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Hexagonal $BaTiO_3$ (h-$BaTiO_3$) Single Crystal growth by Optical Floating zone technique

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Abstract: $BaTiO_3$, a well reported perovskite ferroelectric material undergoes structural phase transitions under various temperatures. Growing crystals of $BaTiO_3$ from stoichiometric melt always results in the hexagonal phase which is a high temperature phase, which subsequently remains meta-stable at room temperature. Single crystals of h-$BaTiO_3$ were grown in air and oxygen atmosphere by floating zone furnace using four halogen lamps. The structure of grown crystal was monitored by powder X-ray diffraction. Various measurements like UV-Vis, Raman scattering, were carried out in order to analyse the optical and vibrational properties of h-$BaTiO_3$. Efforts were made to grow single crystals of $Ba_{0.9}Zn_{0.1}Ti_{0.9}Mn_{0.1}O_3$ composition in order to induce ferromagnetism in $BaTiO_3$.
Keywords: Hexagonal $BaTiO_3$ (h-$BaTiO_3$), Single Crystal growth, Optical Floating zone technique.

Introduction and Experimental:

Extensive research has been carried out on ferroelectric perovskite $BaTiO_3$ with higher permittivity, but less attention is being given to polymorphic hexagonal $BaTiO_3$. Growing crystals of $BaTiO_3$ from stoichiometric melt always results in the hexagonal phase which is a high temperature phase, which subsequently remains meta-stable at room temperature [1]. Hexagonal $BaTiO_3$ crystallizes in the space group $P6_3/mmc$ with cell parameters a = 5.7238 A^o , c= 13.9649 A^o and V = 396.22 A^{o3}[2]. Hexagonal $BaTiO_3$ can be stabilized by two ways, one by melting at higher temperatures [3] and other by doping it with transition metals likeMn, Fe, Coetc. [4, 5]. We have chosen both ways to bring about room temperature hexagonal phase in $BaTiO_3$. Single crystals of $BaTiO_3$ with stoichiometric melt were grown by optical floating zone technique. Attempts were made to grow single crystals of $Ba_{0.9}Zn_{0.1}Ti_{0.9}Mn_{0.1}O_3$ which possessed hexagonal phase at room temperature in its ceramic form.

Polycrystalline powders of the feed and seed rods for the floating zone crystal growth were $BaTiO_3$. Stoichiometric amounts of the raw materials were ball milled and the mixture was calcined at 950^{o}C for 10hrs in air with an intermediate grinding for homogeneity. After the confirmation of the single phase by X-ray diffraction the resultant powder was then isostatically pressed in the form of rods and sintered at 1200°C for 24hrs. Crystal growth was carried out in an optical image furnace (FZ-4000-H-HR-I-VPO-PC) equipped with four halogen lamps focused by four ellipsoidal mirrors. Phase identification was carried out using powder X-ray Diffraction (XRD) technique. To study optical transmission behaviour of grown crystals, absorption spectra were recorded in the region of 190–1100 nm using ELICO SL 218 double beam spectrophotometer.

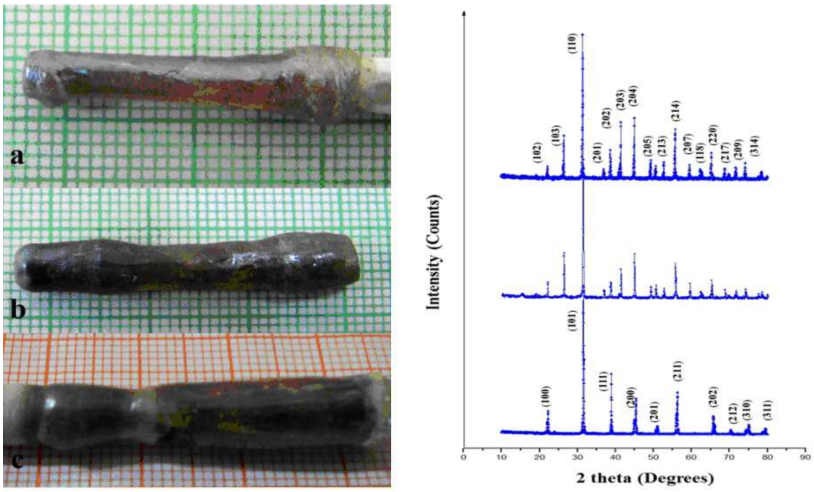

Fig 1. (a) & (b) Grown h-$BaTiO_3$ Crystal in Air Atmosphere (c) Oxygen Atmosphere (d) powder XRD patterns

