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Investigation and characterization of Nano clay structures

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ABSTRACT

Nano clays are synthesized by the sol-gel method while ethanol and some acids are used as organic solvents and matrail treatments in the synthesis processes. The X-ray diffraction (XRD) analysis and Atomic Force Microscopy (AFM) techniques points out that the obtained nanopowders possess a well crystallized hydrotalcite – like anionic clay structure. They reveal that the features of the some dominate kind of clay in particularly montmorillinite (MMT), eillit (psedu quartz) and kaolinite crystal phases which are dependent on the nature of the organic solvent and acid treatment materials. After treatment, the obtained results show an emerged nanoclay with a relatively uniform porous structure with expanding nano clay layers. These results point out that the nature of the organic solvent and acid treatments are important for tailoring the textural and porous properties of nano clay nanostructures which can enhances the structural integrity, and provides a generic framework to construct functionally graded materials.

Keywords: Nanocomposite, Nano Clay, Sol-gel method, X-ray diffraction and AFM techniques.

INTRODUCTION

The sol-gel process is a wet-chemical technique (chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network clays.

Clay may form a sol (quick clay) if it is washed sufficiently to remove the counter ions. Quick clay may be gelled if enough counter ions are added, so that the colloidal particles aggregate. Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

By adsorption of charged species onto the surface of the particles, repulsion between the particles will increase and agglomeration will be prevented. The surface of a particle is covered by ionic groups, which determines the surface potential. Counter ions in the solution will cover

this layer, shielding the rest of the solution from the surface charges, by increasing the number of counter ions. An increase in the concentration of counter ions result in a decrease of the thickness of the double layer.

Systematical investigations of the synthesizing the nano scale materials reveals unique underlying mechanisms for electrostatic-assisted synthesis of sol-gel films. The synthesis of the nanoclay, in particularly, sol-gel MMT depends on procedure time and treatments which can affect to the synthesis rates of sol-gel acids on MMT surfaces. These observations suggest a surface-mediated synthesis of sol-gel oxide, nitride layers on MMT surfaces, one that is likely controlled by electrostatic interactions. These new findings significantly advance the general understanding of the electrostatic assembly process. For the aged precursors, the synthesis mechanism differs; the synthesis of sol-gel oxide layers is controlled by hydrodynamics and follows [1-5].

Therefore, as XRD patterns and AFM images show, the expansions in clay layers can be due to changes in elastic modulus of the multilayers. It can be intentionally tuned by changing the multilayer design and that significant porosity is present in the multilayer even after heating and acid treatments, in where the improved mechanical stability of the nanoclay structures yields to the formation of so strong C–O–C bonds and Si–O–Si bonds between the two silanes of dense structure. This is the resion people believe that the structures with nanoclay may be used for removal of unwanted bonds on the surface of materials such as epoxy primers and polyurethane topcoats from very sensitive metal or composite substrates with better efficiency than was previously available [6 - 9]. The ultra thin layer of MMT on top of substrate such as thin composite surfaces is high and thus can cause the uniform distribution of nano particles. Coatings can be removed with virtually no damage to such substrates, leaving protective coatings such as cladding and anodizing intact.

Experimental procedure and details

The sol-gel process is a wet-chemical technique (chemical solution deposition) and/ or a bottom – up procedure, widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network nano composites. Typical precursors are acetic, nitric, Chloride, formic and sulphuric acids, which undergo various forms of reactions.

Thus, the sol evolves towards the formation of a gel-like diphase system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous networks. In this process, ammonium clay powder ($1 \cdot 16$ g) was dissolved in de-ionized water to which was added citric acid ($0 \cdot 38$ g). The mixture was then stirred carefully using a magnetic stirrer while ammonium hydroxide was added to obtain a pH of 7. The mixture was then heated in a furnace to a temperature of 100°C for 20 h. Initially a zero gel and finally a powder were obtained.

