

Full Length Research Paper

Sodium nano-particle effects on montmorillinite structure

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The main aim of the work is to study the expansion of the inter-layers clay to see what will happen to the mechanical properties of clays. The expansion of clay layers with sodium nano- particles makes for the exfoliation and dispersion of the crystal in fine particles in the clay positions. Patterns obtained by X-ray diffraction (XRD) of nano montmorillinite (MMT) illustrate that its shape is irregular and the range of sizes is very wide as found by X- powder method. XRD patterns represent significant improvement in acid treatment relative to direct or other methods. Mg^{+2} , Ca^{+2} and ammonium are the dominant exchangeable cations which show relatively low dispersion degree and large size of the particle. However, in the present work, Na nano - particles have been inserted in the clays and the extension of the destruction clay layers is revealed.

Key words: Nanostructures, nanoclay, montmorillinite, sol – gel method.

INTRODUCTION

Recently, many researchers (Mani et al., 2005; Quang et al., 2007; Sánchez, 2009; Bahari, 2006; Morgen, 2006; Bahari et al., 2005; Bahari and Pashayan, 2011) have studied polymer layered silicon nano – composites as suitable material both in industry area and in academia, due to their potential for enhanced physical, chemical and mechanical properties compared to conventionally filled composites. Indeed, two categories of clay minerals are: first type known 1:1 clays which is one tetrahedral sheet presented for one octahedral sheet; second type known 2:1 clays with two tetrahedral sheets presented for one octahedral sheet. They have been studied both experimentally and theoretically. The 2:1 clay minerals are further subdivided into smectites, micas, vermiculites, and pyrophyllites. We have studied MMT which is 3:4 clay mineral and classified as a smectite, which is widely used in the preparation of polymer nanocomposites.

MMT is a nano clay and seems something like polymer – based nano compositions because of their suitable charge layer density, 2:1 tetrahedral – octahedral layer structure. From Mani et al. (2005) and Quang et al. (2007), we found that the structure of MMT is derived from clay by the substitution of certain atoms for other

atoms. By looking at their structure, it is clear that the tetrahedral sheet is tetravalent Si with little trivalent Al atoms. But, the octahedral sheet includes divalent Mg which replaces trivalent Al without filling the third vacant octahedral position. In fact, the pointed mineral contains an atom of lower positive valence which is replaced with one of higher valence atom. This resulted in a deficit of positive charge (that is, excess negative charge), excess negative charge as compensated by the adsorption of cations. They are too large to be accommodated in the interior of the crystal. In the presence of water, the compensating cations on the layer surfaces may be easily exchanged by other cations, as expected by looking at the structures using crystal phases of clays and X- powder method.

METHODOLOGY

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 diphasic system containing both a liquid phase and solid phase whose

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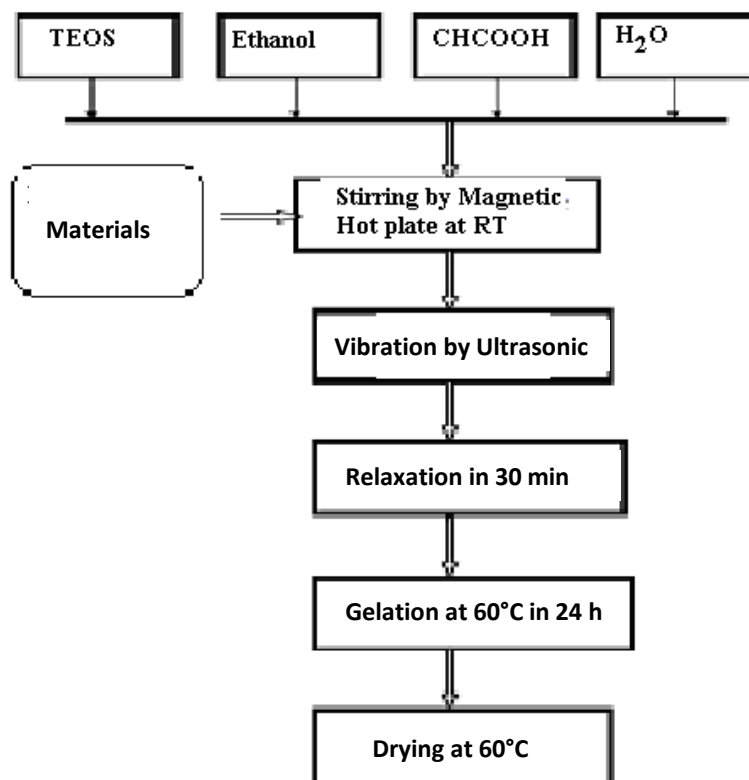


