

# Ferroelectric Nanomaterials Through Mechano-Chemical Processing

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*Ferroelectric perovskite powders pertaining to various oxides were prepared by using mechano-chemical processing followed by heating at low temperatures (200°C – 400°C). The complete process yielded nano (~ 50 nm) to submicron (up to 0.3 μm) sized powders of well formed compound indicating complete formation of the desired phase. It has been shown that mechano-chemical activation substantially increases the solid - state chemical reactions at the milling temperatures. During milling, the reaction zones have not only increased as the particle and grain sizes have decreased, product phases have also formed at low temperatures with smaller amount of external energy compared to conventional processing methods.*

## 1.0 INTRODUCTION

Barium Titanate ( $\text{BaTiO}_3$ ) is one of the most studied ferroelectric, with extensive use as a dielectric ceramic capacitor, embedded capacitance in Printed Circuit Boards, actuators, relaxors and sensors due to its high dielectric constant, thermal stability and low loss characteristics<sup>1,2</sup>. While the dielectric properties strongly depend on the proper element doping at the A-site (with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{La}^{2+}$  ion) or B-site (with  $\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$  ion) in the perovskite-type ferroelectric units like  $\text{BaTiO}_3$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  etc., grain size (GS) also has a pronounced effect on the ferroelectric behaviour<sup>1,3</sup>. The relative permittivity measured at room temperature (~ 1500) for coarse grained ceramics ( $\text{GS} > 10 \mu\text{m}$ ) has been reported to increase as the GS is reduced to micrometers, having a pronounced maximum of  $\epsilon \sim 5000$  at ~ 1 μm. Further reduction of the GS causes reduction in ferroelectric properties which is attributed to structural changes, twinning mechanisms in polycrystalline ceramics and internal stresses induced by the reduction of grain sizes. While small grain size of the order of ~ 1 μm may offer the best suited properties ultra-fine grained crystallites (submicron/nanosized) as starting compositions provide

extremely useful inputs in terms of energy efficiency, consistency in properties and finally diverse possibilities of synthesis of newer compounds. The progress in the modern materials science and technology is governed by stringent requirements imposed on superfine powder production especially in large scale. Ultra fine grained powders in nanometers scale can be synthesized by mechano-chemical grinding of oxides which take superiority over other methods of powder synthesis because it is (i) inexpensive (ii) ecologically clean and (iii) possible to synthesize in mass scale.

Mechano-chemical process (MCP) uses mechanical energy to activate chemical reactions and structural changes. Conventional solid state reactions whether alloying or chemical reactions, involve the formation of one or more product phases that separate the reactants. Diffusion through the product phases is invariably the rate controlling process and consequently high temperatures are normally required to achieve acceptable reaction kinetics. MCP overcomes this diffusion limitation, with the metastable structures developed directly reflecting the diffusion constraints imposed by the low temperature nature of the process.

In the present work, mechano-chemical synthesis processing is employed to synthesize ultra fine powders of oxides, based on Bi, Ta, Ba, Nb, La, and Ti to demonstrate the suitability of the process to synthesize the ferroelectric compounds at as low a temperature of 200°C while the conventional solid state sintering requires calcination temperatures > 1000°C for long durations (24 hours) for phase formation. The compounds synthesized by various routes are LiTaO<sub>3</sub>, BiTaO<sub>4</sub> and BaBiNb<sub>2</sub>O<sub>9</sub> and characterized by X-ray Diffractometry (XRD), Differential Thermal Analysis (DTA) and Scanning Electron Microscopy (SEM) associated with Energy Dispersive X-ray Analysis (EDX).

## 2.0 EXPERIMENTS, RESULTS AND DISCUSSION

### 2.1 Synthesis of Lithium Tantalate (LiTaO<sub>3</sub>) through solid state reaction

Polycrystalline powder of LiTaO<sub>3</sub> was prepared by heating a stoichiometric mixture of Lithium Carbonate (analytical grade, Loba, 99.5%) and Tantalum Pentoxide (99.9% pure analytical grade) in a platinum crucible up to 1000°C for 12 hours, at the rate of 3°/min and then at 1375°C for 12 hours in air with intermittent grinding after each heat treatment. The formation of the compound was confirmed by X-ray powder diffraction studies.

### 2.2 Synthesis of LiTaO<sub>3</sub> through Mechano-chemical method

Fine powders of polycrystalline LiTaO<sub>3</sub> was prepared by ball milling a stoichiometric mixture of Lithium Carbonate (analytical grade, Loba, 99.5%) and Tantalum Pentoxide (99.9% pure analytical grade) in a planetary ball mill (Model Retsch 4000) with Zirconia balls as grinding media in a Zirconia jar in acetone medium. The Zirconia material was chosen as the milling medium to avoid contamination during milling. The ball to powder weight ratio was maintained at 1:10 to achieve proper milling during which period the energy transfer from grinding media to the reactant mixture takes place. Further, three different sizes of balls were used viz.; 20 mm dia, 10 mm dia and 5 mm dia which again helps in formation of the compound at much lower

temperatures than in conventional reactions. Ball milling was carried out for 10-75 hours and samples were collected at regular intervals for phase and particle size analysis. Care was taken to see that stoichiometry is not lost during continuous milling. Complete phase formation of LiTaO<sub>3</sub> was observed on heating the mechano-chemically milled raw materials at as low a time and temperature of 2 h at 400°C, whereas in the conventional method complete phase formation occurred only after heating to 1375°C for 12 hours. XRD patterns pertaining to various phases formed at different stages of milling including the raw materials and final compound are shown in Fig. 1.