Results and Discussion:

The crystals shown in Fig 1.were grown at higher growth rates of 20mm/h in Air and Oxygen atmosphere with feed rod and seed rod shaft rotation at 20-30rpm. The grown crystals are black in colour due to oxygen deficiency but became transparent after annealing at higher temperature of 1000°C.

It is evident from the pattern that the grown crystal possesseshexagonal structure (JCPDS #340129), while the polycrystalline seed material has a tetragonal structure (JCPDS #050626). The phase composition of the grown crystal was investigated by Raman spectroscopy, which is a highly sensitive spectroscopic technique to probe the local structure of atoms. Raman spectra for the grown h-$BaTiO_3$ crystal are shown in Fig .2.The symmetry of the optical phonon modes at the zone centre are calculated by factor group analysis is as follows [6],

$$5A_{1g} + 2A_{2g} + 6B_{1g} +B_{2g} + 6E_{1g} + 8E_{2g} + A_{1u} + 6A_{2u} + 2B_{1u} + 6B_{2u} + 8E_{1u} + 7E_{2u}$$

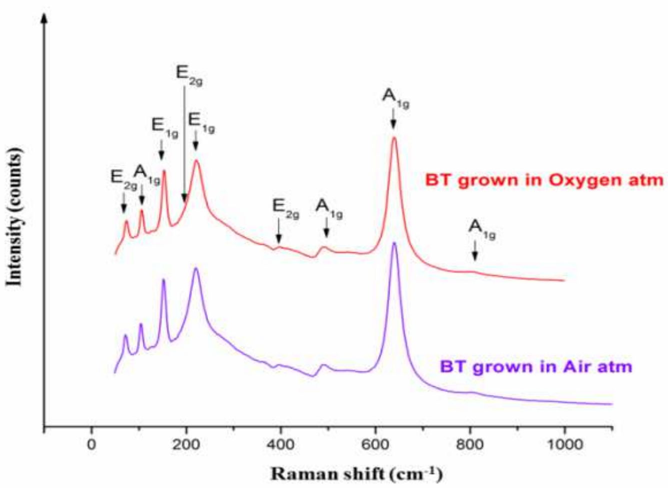

Fig 2. Raman spectra of h-$BaTiO_3$Crystals grown in Air & Oxygen atmosphere

All the spectra exhibit bands at 811, 640,501,411,220,196,151,105,71cm^{-1}, respectively which are characteristic of the hexagonal phase of $BaTiO_3$[6]. Thus it can be proven through Raman spectroscopy that the grown crystal possess hexagonal phase. The absorption spectra of the grown crystal was recorded for 1.5mm thickness crystal in the range 200-1100nm in Fig.3. The crystal has no significant absorption in the range 414 -1100nm. The cut off wavelength is 413nm.The optical absorption coefficient (α) was calculated by the transmittance data using the following relation

$$\alpha = 2.303 \log\left(\frac{1}{T}\right) / t \qquad (1)$$

where α is the absorption coefficient, T is the transmittance and t is the thickness of the crystal. The optical band gap of the grownh-$BaTiO_3$ crystal is evaluated from the absorption coefficient (α) andtransmission spectrum using the relation Eq. (2).

$$\alpha h\gamma = A\,(h\gamma - E_g)^{1/2} \qquad (2)$$

whereE_g is the optical band gap, A is a constant, γis the frequencyof incident photons and h is the Planck's constant. Using Tauc's method, the graph (Fig. 3b) has been plotted for the product of absorption coefficient (α) and incident photon energies (hγ). The band gap measured was 2.85 eV for the grown crystal. Based on the energy dependent absorption coefficient in the graph, it is confirmed that the grown crystal has direct band gap (E_g).