Figure 1. Flowchart of synthesis stainless steel nano- particles.

Table 1. The procedure of experiment in sol – gel method with H₂O₂, acetic chloride and sodium treatments.

Specimen	Composites and procedures	MMT d ₍₀₀₁₎ (nm)
MMT -0	Natural clay	6.65
MMT -1	MMT -0 with H ₂ O ₂	7.85
MMT -2	MMT -1 with acetic chloride	5.36
MMT -3	MMT -1 with Na	8

morphologies range from discrete particles to continuous networks. In this process, sodium clay powders are dissolved in de-ionized water to which is added citric acid. The mixture is then stirred carefully using a magnetic stirrer while ammonium hydroxide is added to obtain a pH of 7. Initially a zero gel and finally a powder are obtained. MMT powder is synthesized via simple sol – gel method as summarized in Figure 1.

RESULTS AND DISCUSSION

XRD technique is used for crystal phase identification and estimation of the crystallite size. XRD patterns are measured on a (GBC-MMA 007 (2000)) X-ray diffractometer. The diffractograms are recorded with 0.02° step size in which the speed is 10°/min radiations over a 2θ range of 10 to 80° at a sampling width of 0.2° and a scanning speed of 10°/ min. The XRD patterns of MMT are composed of calcined at different treatments.

The crystalline peaks corresponded to MMT in the form of either highly pure mixed MMT - quartz, except the as – prepared nanostructure showing amorphous phase. This point indicates that increase in MMT - quartz transformation of clay peak place with some materials is given in Table 1.

Crystallite size, lattice micro strain and lattice parameter of each nano clay powder have been calculated from the XRD peak broadening. Following Scherrer equation, the crystallite sizes have been determined for MMT and clays powders (Bertoluzza et al., 1982; Ramez and Occurrence, 1996; Bahari et al., 2008; Hernandez-Torres and Mendoza-Galvan, 2005).