The powder was then heated to a temperature of 60°C for 24 h to obtain a pale yellow powder. The characterization of clay synthesized by the sol – gel method was studied by using XRD and FTIR techniques. It is worth noting that the samples are cleaned inside the ultrasonic bath after rinsing and washing in heated acetone then ethanol the surface cleanliness is checked with XRD technique. MMT powder is synthesized via simple sol – gel method as summarized in figure 1.

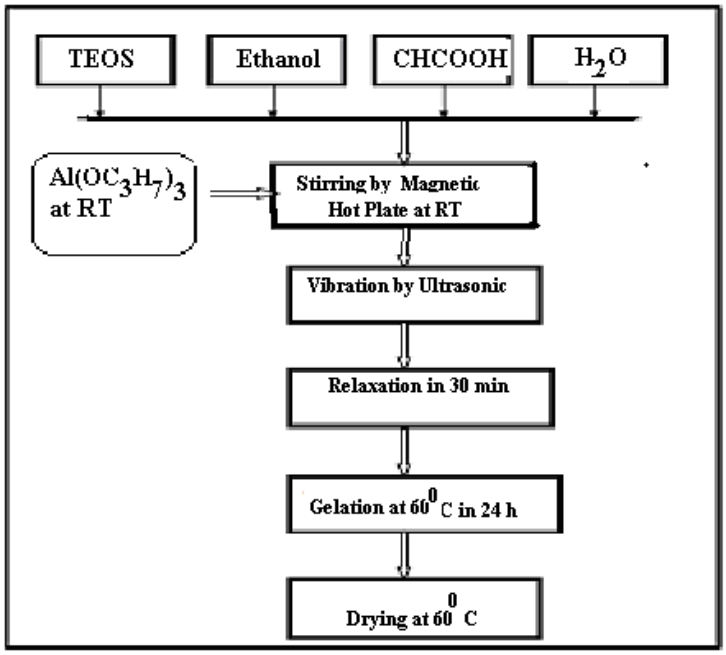

Figure 1 - Flowchart of synthesis stainless steel nano particles.

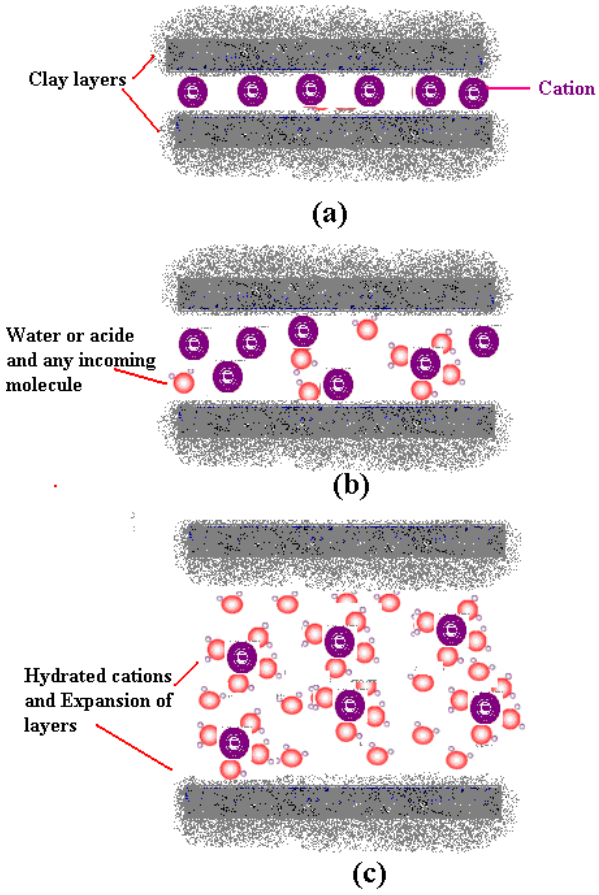

Figure 1: The schematic processes which show how incoming molecules can penetrate through the caly and expand clay layers. (a) Dry condition (interlayer), (b) The incoming molecules like water molecules wedge into the interlayer after adding water or acid and (c) The cations are hydrated which results in repulsive forces and expanding clay layer (Hydration energy)

