annealing on conduction and the effect of high electric field on conduction mechanism is a subject of great importance because the results of such studies provide ways to control conductivity effectively. The density of localized states in the mobility gap controls many physical properties of amorphous semiconductors. The determination of density of states near the Fermi level N (EF) has been an important issue in these materials. One of the direct methods for the determination of N (EF) involves the measurement of space charge limited conduction (SCLC) which can be easily observed in low conductivity semiconducting materials. The electrical transport properties of these nanostructures materials will be studied in the temperature range from room temperature to 500K. We shall use ohmic method to measure I-V characteristics at different temperature and R-T characteristics to explain the transport mechanism.

(d) Dielectric properties measurements
A specially designed metallic sample holder is used for DC as well as AC measurements. The sample holder consists of two parts; the upper part contains two steel electrodes passes through Teflon feed, between which the samples were mounted via a screw arrangements. The lower part contains a heating element in the bottom to heat the sample. For both DC and AC measurements, the vacuum of the order 10^{-3} Torr maintained inside the sample holder. The temperature was measured by mounting a k-type Chromel-Alumel thermocouple near the sample. A Keithley picoammeter (model 6485) was used to measure the currents between temperatures from room temperature to 5000K. For dielectric properties, the capacitance C and dissipation factor D is measured by using Wayne Kerr 4300 LCR meter (frequency range 20 Hz-1 MHz with 0.1% basic accuracy).

3. Result and Discussion

Structural Characterization
In fig-1, the microstructure of the powdered samples is shown in the SEM images of fractured surface of the samples. The volume of pores and grain size can be seen clearly. The surface of this particular elongated grain shows distinct evidence of crack growth along the surface of the grain. Such a growth mode helps to produce a complex crack path, which in turn contributes to crack deflection and bridging, thereby improving the toughness of these samples. The large grains surrounding some fine grains can form open as well as closed pores. This effect results in the rearrangement stage and rapid initial densification. So these dense samples confirm certain electrical and dielectric properties at high temperature. X-ray diffraction techniques are used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. X-ray diffraction techniques are superior in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of materials largely depend on the crystal structures. X-ray diffraction techniques have, therefore, been widely used as an indispensable means in materials research, development and production.