$$\Gamma = \frac{K \lambda}{\beta \cos \theta}$$

Where Γ , K , λ , β and θ is mean crystallite dimension, X-

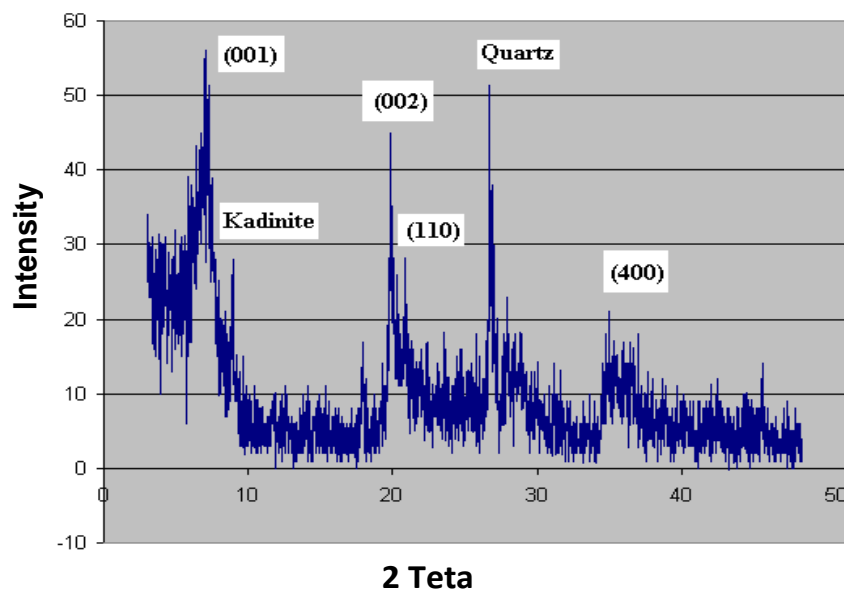


Figure 2. XRD pattern of nano clay before adding Na nano-particles corresponding to Table 1.

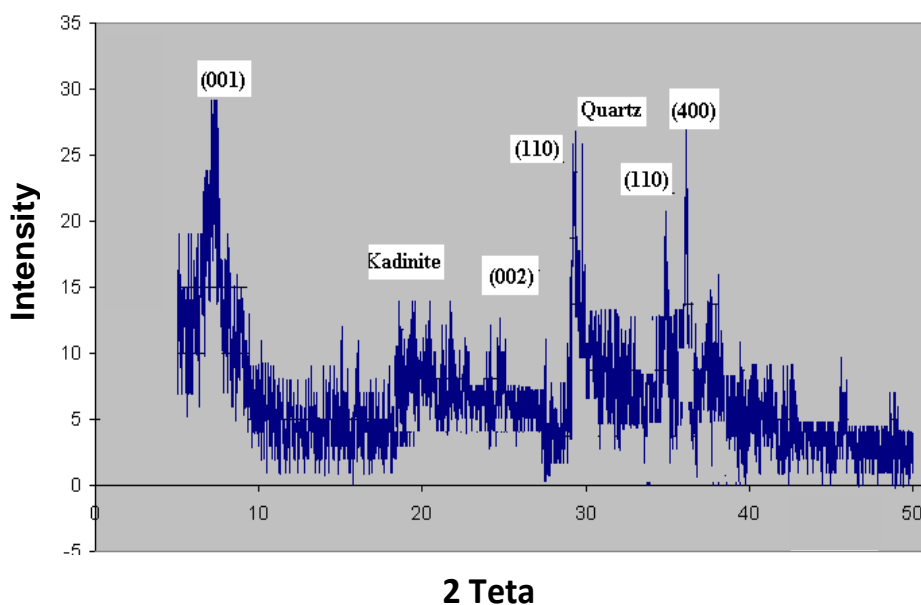


Figure 3. XRD pattern of nano clay after adding Na nano-particles corresponding to Table 1. The shifted peak around 20° Indicates the extend spacing between layer.

ray wavelength, FWHM (in radians) and Bragg angle, respectively.

Based on the diffraction peak of MMT in XRD patterns (Figures 2 to 5), 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 MMT (100); such peak interdistance is expressed by d_{100} .

Because the Scherrer relation cannot determine the accurate size of nano - particles, we have thus used X-powder method (Figures 6 to 9) and found the accurate crystalline size.

From the diffraction patterns in Figures 2 to 5, we can see that the peak, MMT (001) is shifted to a lower angle compared to the natural MMT (001) peak. This shifted peak indicates some expansion of the clay gallery with

