MORPHYLOGICAL STUDY OF $KNBO_3$ SINGLE CRYSTALS

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Abstract: It is clear from the earlier efforts to grow $KNbO_3$ single crystals that the flux method of growing single crystals of $KNbO_3$ could be attractive under the condition of appropriate solvent ,composition of molten solution. Scanning electron micrograph of the sample was recorded at different magnification of different regions. One of the micrograph of the sample from the Fig. III.3 to III.8.Form the SEM of sample synthesized at 400˚C it is observed that the grain size of the sample is in the range 1.2 to 2.5µm.

Key Words: **- ferroelectric material, single crystals, perovskite ,orthorhombic. Piezoelectric.**

I. INTRODUCTION

Potassium niobate $KNbO_3$ is an important ferroelectric material with the perovskite structure. Similar to the more extensively studied isomorphous analog, $BaTiO_3$, it shows the same sequence of structural phase transformations on cooling from high temperature with the crystallographic symmetry being reduced from cubic - tetragonal -orthorhombic - rhombohedral. The mechanisms for the phase transformations (i.e., their displacive or order-disorder character) are still under discussion. Unlike tetragonal $BaTiO_3$, $KNbO_3$ is orthorhombic at room temperature, with space group and the crystallographic lattice parameters a=5.695 Å, b=3.973 Å, and c=5.721 Å. The spontaneous polarization vector is parallel to the c axis (i.e., parallel to the [110] direction of the prototypic high-temperature cubic state).

These materials have successful applications of piezoelectric, ferroelectric and electro- optic ceramics is highly dependent on relative case with which materials can be useful and reliable devices .The reason behind these materials have been so successful over the years in finding increasing number of application is their simplicity, small size, low cost and higher reliability to the design engineering.

Ferroelectrics have been used for piezoelectric and pyroelectric applications, miniature capacitors, memory devices, circuit elements, electro-optic applications, and for acousto-optics and opto-electronics. A good account of these applications has been given by Lines and Glass [1] and by Burfoot and Taylor [2].

Ferroelectric materials are used in the form of ceramics, single crystals or thin films. Recent development in the ceramics field is the formation and used for multilayer ceramic capacitors have been modified $BaTiO_3$. Relaxor material that have high dielectric constant and low temperature variation near the Curie point have been developed [3], as for example $[Pb(Mg_{1/3}Nb_{2/3}]_{0.93}[PbTiO_3]_{0.07}$.This has vastly improved the dielectric , electro –optic and piezoelectric properties of the ceramics.

The composites are mainly used as acoustic transducers. A variety of techniques have been devised to fabricate them. The ceramic rod are aligned in a fixer and the polymer is cast around them ,or the polymer is poured into deep grooves cut in to a ceramic block , or alternate layers of polymers, and ceramic are glued together. In a cast wox method, a ceramic are injected in to a performed mould. When the spatial scale of the composite finer than all relevant a caustics wavelength, the properties of the individual component are accurately subsumed into a new set of material parameters for the composite material. These material properties can be tailored by choosing the composite materials, their relative proportions, and the spatial scale of the composite structure. Important properties like electromechanical coupling, specific acoustic impedance, hydrostatic response, dielectric permittivity and sound speed can be readily adjusted. The spacing between ceramic rods can be adjusted in to suppressed waves running perpendicular to the rods .This help decoupled parasitic radial resonance from the thickness resonance in the pulse echo transducers. It also reduces acoustic cross –talk in monolithic arrays , and suppressed flow- noise in hydrophones , Also a given physical property can be optimized in the designed in particular application [4]. Use of piezoelectricity active polymers like PVDF (Polivinylidene Fluoride), ceramic - copolymer, composites, and gel formed piezoelectric represent significant effort in the development of composite flexible polymer composites[5] using PVDF and PZT have been developed for use in transducer, memory, and display applications.

Thin films are produced by evaporation, sputtering, chemical vapour deposition, and laser deposition techniques. Recently, solution-gelation processing[6] have been developed for integration of ferroelectrics thin film layer of variety of substrate materials. A successful integration of ferroelectric memory capacitor with both the GaAs and silicon semiconductor technologies has been achieved for realization of high densities non volatile random access memories [7]. In the ferroelectric memories technology, PZT is often the material use. Efforts to develop nondestructive Read out by using different type of materials have shown that $BaMgF_4$ hold a promise .these films are prepared under high vaccum conditions.