The difference in the FTIR results may be attributed to polarity of the structure, which causes difference in internal phase separation from that of natural clay. Based on the diffraction peak of MMT (in XRD patterns (figures 3-6), under different treatments , their X- ray peaks are calculated to obtain the interlayer distance change as shown in Table 1. The characteristic peak for the pristine clay is that of the diffraction at (100), such peak interdistance is expressed by $d_{100.}$ Because the Scherrer relation can not determine the accurate size of nano particles. We have thus used X – Powder method (see figures 3 through 6) and found the accurate crystalline size.

X - ray diffraction (XRD) patterns were recorded using a Philips PW 1840 diffractometer under the following conditions: 40 kV, 30 mA, monochromatic CuKα radiation (λ = 0.15418 nm) over a 2θ range from 4 to 70º. The nitrogen adsorption – desorption isotherms were recorded at 77 K on a Coulter SA 3100 automated gas adsorption system on samples previously degassed at 383 K for 7 h under vacuum.

Microcomputer processing controlled the analysis. Specific surface areas (SBET) were determined with the Brunauer–Emmett Teller (BET) method on the basis of adsorption data.

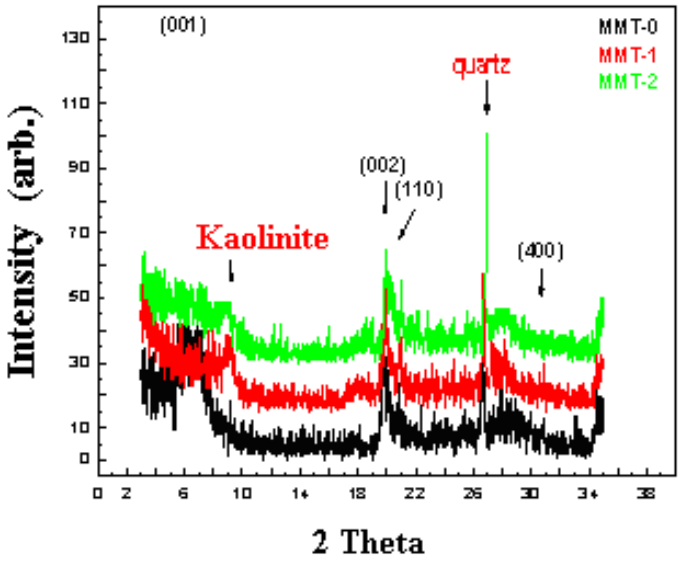

Figure 3: XRD pattern of nano clay correspond to Table 1.

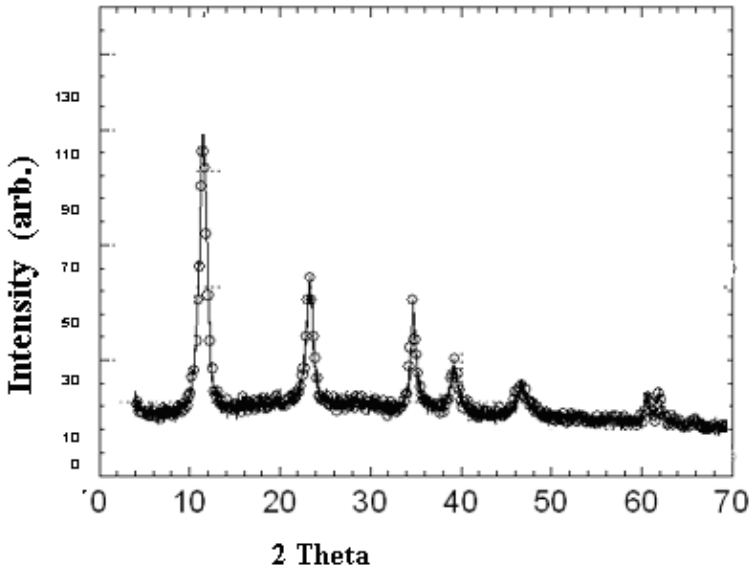

Figure 4: XRD pattern of nano clay correspond to Table 1.