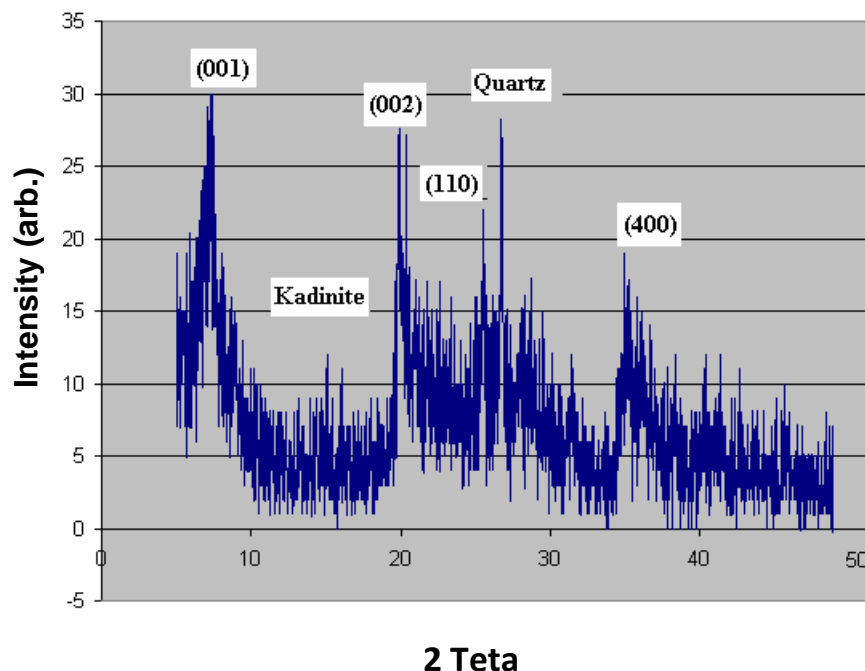


Figure 4. XRD pattern of nano clay which shows lower intensity of MMT (001) due to fifty – fifty Na nano-particles- acids in Table 1.

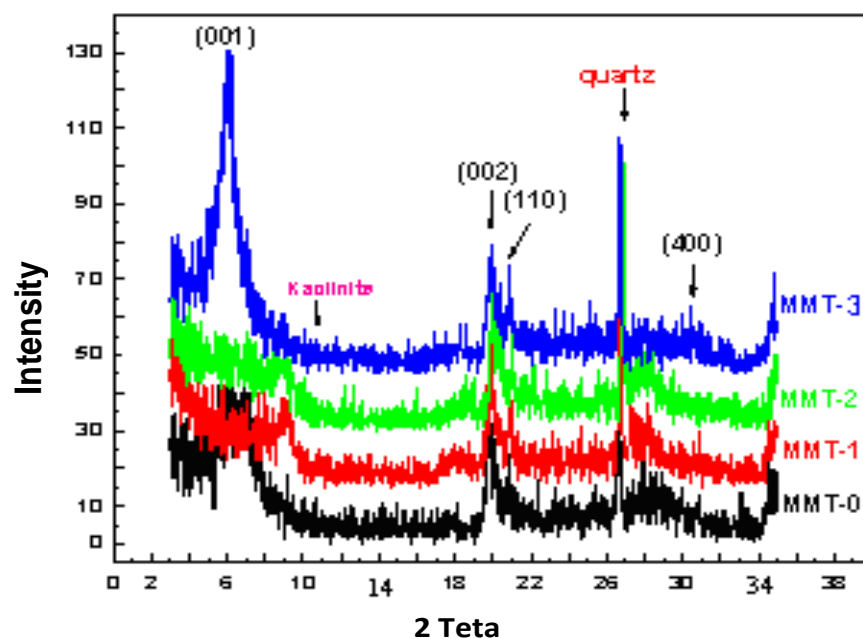


Figure 5. XRD pattern of nano clay corresponding to Table 1.

the diffusion of Na- nano- particles chains into the clay galleries. Comparing the diffraction patterns of the Figures 2 and 3, we see that the peak of sample prepared is shifted, which leads us to believe that the expansion at the clays is due to Na nano- particles. On the other hand, XRD patterns of extruded samples

(Figures 2, 4 and 5) prepared via Na cations show no significant shifting issues peaks, which may indicate fully exfoliated nanostructures. From this observation, we can conclude that the exfoliation of the layered silicate that resulted from Na - nano- particles is not caused by the foaming of the Na - Si bonds when exiting the extruder.