Single crystal fibers hold promise for a variety on nonlinear electro-optic and laser device applications, where enhance optical light guiding is required. A miniature float zone process using a laser heat source has been found very useful for preparing single crystal fibers.

Disorder ferroelectrics are finding greater use on account of their electrostrictive properties. The advantages of these devices in contrast to piezoelectric ones are the absence of electro-mechanical hysteresis, high level of temporal stability and technological simplification. Hence these materials are increasing being used for precise micromanipulators, force actuators, adaptive mirrors [8], etc.

Another interesting development is that of smart ferroelectrics that have both sensors and actuator capacities [9]. These materials can be used for heavy machinery vibration control or for acoustic absorption in hydrostatic pressure situations.

Presently, magneto-optics thin film devices are used for optical information store and processing .Ferroelectric PZT and PLZT thin films have been shown this type of capability. Their erasable / rewritable optical memories have fast switching and potentially long life times [10].

Lu Zheng [11]has observed Localized reversal of patterns formed by ferroelectric domains on the naturally grown surface in an iron-doped potassium niobate (Fe: $KNbO_3$) single crystal and discussed the mechanism of forming this domain structure.

Adachi M.[12] Potassium niobate (KN) single crystals were successfully grown from a melt with potassium enriched composition 51.2 mole % K_2CO_3 using the TSSG technique. Colorless and crack-free crystals up to 27 × 27 × 10 mm 3 in size are reproducibly grown using a platinum crucible of 50 mm in diameter and 50 mm in height. The crystal was allowed to grow laterally from around 30 h to obtain the cross section desired. The growing crystal was then lifted up above the melt surface or lifted intermittently at the rate of about 0.5 mm/h, while the melt was cooled. Cracking occurred at the phase transition temperatures of 435 and 225˚C. Slow cooling fairly eliminated the cracking at the both phase transition points.

Baier-Saip J.A. et.al.[13]the influence of grain size on the phase transitions of ferroelectric $KNbO_3$ was studied by micro Raman spectroscopy. It was found that the three transitions observed are not sharp for small particles (w50 mm). The transition temperatures depend on the size and all particles show hysteresis. From these experiments he obtained some evidence that in small particles monodomains of the rhombohedral and orthorhombic phases coexist in a range of temperatures.

Makovec Darko et.al.[14]studied sintering of $KNbO_3$ ceramics was achieved by using small additions of TiO_2. This improved densification can be explained on the basis of high-temperature chemical reactions in the system. X-ray diffractometry and electron microscopy were used in combination with diffusion-couple experiments in order to elucidate the chemical reactions between $KNbO_3$ and TiO_2. TiO_2 reacts with $KNbO_3$ forming $KNbTiO_5$, and a low concentration of Ti incorporates in the $KNbO_3$ structure resulting in the formation of oxygen vacancies and, consequently, in an improvement in the densification. At 1037 °C eutectic melting between the $KNbO_3$ and the $KNbTiO_5$ further improves the densification of the $KNbO_3$ ceramics.

Wada Satoshi [15] the engineered domain configuration was induced into potassium niobate ($KNbO_3$) crystals, and the piezoelectric properties were investigated as a function of domain size. First, single-domain treatment was investigated. Finally, the engineered domain configurations were induced into $KNbO_3$ crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these $KNbO_3$ crystals with the engineered domain configurations showed much higher values than those of the single-domain crystal. Moreover, the piezoelectric properties increased with decreasing the domain sizes of the engineered domain configuration.

Evans D. R.[16]studied optical and electrical measurements have been made on a new codoped potassium niobate crystal ($KNbO_3$: Fe, Ag) that yields a significant enhancement of the photorefractive and photovoltaic effects when compared with the published results for singly doped potassium niobate crystals. The codoped Ag impurity enters the K site, rather than the typical Nb site, thus changing the local field in the lattice. An enhanced trap density is likely the cause of the increased photorefractive counter propagating two-beam coupling efficiency.

Hirohashi Junji[17] studied a new electric poling concept called the `embryonic nucleation method' to $KNbO_3$, 1-mm-thick uniform periodically poled $KNbO_3$ (PPKN) with domain inverted period of 35.5 μm and an interaction length of 10 mm has been successfully fabricated by applying only 300 V/mm without the generation of unwanted domains. SHG using PPKN fabricated by this method was demonstrated and 100 mw second-harmonic laser generations at a wavelength of 532 nm was obtained from 1 W pumping without photorefractive damage at approximately 40˚C.

