Novel nano scale synthesis and electrical features of free fluoride HP mica clay for water remediation

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ABSTRACT

Mixed solid state/solution routes were applied to synthesize new family of free-fluoride synthetic clay for water remediation applications. The selected samples of synthetic free fluoride -Na-4-mica were having the general formula ($Na_4Mg_6M_4Si_4O_{22}.nH_2O$) where M=Al, Bi and Cr^{3+}. Structural and micro-structural properties were monitoring by using both of XRD and SEM evaluating, grain size of the mica bulk was found to be in between 2.37-3.43μm which are lower than those reported in literatures. Electrical investigation proved that clay I &II exhibited semi-conducting behavior while insulating behavior with clay III that confirm the energy gap ΔE_g is maximum for chromium clay.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

The "swelling micas". This group of synthetic clays, of which Na-4-mica is only one, were originally developed expressly for water treatment. They expand as they absorb metal ions, then collapse, sealing the metals inside. Na-4-mica is formed by combining kaolinite, a soft clay mineral used in the ceramics industry, with magnesium oxide in sodium fluoride at a temperature of 890°C. The resulting product has natural mica's sheet like structure and brittle composition, but the space between the layers[1-3].

Waste streams encountered in mining operations, and various chemical processing industries, contain heavy metals which are non-biodegradable, toxic priority pollutants. Due to their tendency to accumulate in living organisms, causing various diseases and disorders, the treatment methods for metal-bearing effluents are essential for environmental and human health protection. Among numerous commonly used techniques for water purification, adsorption technologies have gained the most attention because of their low cost and easy operation[4-18].

In recent years, an intensive research was conducted focusing on the selection and/or production of low-cost adsorbents with good metal-binding capacities, which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment-activated carbon. Natural materials of both organic and inorganic nature (such as chitosan, zeolites, minerals, etc) and

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certain waste products from industrial operations (such as fly ash, coal and oxides) are classified as low-cost adsorbents because they are economical and locally available[19-28] Na-4-mica has much the same composition as natural mica, containing aluminum, silicon, and magnesium. But natural mica also contains potassium ions, which sit in hexagonal holes in the mineral's layers, superimposed upon one another, bonding the sheets tightly together. This "closed" structure makes natural mica a poor ion exchange medium[1,2].

The major goal in the present article is to investigate the effect of solution route synthesis on; Structural and Nano-structural properties of $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ mica clay sample.Electrical properties of $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ mica clay sample.Application of free-fluoride environmentally friend mica clay for water remediation in the near future as new synthetic mica clay for cation selectivity of some toxic heavy metals.

EXPERIMENTAL

Samples preparation

The selected samples of synthetic free fluoride - Na-4-mica which having the general formula $(Na_4Mg_6M_4Si_4O_{22}.nH_2O)$ where M=Al, Bi and Cr^{3+} were synthesized by applying solution route and sintering procedure using the molar ratios of $Na_2O.2SiO_2.2H_2O$, $MgCO_3$, Al_2O_3,Bi_2O_3 and Cr_2O_3 each of highly pure chemical grade purity. The mixture were ground carefully then disolved in few drops of concentrated nitric acid forming nitrate extract which diluted by distill water. The nitrate solution was neutralized by using 45% urea solution and pH becomes~6.5.

Mixture I was for sodium silicates solution and mixture II was for rest of component (Al+Mg+Bi+Cr) nitrates according to chemical formula desired. Mixture I was diluted by distill water to be 100 ml then pH was adjusted to be 8.5 concentrated solution of ammonia was added carefully till heavy white precipitate from Metals hydroxide is obtained and the pH must be higher than 8. The precursor is filtered and washed by 2.5% ammonium nitrate solution.Mixture II of (Al+Mg+Bi+Cr) was passing through the same treatment but in present of ethylene glycol as complexing agent to produce gelatinous precipitate of metals cations hydroxide precursor.

The Mixture I+Mixture II precursors were forwarded to muffle furnace and calcinations process was performed at 880°C under a compressed air atmosphere for 15 hrs then reground and pressed into pellets (thickness 0.2cm and diameter 1.2cm) under 10 Ton/cm². Sintering was carried out under air stream at 1050°C for 10 hrs. The samples were slowly cooled down (20°C/hr) till 500°C and annealed there for 5 hrs under air stream. The furnace is shut off and cooled slowly down to room temperature.Finally the materials are kept in vacuum desiccator over silica gel dryer.

