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X-Ray Diffraction Studies of PZT- SiO_2 Ceramic Glass Composites

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Abstract

PZT ceramic of morphotropic phase boundary (MPB) compositions was prepared by a conventional oxide method and its composite with glassy SiO_2 was prepared. X-ray powder diffraction (XRD) analysis was carried out at room temperature to determine phase structure and lattice parameters. In the present study the JEOL model JDX-3530, Ni filtered CuK_α radiation at 30kV, 40 mA, was used. It is observed from the XRD that sharpness of the lines and tetragonality of the lattice decrease with the increase of the Silica percentage. The presence of SiO_2 as a glassy matrix improves its usability in micro electromechanical devices.

Keywords: XRD, ceramic, Composite, Electroceramic Materials.

Introduction

Use of ceramics in electronic components is growing rapidly as a result of their superior physical properties and recent technology development. The markets and material technologies for ceramics used as insulators, substrates, packages, capacitors, resistors, semiconductors, piezoelectric devices, and superconductors have shown an outstanding growth during the last three decades [1]. For each type of material, market factor, segmentation and trends are strongly connected with technology and developments. The electronic ceramics industry is a highly technological one characterised by rapid innovation and constant changes. Working with a wide variety of functionally different materials, the electronic ceramic industry is still in the process of strong expansion and redirection. It interfaces directly with the electronic industry through the widespread use of ceramic components as an integral part of electronic devices and packages[2]. Several of the electronic ceramic market segments have matured, yet they are still growing at a steady pace.

Electronic ceramics provide basic components as well as support a variety of electronic products including computers, industrial controllers, consumer automotive devices and digital switches. They can be also used as active components, such as semiconductors to control voltage and electrical currents, and as passive components, such as capacitors and resistors to control electrical currents or voltages, or electromechanical applications[3], such as ferrite magnets or piezoelectric devices. The significance of electroceramic materials can be gauged with respect to the present demand of electroceramics in the global market and projected demand[4] in the future.

Although research and development in advanced ceramics and related components has been going on for more than twenty years in India, its requirements towards competitive commercial needs have neither been systematically studied nor understood. The onset of globalisation and liberalisation had put great emphasis on indigenous research and development which has to gear up to the exacting global standards. Global standards are ever increasing, therefore to keep up breast with the demands, we need considerable inputs in the form of substantial increase in technical manpower as well as cutting edge infrastructure. One needs to maintain a day to day updated database on the consumption and market demands of the ceramics in question. The commercial interest generated for a particular type of advanced ceramic has to be gauged and the research, development as well as manufacture has to be planned accordingly.

In the present study we had tried to develop a ceramic composite with silica glass as a matrix and a piezoelectric ceramic viz. Lead Zirconate Titanate[5] (PZT) dispersed in the matrix and its characterization by X-ray powder diffraction (XRD).

Review of Literature

PZT is one of the most widely used piezoelectric materials. It is noted that most commercially available ceramics (such as barium titanate and PZT) are based on the perovskite structure[6] (Figure 1).

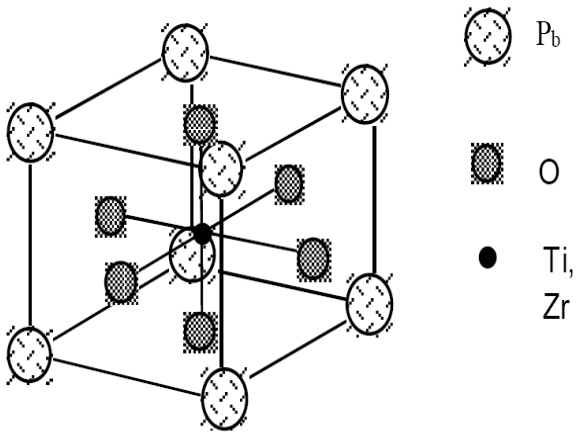

Fig. 1 The perovskite structure[6]

The perovskite structure (ABO_3) is the simplest arrangement where the corner-sharing oxygen octahedra are linked together in a regular cubic array with smaller cations (Ti, Zr, Sn, Nb etc.) occupying the central octahedral B-site, and larger cations (Pb Ba, Sr, Ca, Na etc.) filling the interstices between octahedra in the larger A-site. Compounds such as $BaTiO_3$, $PbTiO_3$, $PbZrO_3$, $NaNbO_3$ and $KNbO_3$ have been studied at length and their high temperature ferroelectric and antiferroelectric phases have been extensively exploited[7]. This structure also allows for multiple substitutions on the A-site and B-site resulting in a number of useful though more complex compounds such as $(Ba,Sr)TiO_3$ $(Pb,Sr)(Zr,Ti)O_3$, $Pb(Fe,Ta)O_3$, $(KBi)TiO_3$ etc. see Fig. 1. PZT is currently the primary material used in naval sonar devices[8], and it has also been investigated for possible use in FRAM memory modules. PZT is a perovskite alloy of lead zirconate (PZ) and lead titanate (PT)[9]. PZ and PT are relatively simple to characterize and have been thoroughly investigated both experimentally and by means of theoretical calculations. PT is a ferroelectric (FE) material with a simple tetragonal structure, while PZ has a complex antiferroelectric (AFE) ground state. By themselves, neither PZ nor PT are particularly good piezoelectrics, but mixing these materials in a disordered solid solution gives rise to excellent piezoelectric response.