Hirohashi Junji [18]studied the controllability of specific domain structures in $KNbO_3$ single crystals was investigated by electric poling to several different orientations at room temperature. By applying electric field to the direction corresponding to the differential direction between the original and intended spontaneous polarization directions (differential vector poling method), 60˚-, 90˚-, and 180˚-domain pairs were successfully fabricated under control in $KNbO_3$.

Wada Satoshi et.al.[19] studied the engineered domain configurations were induced into $KNbO_3$ crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these $KNbO_3$ crystals with the engineered domain configurations showed much higher values than those of the single-domain crystal. Moreover, the piezoelectric properties increased with decreasing the domain sizes of the engineered domain configuration.

II. EXPERIMENTAL DETAILS

The lack of information on the domain structures in $KNbO_3$ is probably because of the difficulty in growing good single crystals that are not highly twinned. Moreover, the crystals with plate like habit, suitable for the domain studies are not easily obtained. We have grown these single crystals, following the method of Wood (1951) with some modifications K_2CO_3 and Nb_2O_5 were taken in the molar composition 1.2:1 and the dry materials were grounded together in a mortar and packed into a 50 cc. flat bottomed platinum crucible. The crucible with its charge was introduced in the furnace.

Another method, potassium carbonate and niobium pentaoxide were used in mortar composition 1.2:1.0. Another grade niobium pentaoxide has been used. Potassium carbonate was dried at 300˚C for two hours before its use. This particular composition was selected following Reisman et.al., and Miller can indeed be expected to give good results for the reason that it is always desirable to effect nucleation from the melt, as rich in $KNbO_3$ as possible.

Another method, by taking dopant in required mixture is as follows by S. G. Ingle [20]. The dopant Al_2O_3 was added to the mixture of K_2CO_3 and Nb_2O_5.

The materials were mixed thoroughly by growing them together in the mortar for a sufficiently long time (4 to 5 hrs) and mixture packed in a 50 ml flat bottom platinum crucible. The crucible with its charge was covered with a lid and introduced in a furnace up to 1100˚C. The soaked period was 24 hrs. The socked time was expected to set the on this temperature melt in an equilibrium state. The temperature of the crucible was measured by platinum - platinum rhodium thermocouple. The platinum crucible was adjusted in an inclined position.

After soaking the mixture cooled slowly at the rate of 14-17˚C per hour up to 840˚C. Then the crucible is reheated up to 1000˚C and kept there for 18 hrs. A sufficiently nucleation and growth must have occurred during this interval. The eutectic temperature is reached at 840˚C and if the cooling would have continued up to 840˚C, complete crystallization of $KNbO_3$ would have taken place. It is known however, that the crystals so obtained are small. This is not surprising, as, when the nucleation takes place simultaneously at various places in the liquid the small crystallites grow independently of each other. Since they start with no knowledge of each other. They have different orientations, and when they meet, they may not join to form a big single crystal. It is necessary for the growth of a large single crystal that stray nucleation should be reduced to a minimum. Deshmukh and Ingle hence thought of an alternative procedure which results in large crystals[21].

In the method followed, the cooling is stop at 840˚C. The crucible is reheated to a temperature just below 1000˚C, and kept at the temperature for yet another soaking period of 18 hours. The reheating is expected to re-dissolve the number of small crystals that might be nucleated initially as a result of stray nucleation. The crystallites might have been nucleation. The crystallites might have been nucleated at different times in the cooling process, and as the cooling approached 840˚C, numbers of crystallites of different sizes must have been present. In the reheating process, the smaller crystallites dissolve rapidly, while the larger crystallites are also attached and get reduced in size gradually. At a temperature just below 1000˚C, the liquid us temperature for the composition used, the charge in the crucible is expected to be in a completely molten state, expect for a very few crystallites that remain scattered in liquid.

An equilibrium is reached between them are the rest of the melt during a soaking period of 18 hrs. When cooling is now started slowly at the rate of 30-35 hrs till the room temperature was reached, the small crystallites serve as seeds are favoured, as the growth of the crystal is dendritic and quite rapid. The chances of stray nucleation are consequently considerably reduced, and the large single crystals are observed. The crystal blocks separated from flux was found covered at the top by a thick crystalline layer projecting from the walls of the crucible. (i.e.CO_2 is evaporated from the mixture). A thin layer of small crystals was also found to be growing out of the thick layer. Crystal plates could also be obtained on the bed of flux.