The sample were named as Clay I=($Na_4Mg_6Al_4Si_4O_{22}.nH_2O$),ClayII=($Na_4Mg_6Bi_4Si_4O_{22}.nH_2O$) and ClayIII=$Na_4Mg_6Cr_4Si_4O_{22}.nH_2O$.
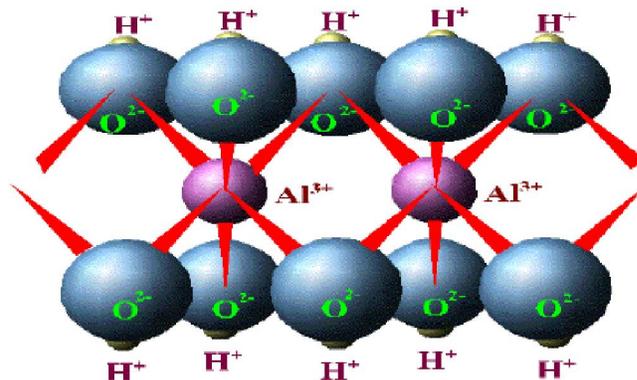
Figure 1 : Structure of Al-Silicates-Clay I

As described in Figure 1, tetrahedral units of silicate are the backbone structure of mica clay indicating that each unit cell surrounded by 4-Na-atoms that can be replaced if it is applied as cations exchanger.

Phase identification

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using Cu-K$_\alpha$ radiation source,Ni-filter and a computerized STOE diffractometer/Germany with two theta step scan technique.

Scannig Electron Microscopy (SEM) measurements were carried out at different sectors in the prepared samples by using a computerized SEM camera with elemental analyzer unit (PHILIPS-XL 30 ESEM/ USA).

Electrical measurements

DC-electrical conductivity of the prepared materi-

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als was undertaken as a function of temperature from room temperature till 520°C and performed on the pellet surface by using two probe circuit and garaphite paste was used as connective matter.

RESULTS AND DISCUSSION

Phase identification

Figure (2a-c), displays the X-ray powder diffraction pattern recorded for synthetic free fluoride -Na-4-mica samples which are having the general formula ($Na_4Mg_6M_4Si_4O_{22}.nH_2O$) where M=Al, Bi and Cr^{3+} respectively. The analysis of the corresponding 2θ values and the interplanar spacings d (A°) were carried out using computerized program and indicated that, the X-ray crystalline structure mainly belongs to a monoclinic phase $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ in major besides few peaks of unreacted starting oxides as secondary phase in minor. The lattice parameters of the unit cell were refined using the least-squares sub-routine of a standard computer program these refined lattice parameters were found typically to those reported in[19-23] literatures. These unit cell parameters are in good agreement with those of the reported ones for $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ structure[6].

It is obviously that, the additions of nono-oxides components have a negligible effect on the main crystalline structure $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ with Fluoride-content (x=0.0) as shown in Figure (2c).

From Figure (2a,b), one can indicate that monoclinic phase of mica-clay $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ is the dominating phase by ratio exceeds than 90% (d_{100}=1.12-1.13nm) confirming that nano-oxides component are successfully reacted and formed monoclinic biotite phase with very good degree of crystallinity.

TABLE 1, explain EDX-elemental analysis data recorded for $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ that prepared via

Figure 2a-c : X-ray diffraction patterns recorded for; (a) Al-clay, (b) Bi-I, clayII and (c) Chromium clay (Clay III)

solution route. It is clear that the atomic percentage recorded is approximately typical with the molar ratios of the prepared sample emphasizing the quality of preparation through solution technique.

On the basis of molar ratio the allowed error in experimental procedures through out solution rout is lesser than those reported in literatures for those synthesized by solid state routes[1,28].

SE-microscopy measurements

Figure (3a-c), show the SEM-micrographs recorded $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ that prepared via so-

TABLE 1 : EDX-Elemental analysis data recorded for Al-clay-I

	Al-Clay-I					
Element	Wt %	At %	K-Ratio	Z	A	F
O K	35.88	56.25	0.1069	1.7394	0.1431	1.0004
NaK	15.29	30.13	0.0479	1.1333	0.7253	1.0131
MgK	18.26	15.48	0.2931	1.0746	0.9907	1.0213
Al L	18.96	14.65	0.0513	0.5181	1.0418	1.1198
Si L	19.68	14.23	0.2364	0.2175	1.0101	1.0212