Specimen	Composites And Procedures	MMT $d_{(001)}$ (nm)
MMT -0	Natural clay	6.65
MMT -1	MMT -0 with H_2O_2	7.85
MMT -2	MMT -1 with Acetic acid	7.89
MMT -3	MMT -2 with Heated at 400^0C	8.34
MMT -4	MMT -2 with Formic acid	6.58
MMT -5	MMT -2 with Sulfuric acid	6.80

Table 1: The procedure of experiment in sol – gel method with H_2O_2, Acetic acid, Magnesium chloride, Nitric acid, Chloride acid, Formic acid and Sulfuric acid treatments.

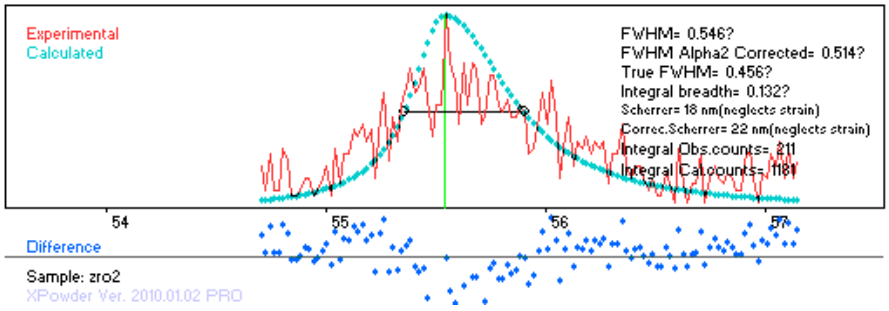

Figure 5: X- powder method has been used for determining the size of nano particles. The size of nano particle at anatas phase is 22 nm.

Figure 1 illustrates the XRD patterns of hydrotalcite – like anionic clay synthesized samples; the diffraction peaks typical of layered double hydroxides structure [1] with sharp and symmetric reflections of the basal MMT(001), Eilit (003) and Caolinite (004), MMT(011) planes and broad, less intense and asymmetric reflections for the nonbasal (102), and (011) planes can be clearly identified. The intensity and the sharpness of the peaks reveal also some differences in the crystalline of the samples. The XRD reflections are indexed using a hexagonal cell with rhombohedral symmetry (R – 3m), commonly used as a description of the nanoclay structure.

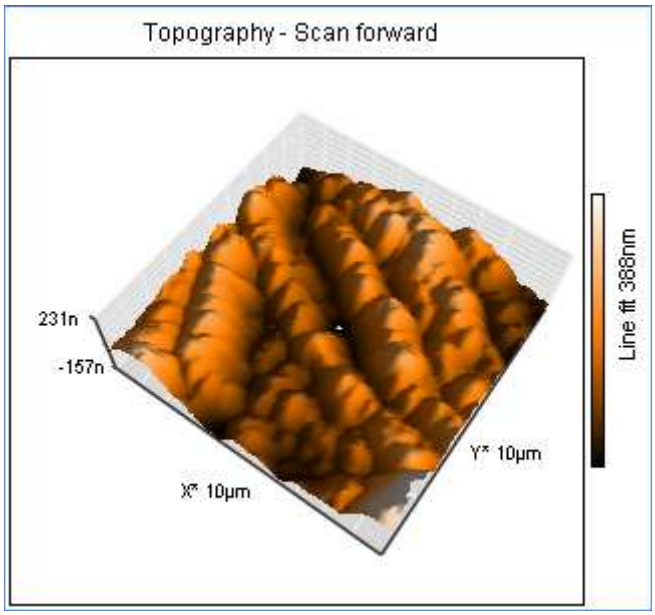

Figure 6- 3D- AFM microstructure of the BFO phase powder ceramics with 10% (left) and 15% (right) Bi.