Inclined position of the crucible is found to be helpful to the crystal, as the diffusion rates are higher at the walls than in liquid, and therefore conditions at the walls are more favorable to the growth of crystals.

The crystal plates found on the bed of the flux are mostly white. Some of them are colorless. The size of the colourless plates range from 2 mm to 50 mm on edge length. The thickness is about 0.4mm. These crystals plates usually show quite simple twinning, and are very good for dielectric as well as domain studies. The white crystal plates are larger in area and smaller in thickness (of the order of 0.1mm.), very fragile and highly twinned usually showing curvature. The large single crystals are in the form of transparent greenish colour. The crystal can be cleared very easily into very thin crystal flakes that appear nearly colourless and their conductivity is quite low of the order of 10^{-9}(Ohm-cm)$^{-1}$.

The rate of cooling is an important parameter in any crystals growth. In general, the crystals growth at low rate of cooling are expected to be more perfect with less strains, since random thermal gradient effects are non considerably reduced. At the low cooling rates, the impurities get time to adjust themselves more favorably in the crystal structure, and the strains in such crystals are correspondingly less. In addition to all these arguments in favoured of the lower cooling rates, one has to balance the thickness of the crystal grown with the attendant cost problem and more importantly the mechanism of crystal growth. The changed rates of cooling can produced drastic changes in the crystal growth. The mechanism of the growth may change, and the twinning habit and the crystal growth habits may also change. Indeed, the whole crystal texture changes by changing a single simple looking parameter, namely the cooling rate. Therefore, in the present investigation the main emphasis was on the study of the changes produced in the crystal textures a result of the changes in the cooling rate. The cooling rates of the order of 60˚/hour were used by Ingle, when he developed the technique which has been the basis for the present work. He had found that crystal surfaces, particularly the small crystals found on the flux bed show dendritic mechanism of growth. It could not be ascertained then if the whole crystal had grown following the same mechanism. Therefore, it was one of the objects of the present investigation to verify this point also.

We, therefore, changed the rates of cooling from 60˚/hr to the various lower values, coming down to as low as 10˚/hrs. The main finding of these experiments is that below 35˚/hr the dendritic growth is generally completely suppressed. There is no sharp transition from dendritic growth to the layer growth as the cooling rates are reduced. The layer growth is found to be caused both by natural kinetics factors and the defects factors. The various facets of the layer growth have been studies[22]extensively.

We have carried out experiments to see the effect of dopants on the crystals growth mechanism and the crystal textures. Aluminum ions produced by using the known amount of Al_2O_3 produced some interesting effects on the domain structures. No change was observed on the mechanism of the crystal growth[23].

III. FINDINGS AND CONCLUSIONS

SCANNING ELECTRON MICROSCOPE (SEM)

When an electron beam strikes the sample, various phenomena occur. Interaction of electron beam with sample is shown in Fig. III.1. The Scanning Electron Microscope (SEM) is a microscope that uses electrons (backscattered or secondary) rather than light to form an image. There are many advantages to using the SEM instead of a light microscope.