TABLE 2 : EDX-Elemental analysis data recorded for Bi-clay-II

	Bi-Clay-II					
Element	Wt %	At %	K-Ratio	Z	A	F
O K	39.68	53.35	0.2269	1.7394	0.1431	1.1114
NaK	16.29	33.13	0.0499	1.1333	0.7253	1.0136
MgK	18.26	14.48	0.2931	1.0746	0.9907	1.0345
Bi L	17.36	13.65	0.0613	0.5181	1.0418	1.2298
Si L	18.68	14.23	0.1364	0.2175	1.0101	1.0312

TABLE 3 : EDX-Elemental analysis data recorded for Cr-clay-III

	Cr-Clay-III					
Element	Wt %	At %	K-Ratio	Z	A	F
O K	37.81	57.25	0.1069	1.7334	0.1481	1.0804
NaK	18.21	35.13	0.0479	1.1733	0.7353	1.0131
MgK	12.22	16.48	0.2731	1.0746	0.9607	1.0813
Cr L	16.66	16.65	0.0513	0.5181	1.0718	1.1498
Si L	18.98	16.23	0.2364	0.2175	1.0501	1.1212

lution route where M=Al^{+++}, Bi^{+++} and Cr^{+++}. The estimated average of grain size was calculated and found in between 2.37- 3.43μm supporting the data reported in[23].
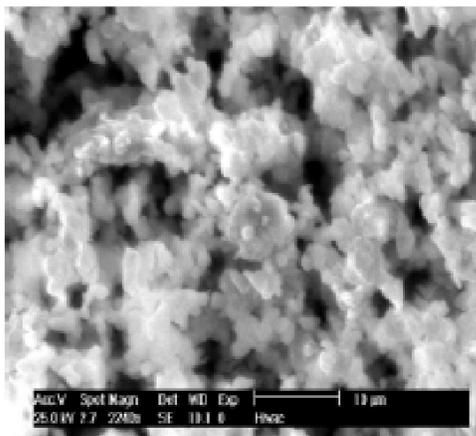
(a) Al-clay-I
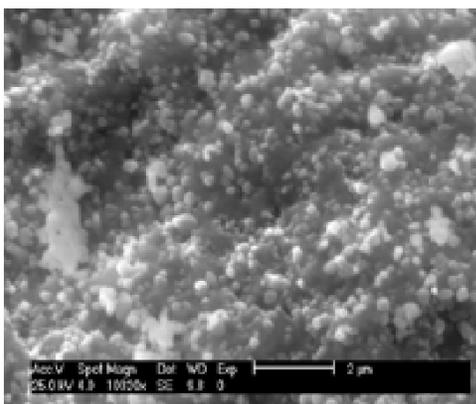
(b) Bi-clay-II
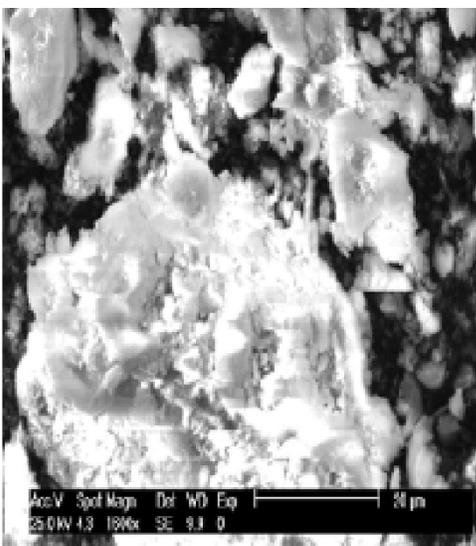
(c) Cr-clay-III

Figure 3a-c : SE-micrographs recorded for with different magnification factors; (a) Al-clay-I, (b) Bi-clay-II and (c) Cr-clay-III

The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ that prepared via solution route, such that the differences in the molar ratios EDX estimated for the same sample is emphasized and an evidence for the existence of mono-clinic-phase with good approximation to molar ratios see (TABLE 1-3).

From figure (2a-c), it is so difficult to observe inhomogeneitiy within the micrograph due to that the powders used are very fine and the particle size estimated is too small.

This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Furthermore, particle size wa estimated from both of XRD and SEM analyses and its average found to be in between 25-124nm confiming that solution route synthesis increases the fraction ratio of nano-particles formation.