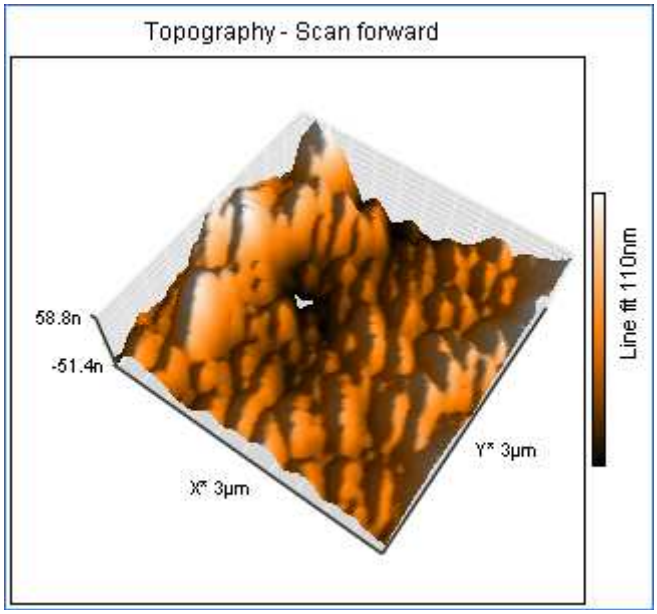

Figure 7- 3D- AFM microstructure of the BFO phase powder ceramics with 10% (left) and 15% (right) Bi.

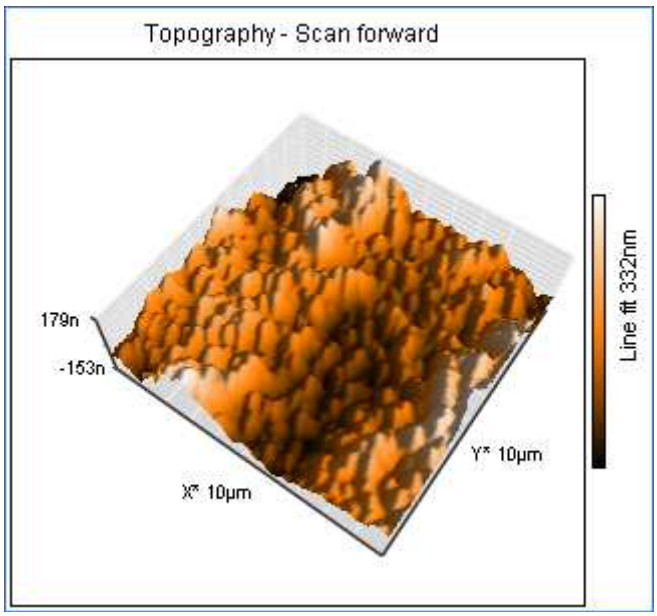

Figure 8- 3D- AFM microstructure of the BFO phase powder ceramics with 10% (left) and 15% (right) Bi.

The calculated interlayer free space are shown in Table 1. The values of the interlayer free space ($d_{(001)}$) values (see Table 1) modify when the organic solvents and acid treatments on clay are used in the synthesis process.

The nanometer-sized montmorillonite clay particles can thus improve surface integrity and provide advantages in the mechanical and thermal properties of the composite. These results are achieved with looking at XRD patterns as shown in figures 1 through 4 and AFM images in figures 5 through 8. The size of nano clay has been determined with X – Powder method as shown in figures 9 through 13. These results demonstrate that the overall increase in efficiency of this media is three to four times faster than unfilled polymer while the durability has more than doubled.When ethanol is used in the synthesis medium the emerged nanoclay present a relatively uniform porous structure.