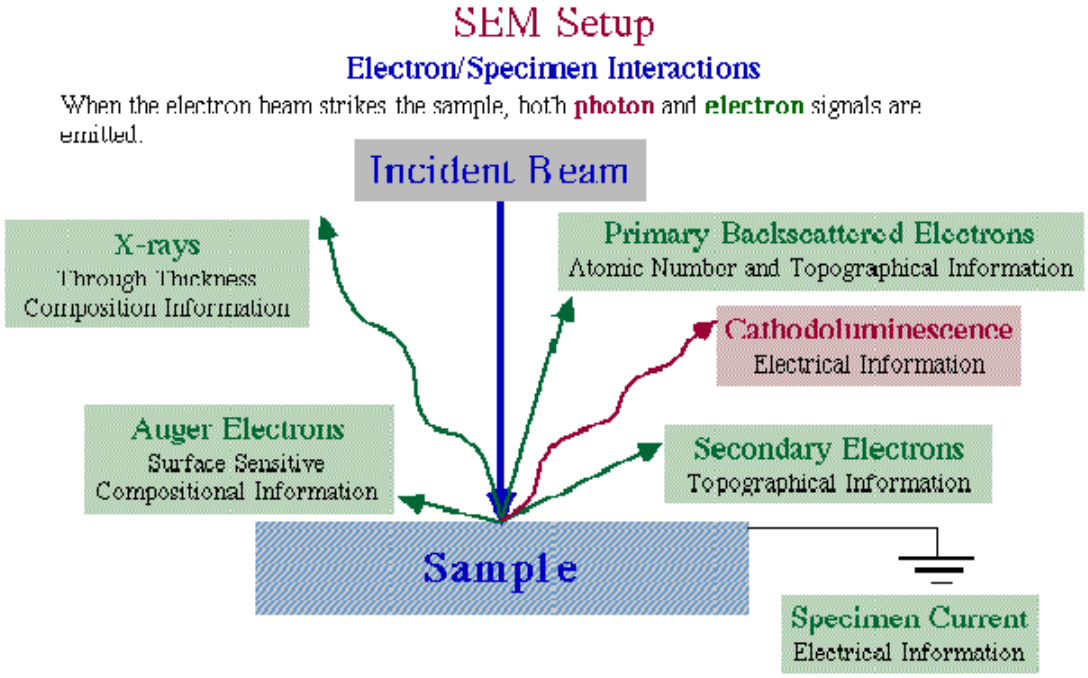

Fig. III.1: Interaction of electron beam with material.

The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. As in any microscope the main objective is for magnification and focus for clarity. An optical microscope uses lenses to bend the light waves and the lenses are adjusted for focus. In the SEM, electromagnets are used to bend an electron beam which is used to produce the image on a screen. By using electromagnets an observer can have more control in how much magnification he/she obtains. The electron beam also provides greater clarity in the image produced.

The SEM is designed for direct studying of the surfaces of solid objects. By scanning with an electron beam that has been generated and focused by the operation of the microscope, an image is formed in much the same way as a TV. The SEM allows a greater depth of focus than the optical microscope. For this reason the SEM can produce an image that is a good representation of the three-dimensional sample.

The sputter coater is used to coat non-metallic samples (bugs, plants, human hair, etc.) with a thin layer of gold. This makes them conductive, and ready to be viewed by the SEM. If the samples are metallic, they can simply be mounted and placed in the SEM. Photograph of scanning electron microscope (SEM) is shown in Fig. III.2 and the specimen of SEM of $KNbO_3$ samples are shown in Figs. III.3 to III.8.