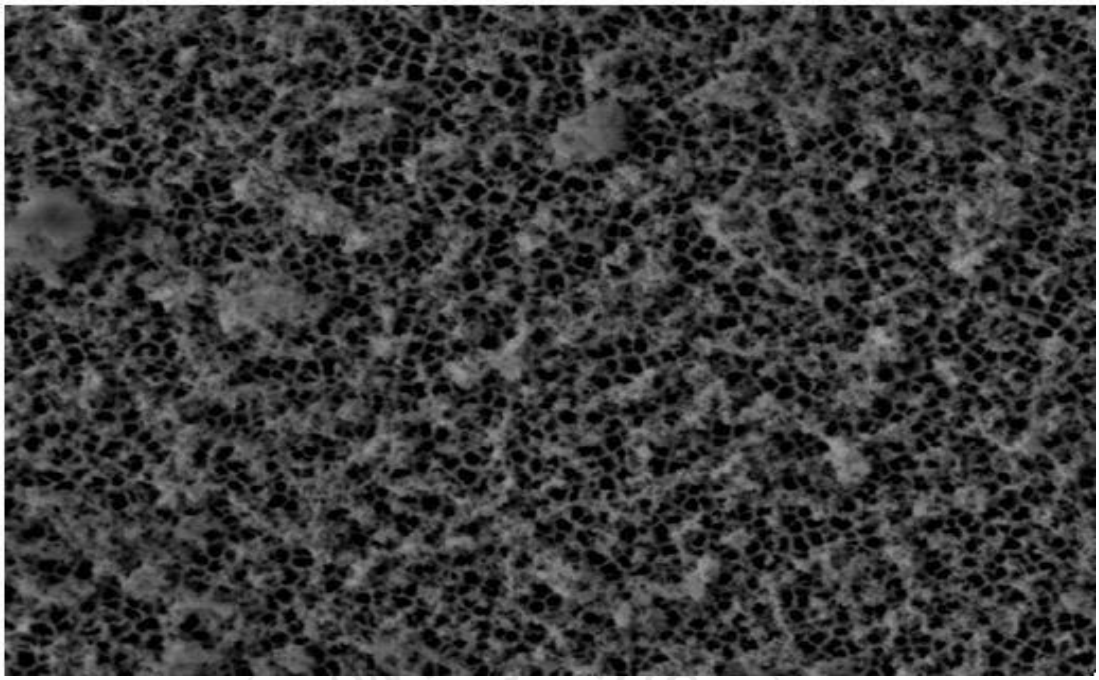

Figure 1: SEM image showing microstructure of the sample

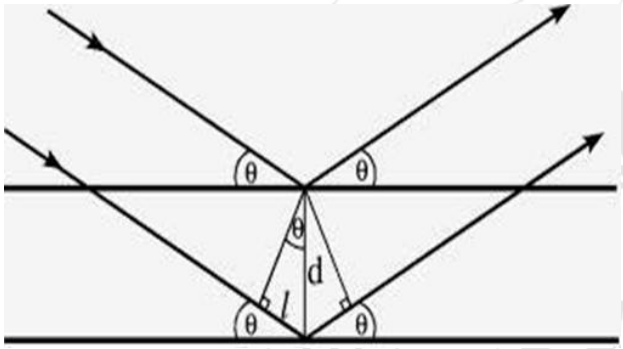

Figure 2: X-ray Crystallography of the sample by Bragg's law

The Bragg equation, $n\lambda = 2d\sin\theta$ is one of the keystones in understanding X-ray diffraction. In this equation, n is an integer, λ is the characteristic wavelength of the X-rays impinging on the crystallize sample, d is the interplanar spacing between rows of atoms, and θ is the angle of the X-ray beam with respect to these planes. When this equation is satisfied, X-rays scattered by the atoms in the plane of a periodic structure are in phase and diffraction occurs in the direction defined by the angle θ. In the simplest instance, an X-ray diffraction experiment fig.2 consists of a set of diffracted intensities and the angles at which they are observed. This diffraction pattern can be thought of as a chemical fingerprint, and chemical identification can be performed by comparing this diffraction pattern to a database of known patterns.

Electrical transport measurements

To measure the DC conductivity (σ_{dc}) of different Mxenes, the temperature dependent current has been measured. The dc conductivity is plotted as a function of temperature as shown in fig.3. In the temperatures region (T<625K), the dc conductivity is nearly temperature independent. In the higher temperatures region (T>625 K), the dc conductivity increases exponentially with temperature.

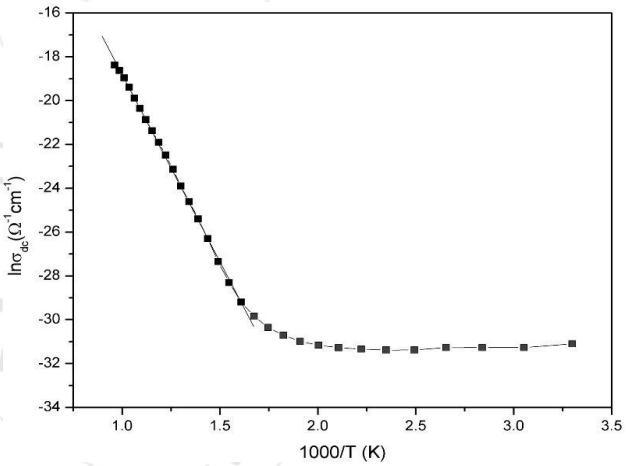

Figure 3: Temperature dependent dc conductivity

Dielectric Properties

The alternative representations of the AC response of Mxenes are dielectric constant. In the presented work the measured quantities are the capacitance C and dissipation factor D. They have the transformation relationships described as below. The real part dielectric constant (ε') and imaginary part dielectric loss (ε'') of the dielectric permittivity are extracted using the established relationships:

$$\varepsilon' = \varepsilon_0 C.A/d \quad \text{and} \quad \varepsilon'' = D.\varepsilon'$$

Where d is the thickness, A is the cross-sectional area of the sample, ε_0 is the permittivity of the vacuum and ω is the angular frequency.