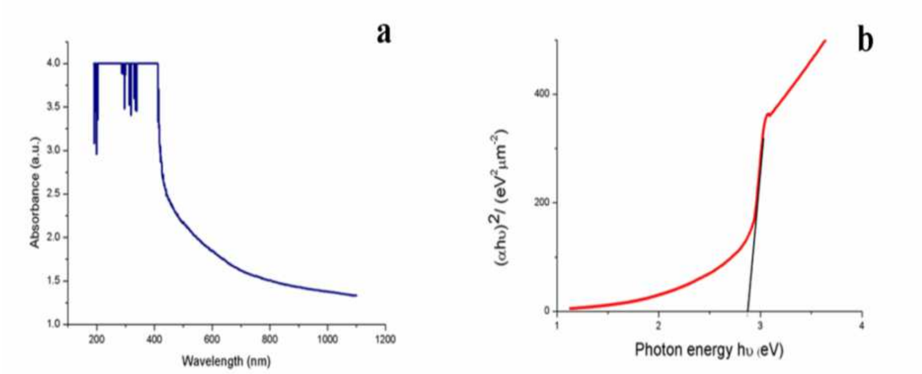

Fig3. a) Absorbance spectra for h-$BaTiO_3$crystal, b) Plot of $(\alpha hv)^2$ vs. Photon energy (hv).

In order to induce ferromagnetism in $BaTiO_3$, Mn was doped in Ti site and Zn was doped in Ba site. The starting materials $BaCO_3$, TiO_2, $MnO_2$and ZnO were grounded and calcined at 1100^{0}C for 10hrs. The powder XRD pattern shown in Fig.4revealed that it possess hexagonal structure (JCPDS#340129).Ceramic rods for crystal growth were prepared and sintered at 1200^{o}C for 24hrs. Crystal growth of $Ba_{0.9}Zn_{0.1}Ti_{0.9}Mn_{0.1}O_3$ was performed using optical float zone technique. Due to the volatilization of zinc at higher temperatures, stable molten zone couldn't be achieved [7]. The melt was unstable which resulted in the failure of crystal growth. Efforts are being made to make use of fluxes like V_2O_5, B_2O_3etc to reduce the growth temperature below 1200^{o}C, in order to suppress the ZnO evaporation during crystal growth.

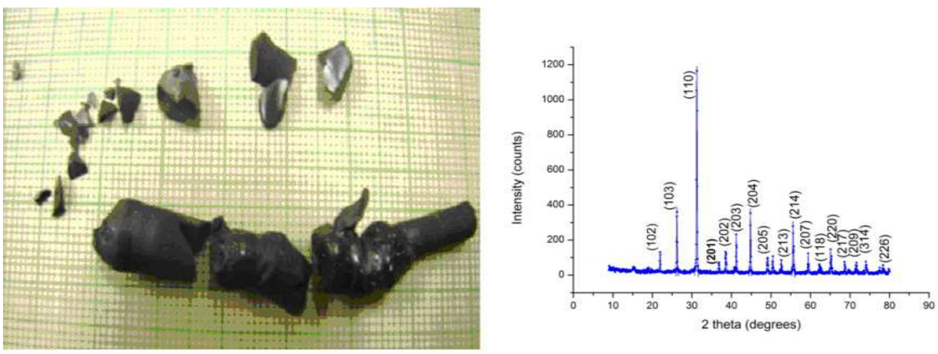

Fig 4. a) Broken pieces of $Ba_{0.9}Zn_{0.1}Ti_{0.9}Mn_{0.1}O_3$crystal b) XRD pattern of $Ba_{0.9}Zn_{0.1}Ti_{0.9}Mn_{0.1}O_3$ polycrystalline powder.

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