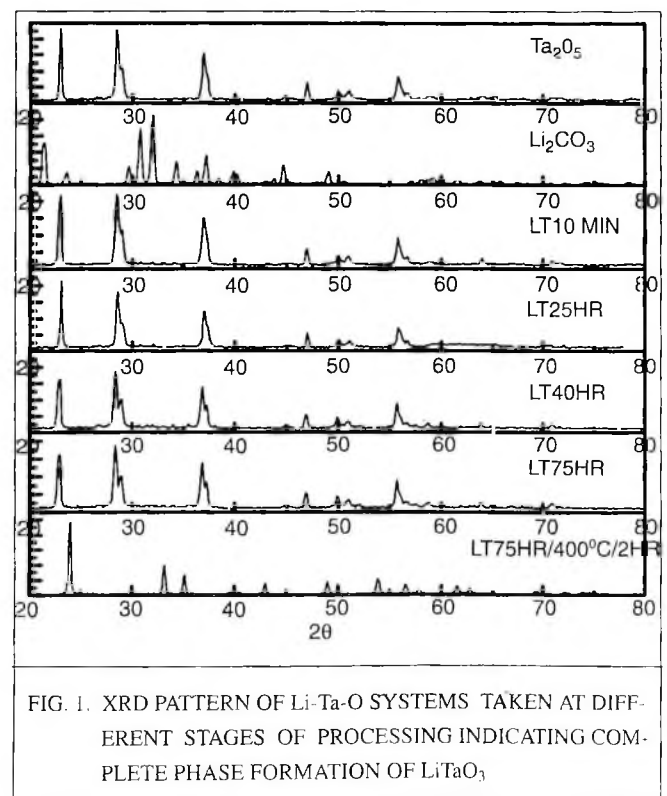


FIG. 1. XRD PATTERN OF LI-TA-O SYSTEMS TAKEN AT DIFFERENT STAGES OF PROCESSING INDICATING COMPLETE PHASE FORMATION OF LiTaO<sub>3</sub>

Figure 2 shows the SEM micrograph of sintered LiTaO<sub>3</sub> pellet (1200°C/8 hours) prepared through mechano-chemical reaction clearly showing grains distributed with very less porosity. The fine grained sintered ferroelectric also exhibits favorable dielectric behavior. LiTaO<sub>3</sub> has a curie temperature of 665°C which is further confirmed from DTA data.

### 2.3 Synthesis of BiTaO<sub>4</sub> Through Mechano-chemical Method

Fine powders of polycrystalline BiTaO<sub>4</sub> was prepared by ball milling a stoichiometric mixture of



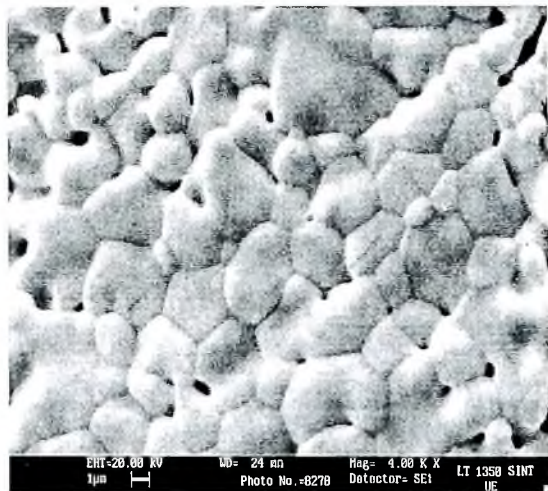


FIG. 2. SEM MICROGRAPH AT 4000X OF  $\text{LiTaO}_3$  SINTERED AT  $1200^\circ\text{C}$  FOR 8 HOURS

Bismuth Oxide (analytical grade, Loba, 99.5%) and Tantalum Pentoxide (99.9% pure analytical grade). The same type of milling as in the case  $\text{LiTaO}_3$  was adopted here. The product phase was achieved after 75 hrs of ball milling followed by heating at  $200^\circ\text{C}$  for 2 hours. Figure 3 shows the SEM micrograph of  $\text{BiTaO}_4$  powder taken at 50,000X. It can be clearly seen here that the average grain size of mechano-chemically synthesized  $\text{BiTaO}_4$  powder is  $\sim 200$  nm.