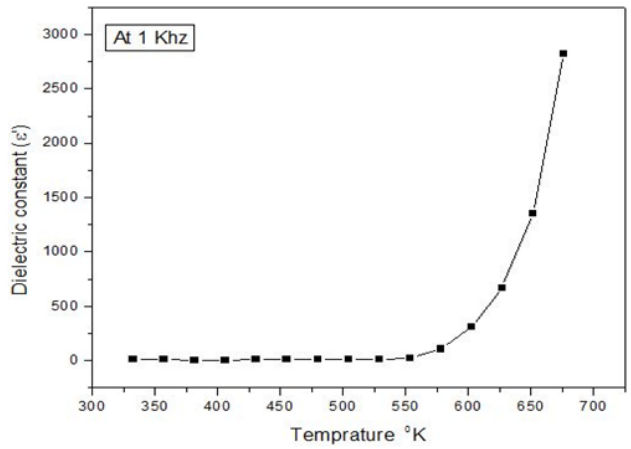

Figure 4: Dielectric constant (ε′) vs. temperature

Frequency and temperature dependence dielectric parameters (ε′ and ε″) of the different MXenes are investigated in the temperature range (300 K-1000 K) at frequencies (100Hz to 1MHz). Fig.4 and fig.5, shows the temperature dependent dielectric constant (ε′) and dielectric loss (ε″) at different frequencies (100Hz to 1 MHz). The values of ε′ and ε″ from room temperature to (> 625K) remain almost independent of temperature. As the temperature are increases, ε′and ε″ increase quite appreciably with temperature.

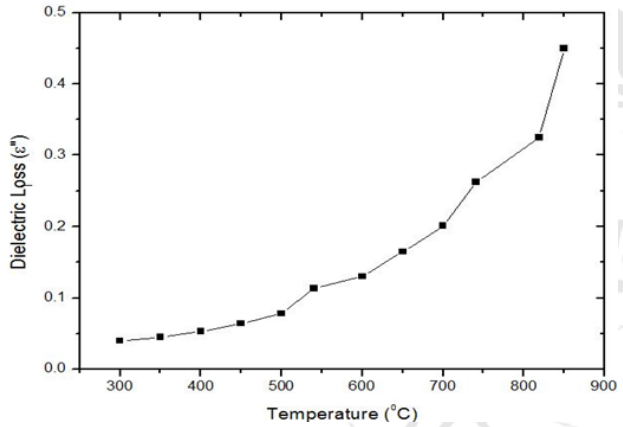

Figure 5: Dielectric loss (ε”) vs. temperature

4. Conclusion

Carbonitrides and nitrides were produced in the past 5 years by selective etching and exfoliation of layered ternary precursors forming a large family of 2D materials named MXenes. In addition of the composition, the electrical conductivity of MXenes depends on the sample preparation method. A variety of MXene structures make them promising candidates for many applications. Energy storage has been the first and most studied application of MXenes. However, there are potentially other applications in which MXenes can outperform other materials. MXenes in energy storage batteries have wide chemical and structural variety. For this reason, MXenes can help to define the most promising candidates for energy-storage applications. Because the ions penetrate between the Mxene so the bonds between M and X are broken easily. The surface terminations are one particular factor than can affect the performance, for example, oxygen terminations deemed most favorable, whereas hydroxyls and fluorine result in lower capacity as well as impeded Li-ion transport. MXenes can provide a range of working potentials, which makes some of them suitable as anodes and some of them suitable as cathodes. This is in agreement with the remarkably high-rate performance experimentally observed for several MXenes. MXene-based composite electrodes hold particular promise for high-performance, high rate batteries. MXenes provide a conductive matrix that accommodates expansion and contraction of particles while maintaining structural and electrical connectivity. Other applications have also been studied such as water purification, reinforcement for composites, electro catalysts and catalysts in the chemical industry, lubricants, photo catalysts, and bio- and gas sensors.

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