Figure III.2 X-ray diffraction of $KNbO_3$ sample**.**

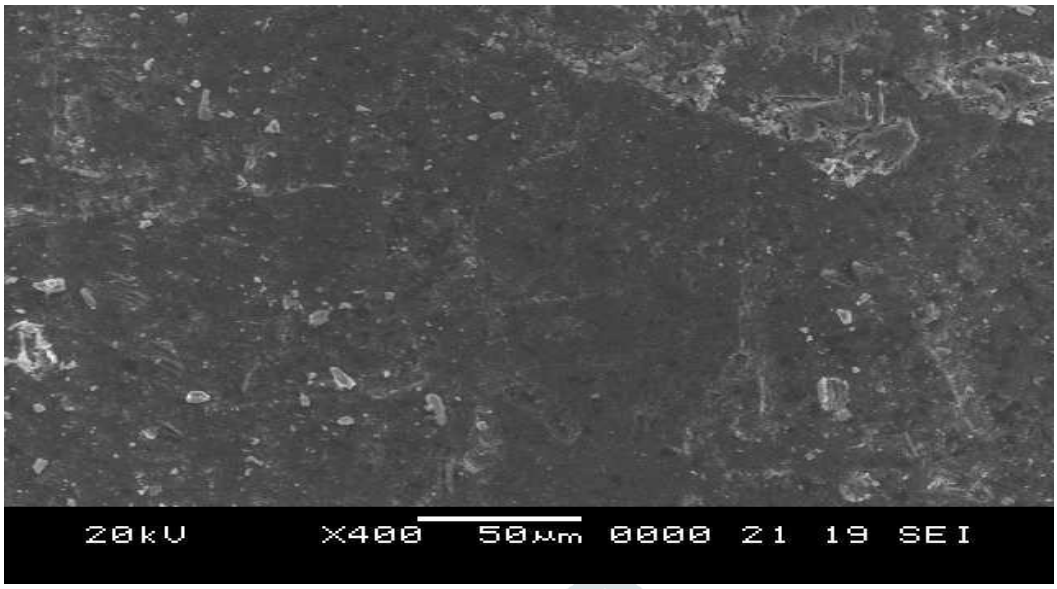

Fig. III.3

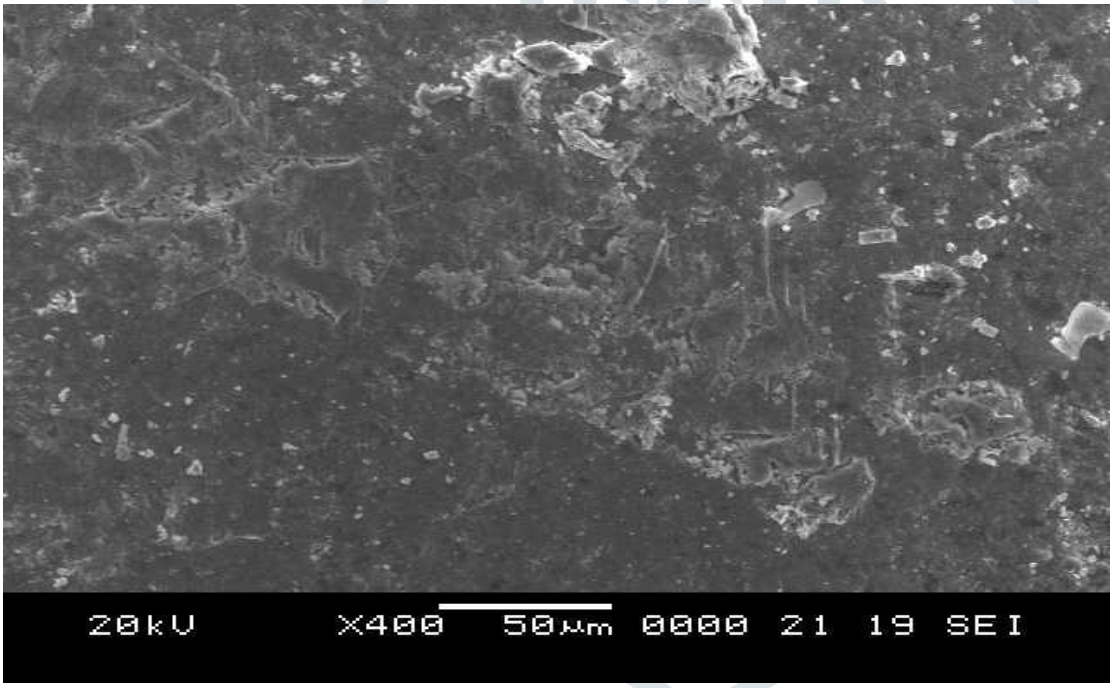

Fig. III.4

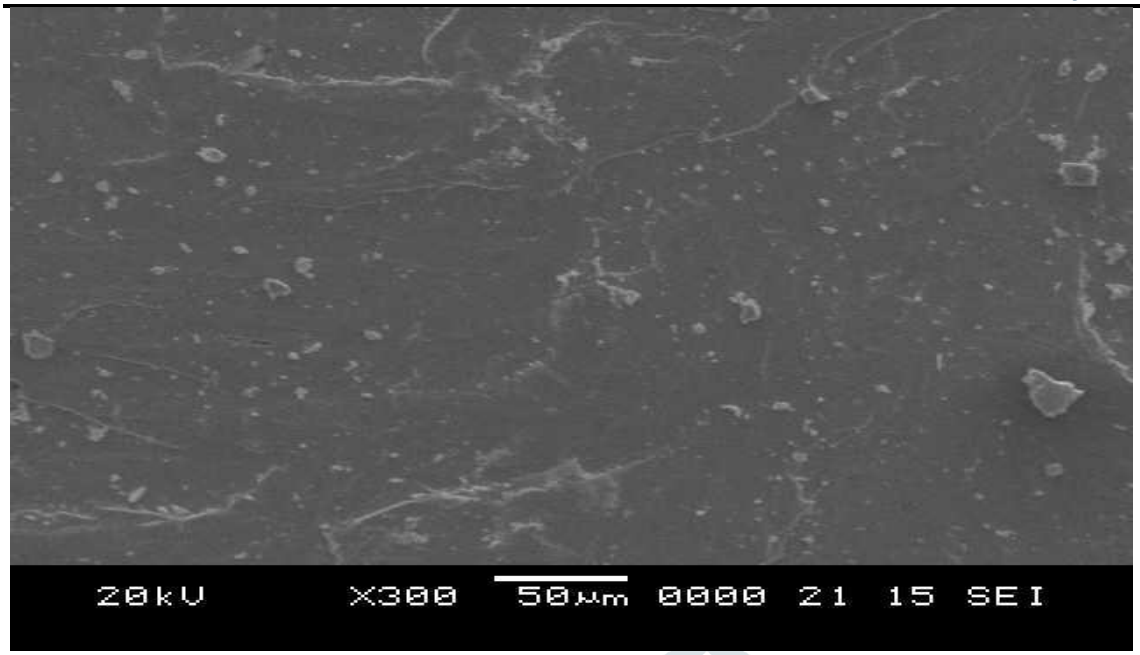