Electrical properties

Figure 4, exhibits DC-electrical conductivity of the prepared mica-material $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ was undertaken as a function of temperature from room temperature till 520°C and performed on the pellet surface by using two probe circuit and garaphite paste was used as connective matter.

It is clear that the conduction increases as temperatures raise reflecting semiconductor behavior of both Al-clay I and Bi-clay II samples, while insulating behavior for Cr-clay III sample.

Although most of mineral silicates-structure clay reported as semiconductors as in literatures[22-25] Cr^{+++}-clay III violate and recorded an insulating behavior through the investigated range of temperature reflecting the bigger of enery gap for Cr-clay III.

Transport properties of the materials obeying Arrhenius equation $\sigma_{ac}=\sigma_0 exp (-E_a/K_BT)$, where the symbols have their usual meanings. It is observed that the conductivity of the material increases with rise in temperature, and shows the negative temperature co-efficient of resistance behavior for both of clay I and clay II. The calculated values of activation energies of the clay compounds are found to be 0.34, 0.41 and 1.31eV for clay I, clay II and clay III respectively.

This behavior suggests that the conduction mecha-

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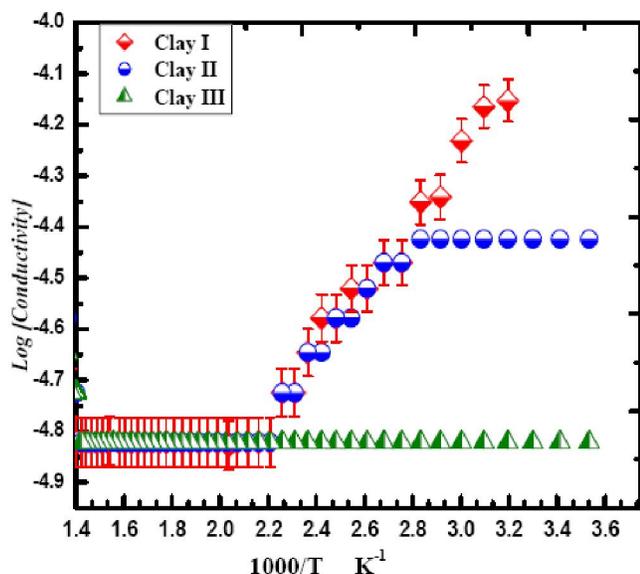
Figure 4 : DC-electrical conductivity as a function of absolute temperature recorded for clay I, clay II and clay III
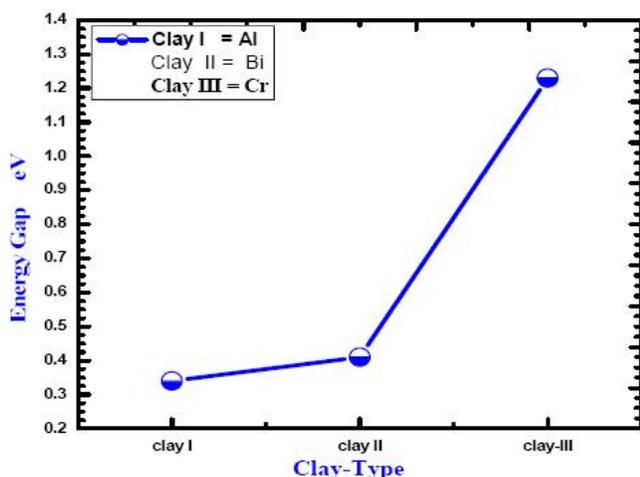
Figure 5 : Variatin of enery gap (Eg) as function of clay-type

nism of the compound may be due to the hopping of charge carrier that enhanced by cations holes and the energy gabs between conduction and valence band increase from clay I to clay III see Figure 5.

From Figure 4, it is clear that Bi-clay-II exhibits semiconducting behavior until 410°C and loss its semiconducting behavior after this temperature due to increasing of its energy gap giving an insulating behavior as shown in Figure 4.

COCLUSIONS

The conclusive remarkes inside this article can be summarized in the following points; Solution technique exhibits structure quality as preparation technique.

Synthetic free-fluoride $Na_4Mg_6M_4Si_4O_{22}.nH_2O$ crystallize in monoclinic phase.

SE-micrographs confirmed that particles size was found in nano-scale (25-135nm) Clay-III ($Na_4Mg_6M_4Si_4O_{22}.nH_2O$ where $M=Cr^{+++}$) has the highest Eg=1.31eV.

HP-synthetic micas can applied as cations selectivity for water remediation.

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