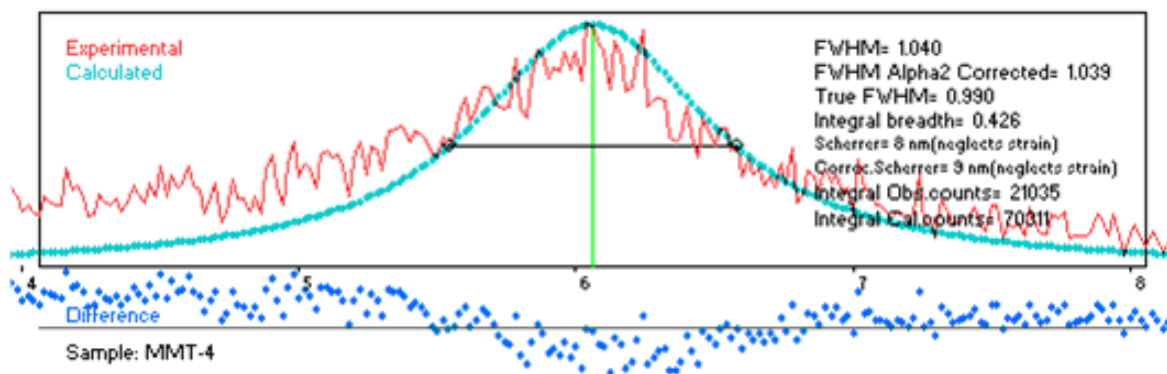


Figure 6. The size of nano - particle is 8 nm as determined with using X- powder method.

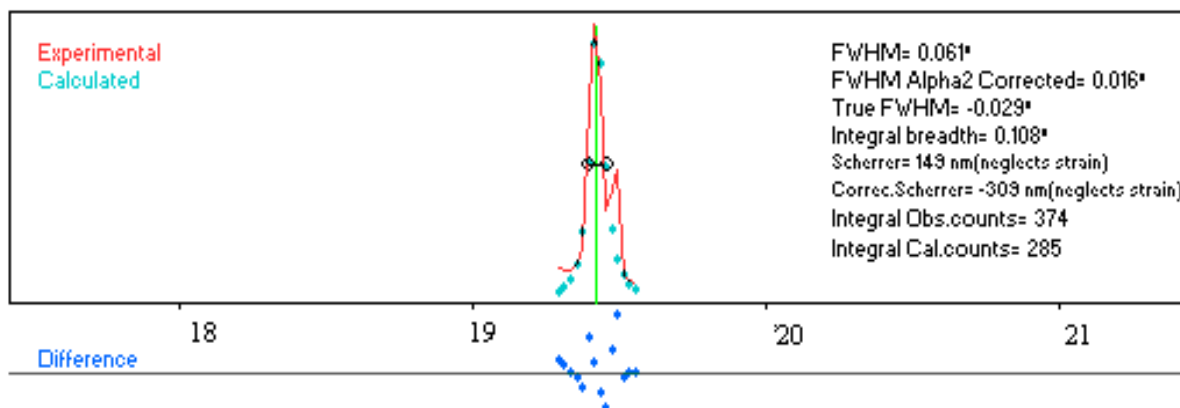


Figure 7. The size of nano- particle is 14.3 nm as determined with using X- powder method.