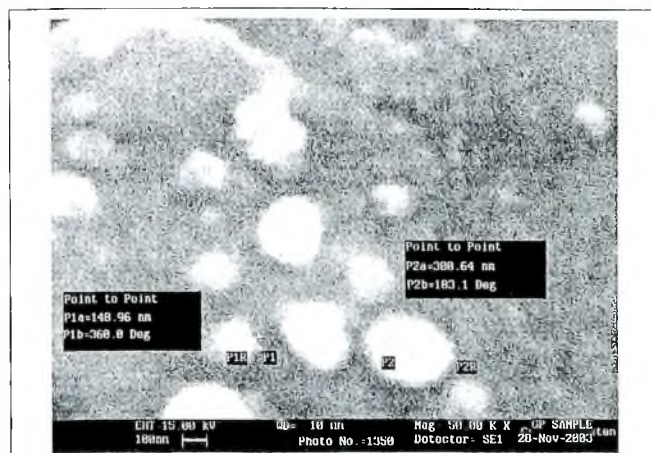


FIG. 3. SEM MICROGRAPH OF  $\text{BiTaO}_4$  FORMED AFTER 75 h OF MILLING FOLLOWED BY HEATING FOR 2 HOURS AT  $200^\circ\text{C}$  (AT 50,000X)

## 2.4 Synthesis of $\text{BaBi}_2\text{Nb}_2\text{O}_9$ by Mechano-Chemical Processing

The layered structures of  $\text{BaBiNb}_2\text{O}_9$  and  $\text{BaBi}_2\text{Ta}_2\text{O}_9$  have recently received considerable

interest in view of their potential application as low voltage, high speed non volatile random access memory (NVRAM).  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  was synthesized by the mechano-chemical processing (10 hours) with average particle size of 50 nm. This was followed by calcination at as low a temperature as  $250^\circ\text{C}$  for 10 minutes whereas the conventional solid state sintering route requires soaking at  $900^\circ\text{C}$  for 2 hours to obtain a pure compound<sup>4</sup>. Such prolonged heat treatment cause unfavorable growth of particles which not only affects the physical properties like sinterability and density, but also the dielectric characteristics including performance in the intended applications. Fig. 4 shows the SEM micrograph of the nanosized powder of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  and Fig. 5 shows the DTA pattern of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  powder indicating an exothermic peak at  $258^\circ\text{C}$  depicting phase formation.

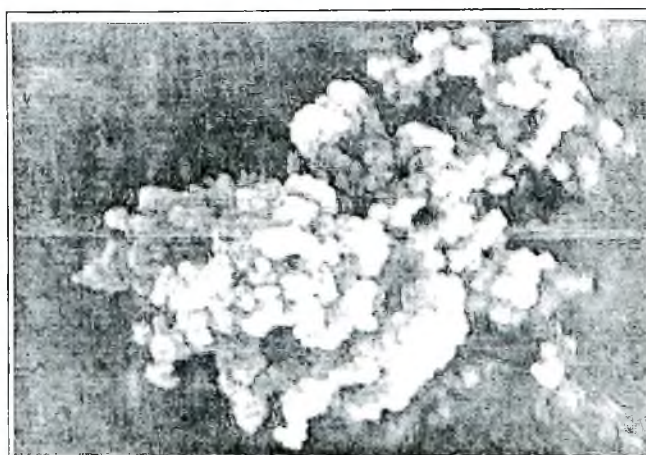


FIG. 4. SEM MICROGRAPH OF NANO-SIZED  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  POWDER (40,000X)

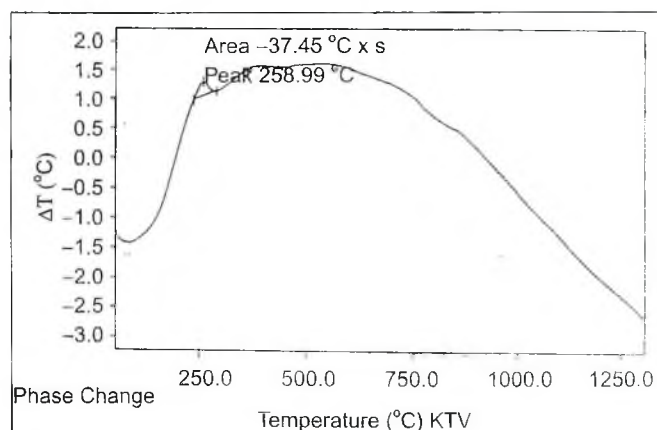


FIG. 5. DTA PATTERN OF  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  POWDER INDICATING AN EXOTHERMIC PEAK AT  $258^\circ\text{C}$  DEPICTING PHASE FORMATION

### 3.0 CONCLUSIONS

Ferroelectric perovskite compounds such as  $\text{LiTaO}_3$ ,  $\text{BiTaO}_4$ , and  $\text{BaBi}_2\text{Nb}_2\text{O}_9$ , have been prepared by the mechano-chemical processing route followed by heat treatment at temperatures varying between  $200^\circ\text{C}$  and  $400^\circ\text{C}$ . While mechano-chemical milling process indicated partial formation of the desired compound and nano-sized particles, complete phase formation occurred on applying some amount external source of energy with sub micron sized grains yielding a dense microstructure on sintering. The energy efficiency of the process as well as enhanced ferroelectric properties is significant.

### REFERENCES

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