In fact, the solvents bring in the synthesis medium their own electrostatic properties that are able to develop new electrostatic features of the synthesis medium thus to establish new electrostatic interactions not only between the reactants but also between the clay layers; this can modify the distance between the clay layer and change the values of *c* parameter. Therefore the value of *c* parameter is equal to 23.37 Å for HT_1 but increases. to 23.54 Å when phenol is also present in the synthesis medium. The interlayer free spacing (IFS) values are calculated by subtracting the thickness of the LDH layer (4.8 Å, [1]) from the calculated d_{003} spacing. The values increase from 2.99 Å for HT_1 to 3.04 Å for HT_2, respectively. The decrease in IFS values point out that the nature of the solvent influences the space between the anionic clay layers.

However, the degree of crystallization is different in each case,HT-Ashows the broadest diffraction peaks and in HT-C the peaks are well-defined and sharp.

The characterization of nano clay synethesized by the sol – gel citration method was studied by using XRD and AFM techniques. It is worth noting that the samples are cleaned inside the ultrasonic bath after rinsing and washing in heated acetone then ethanol the surface cleanliness is checked with AFM technique.

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XRD technique is also used for crystal phase identification and estimation of the crystallite size. XRD patterns were measured on a (GBC-MMA 007 (2000)) X-ray diffractometer. The diffractograms were recorded with 0.02^o step size in where the speed was 10 deg/min radiation over a 2θ range of 10°–80° at a sampling width of 0.2^o and a scanning speed of 10 deg/ min. The XRD patterns of clay compose calcined at different temperatures . The crystalline peaks corresponded to MMT in the form of either highly pure austenite phase or mixed austenite–martensitic, except the as – prepared nanostructure showing amorphous phase. This point indicates that increase in austenite-to-martensitic transformation of clay peak place when the amount of MMT nanoparticles (10%) in SS content is added.

The significant broadening of the clay peaks may be due to the reduction and refinement of the grain size and the increase in the internal strain induced from the repeated fracturing and welding process during mechanical alloying. Crystallite size, lattice microstrain and lattice parameter of each alloy powder has calculated from the XRD peak broadening. Following Scherrer equation, the crystallite size and the lattice strain have been determined for milled samples.

$$\Gamma = \frac{K\lambda}{\beta \operatorname{Cos}\theta}$$

Where Γ , K, λ, β and θ is mean crystallite dimension, x- ray wavelength, FWHM (in radians) and Bragg angle, respectively.

The crystallite size estimated from the XRD analysis of the powder was close to 30 nm. This suggests that major structural changes and dissolution of the alloying elements almost completed by 25 h, and further milling refined the product by MA.

This is because of the entrance of Si and Ni atoms into the lattice of the Al which causes distortion in it. Therefore, two factors determine the hydrolysis and condensation rates. First factor is the acetic acid, which promote the hydrolysis of TEOS; the second is the titanate formed by the chelate of acetic acid and titanium, which accelerate the condensation of TEOS

[22,24].With respect to acetic acid, it plays two roles in the system. One side, it acts as the catalyst to promote the hydrolysis of TEOS; on the other side, it chelate with titanium to form titanate, which accelerate the condensation of TEOS and retard the hydrolysis and condensation of TIOT. In the present work, the TEOS is partially hydrolyzed in methanol, water and hydrochloric acid under controlled conditions that allow the solution, i. e., sol, to yield a formable, loosely cross-linked matrix, i.e., gel. Then, titanium chelate compound (PTP) was added to form polytitanosiloxane solution (TiSi) via polycondensation reaction.

CONCLUSION

The sol – gel method provide an excellent technique to prepare nano particle material. Experimental results indicated that the homogeneous hydrolysis of tetra isopropy ortho titanate via sol-gel route is a promising technique for preparing photosensitive material with uniform nano particles. In this study, nano crystalline SS particles have been successfully synthesised by chemical method and heat treatment process.

The present work provides a method for processing nano structured MoO3 with enhanced gas sensing capabilities.

Nano-sized MoO3 was synthesized using the citrate sol–gel method and the same was characterized using AFM, SEM and XRD techniques.

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