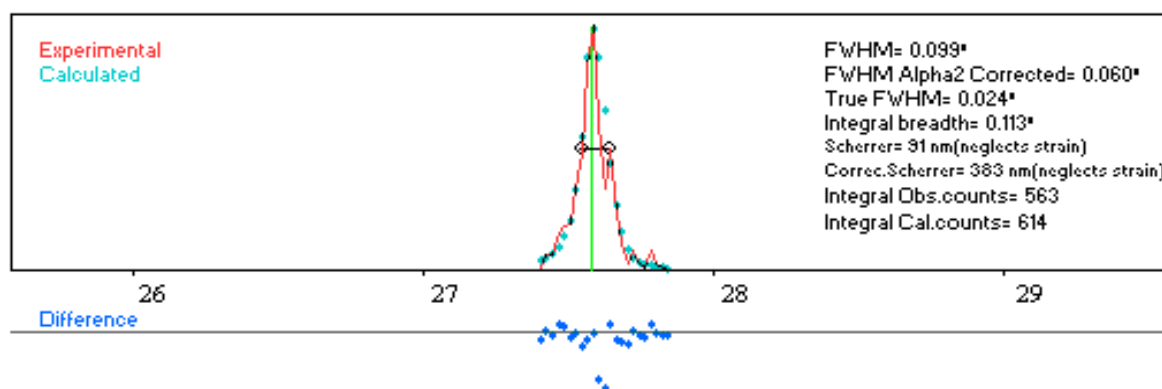


Figure 8. The size of nano- particle is 31 nm as determined with using X- powder method.

Due to the limitation of the current technique, that is, chamber design, we are not able to get exfoliated structure for clay concentration XRD pattern for the nano-composite as this concentration clearly indicates expansion of the d-spacing as given in Table 1.

The crystallite size estimated from the XRD analysis of the powder is close to 8 to 31 nm. The MMT (001) peak intensity in Figure 5 increased by adding Na content as shown with broaden peak. It can be observed that after adding Na nano-particles, kaolinite peak appeared which

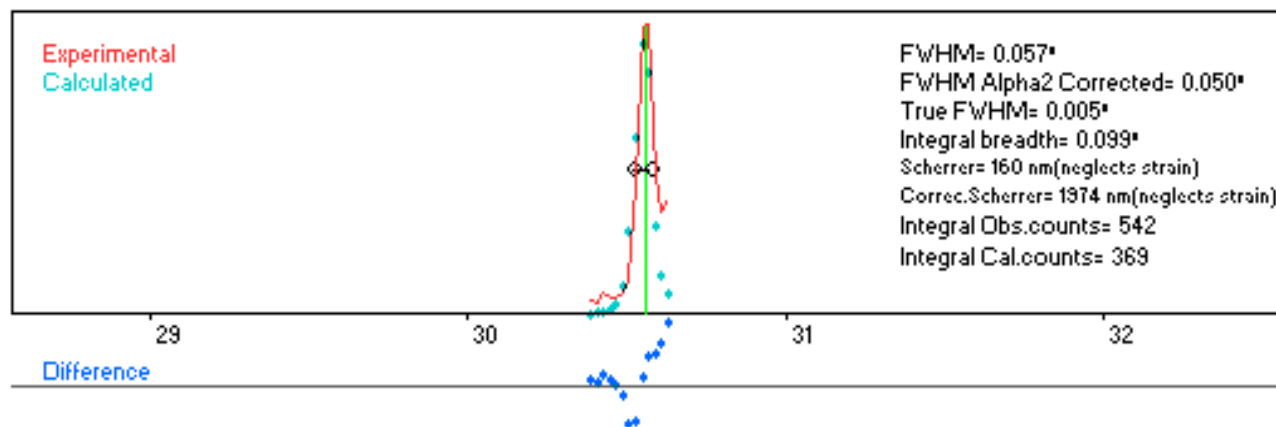


Figure 9. The size of nano- particle is 16 nm as determined with using X- powder method.

demonstrates the presence of the other crystal phase besides the other major crystal phases in the diffraction patterns and suggests only complete solubility. As shown in X - powder peaks (Figures 6 to 9), the significant broadening of the MMT 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. This suggests that major structural changes and dissolution of the clay elements were almost shifted, due to the entrance of Na atoms into the lattice of the clay which changes distortion structure to expanded structure in it.

The hump peaks MMT (001), MMT (004) and quartz originate due to nonreversible relaxation by partial chain movement and clay - sodium nano - particles interaction and also for polar – modified samples due to entire movement of MMT (004) peak in the clay layers. The sample is pillared which is proven by the change in d_{100} distance from 8 nm for MMT (001) to 31 nm for MMT (002). The rearranged structure is only partly accessible to Na atoms or molecules.