Fig. III.5

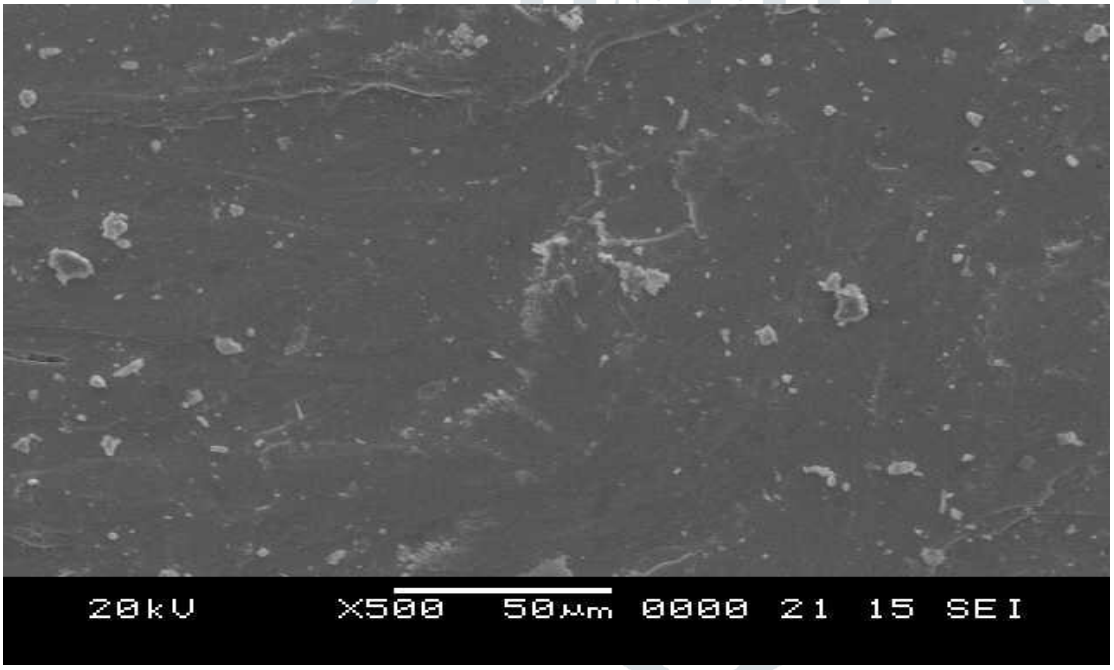

Fig. III.6

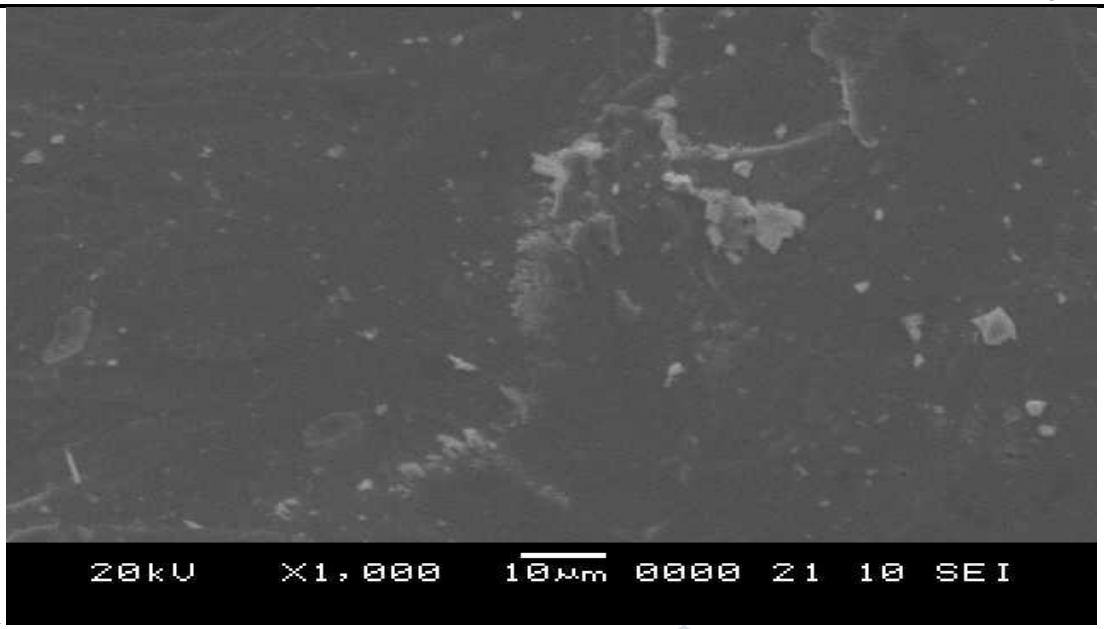

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Fig. III.7

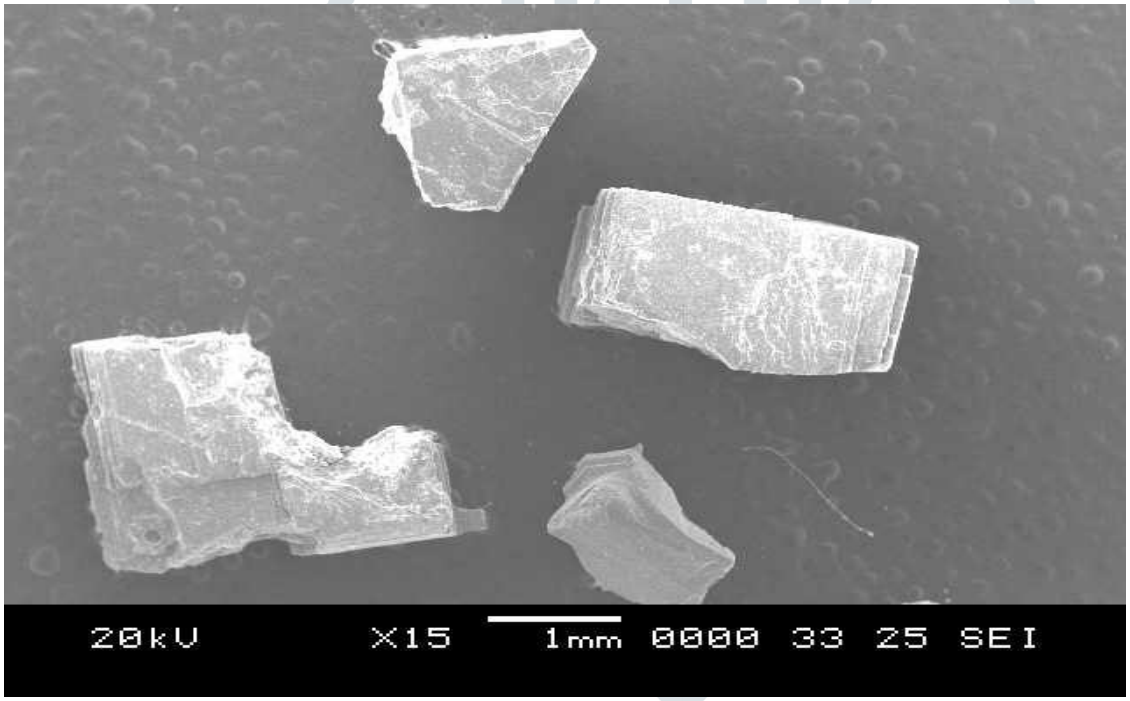

Fig.III.8

Form the SEM of sample synthesized at 400˚C it is observed that the grain size of the sample is in the range 1.2 to 2.5µm.

IV ACKNOLEDGEMENT

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