Indeed, network porosity may have a key role in the nano clustering size, because they are in the same time an efficient surface and interface for absorbing water and/or the other unwanted materials (hydrophobic materials), and also a suitable morphological unit for the nucleation of nano clay charges via trapping some cations to replace Mg^{2+} (Mani et al., 2005; Quang et al., 2007; Kuznetsov et al., 2010; Zhongzhong, 2008).

The difference in the miller index and the shifted crystal phase can be attributed to polarity of the structure, which causes difference in internal phase separation from clay layers. Based on the diffraction peak of MMT, the inter-layer distance change is increased as calculated with X-powder method as shown in Table 1. Nano- structural analysis of MMT reveals the different forms of MMT orientations. The characteristic peak for the MMT clay is that of the diffraction at MMT (100); such peak inter-distance is expressed by d_{100} .

Conclusion

The dispersion of the nanoclay- MMT particles is studied with XRD technique. An increased d-spacing value of the clay particles in the nanocomposites is observed with Nano-particles treatment.

The obtained results with XRD patterns indicate that number of intercalated layers in a single clay crystallite is increased to three nano- crystal phases of clays. Each phase can be used for two distinct areas of materials science: MMTs and ceramics due to their nano- structural properties.

REFERENCES

- Bahari A, Morgen P, Li ZS, Pederson K (2006). Growth of a Stacked Silicon Nitride/Silicon Oxide Dielectric on Si (100), *J. Vacuum Sci. Technol., B*, 24: 2119-2123.
- Bahari A, Morgen P, Li ZS (2008). Ultra thin silicon nitride films on Si (100) studied with core level photoemission, *Surface Sci.*, 602: 2315-2324.
- Bahari A, Pashayan M (2011). Nano structural properties of stainless steel for Ultra high vacuum chambers, *Chem. Tech.*, 3: 403-407.
- Bahari A, Robenhagen U, Morgen P (2005). Growth of Ultra thin Silicon Nitride on Si (111) at low temperatures, *physical Review B*, 72: 205323-205329.
- Bertoluzza A, Fagnano C, Morelli MA, Gotfardi V, Guglielmi M (1982). Raman and Infra-Red spectra on silica gel evolving towards glass, *J. Non Crystalline Solids*, 48: 1-17.
- Hernandez – JT, Mendoza – AG (2005). Formation of NiO – SiO₂ nano composite thin films by the sol – gel method, *J. Nan crystalline solids*, 351: 2029-2035.
- Kuznetsov DV, Lysov DV, Levina VV, Kondrat rva MN, Byzhonkov DI, Kaloshkin SD (2010). Structural special features in nano dispersed Ni – SiO₂ composite materials produces by method of chemical dispersion, *Inorg. Mater. Appl. Res.*, 1: 57-63.
- Mani GQ, Fan S, Ugbolee C, Yang Y (2005). Morphological Studies of Polypropylene–Nanoclay Composites, *J. Appl. Polymer Sci.*, 97: 218-226.
- Morgen P, Bahari A, Pederson K (2006). Functional properties of Nanostructured Material, Springer, 223: 29-257.
- Quang T, Nguyen T, Baird DG (2007). An improved technique for exfoliating and dispersing nanoclay particles into polymer matrices using supercritical carbon dioxide, *Polymer*, 48: 6923-6933.
- Ramez A, Occurrence M (1996). Mineralogy of a deposit of

- Shampoo-clay in southern Iran, *Appl. Clay Sci.*, 11: 43-45.
- Sánchez LC, Beltran JJ, Osorio J, Calle AM, Barrero CA (2009). Fe-doped SnO_2 nanopowders obtained by sol-gel and mechanochemical alloying with and without thermal treatment, *Phys. Astron.*, 185-189: 1-29.
- Zhongzhong Q (2008). Preparation and xharacterzation of MMT-sillica nanocomposite: A sol-gel approach modifying clay surface, *Physic B*, 403: 3231-3238.