Aim of the Study

PZT is especially attractive for material properties designing. Wide range of physical properties can be obtained by variation of Zr/Ti ratio, particularly in so-called morphotropic phase boundary (MPB) region. In addition, PZT ceramics are almost always used with a dopant or a modifier to improve and optimize their basic properties for specific applications. Considering the demand for composite material it is worth the extra effort put into the preparation, manufacture and characterization of the material. In fact most modern appliances and probes have switched over to ceramic polymer or ceramic glass composites because of its superior performances. The top of the line medical electronics rarely use conventional PZT ceramics, instead most of the probes have either 1-3 or 3-3 connected composites, because it simplifies and eliminates the need for complex circuitry needed for noise cancellation, since the signal to noise ratios given out by the composites elements are more than an order of magnitude better than their plain ceramic counterparts[10]. The aim of this paper is the structural characterisation of PZT-SiO_2 composites. Here MPB composition of PZT is used. It is expected that this composite can lead to integration of silicon technology (semiconductors) with ceramic technology through an interface viz. silica glass. Once the figures of merit of the material (composite) are known, and found to be acceptable then, one can easily fuse the material onto the silicon substrate. Powder X-ray Diffraction (XRD) is one of the primary techniques used in material science to examine the physico-chemical make-up of unknown materials. In the present study X-ray diffraction is used for phase identification and phase fraction analysis of PZT-SiO_2 composites

Preparation of the Samples

To characterise the material we need to prepare the samples of the composite at different proportions. So as to find out the appropriate ratio at which the material exhibits the optimum figures of merit. The method of preparing the samples are mentioned graphically using a flow diagram below in Fig. 2. Here the preparation of PZT ceramic is omitted since standardised procedures were followed[11].

Different proportions of the PZT : Glass were prepared viz. 100% PZT, 5% silica glass, 10% silica, 15%, 20%, 25% and 30%. Higher percentages of glass were ignored, because a preliminary study carried out with high glass contents in the composites led to a large reduction in piezoelectric and dielectric properties of the composites so obtained. Also silica in its glassy form does not exhibit any piezoelectric behaviour.

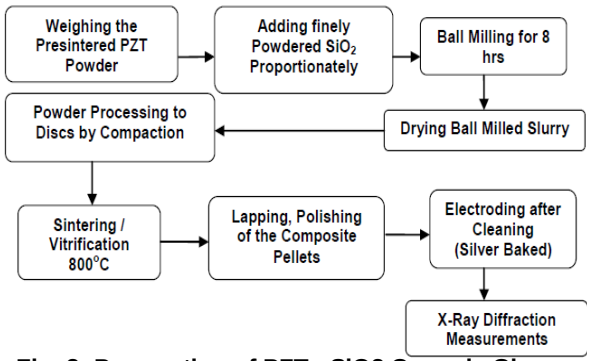

Fig. 2: Preparation of PZT : SiO2 Ceramic Glass Composites

Experimental

The studied ceramics of morphotropic phase boundary (MPB)[12] compositions were prepared by a conventional ceramic mixing method, the general formula: $Pb(Zr_{0.54}Ti_{0.46})O_3$,. The commercially available oxide powders of high purity (all 99.9% purity) were used. PbO, ZrO_2, and TiO_2 (Fluka chemika) of the required amounts were carefully weighed and mixed by wet ball milling for 24 hours

using zirconia balls and acetone as media. The mixture powder was dried at 100°C for 12 hours. After drying, the mixture powder was calcined in a closed alumina cup at 800°C for 4 hours at a constant heating rate of 300°C/h. The calcined powder was then ground in a mortar and pestle to crush agglomerates to pass through a 100 mesh sieve and was filled in a covered alumina crucible, a $Pb(Zr_{0.54}Ti_{0.46})O_3$ atmosphere powder were placed on the top, bottom and in the vicinity of the crucible in order to maintain stoichiometries as closely to the nominal compositions as possible. Moisture contents and binder were removed by heating the sealed alumina crucible at 500°C for 1 hour at the constant heating rate of 300°C/h. Then, the lightly compacted powder in three sealed alumina crucibles, were sintered for 1hour each. Sintering temperature was set at 1200°C. The samples were characterized for weight loss and sintered density. X-ray powder diffraction (XRD) analysis was carried out at room temperature to determine phase structure and lattice parameters. The JEOL model JDX-3530, Ni filtered CuK_α radiation at 30kV, 40 mA) were used. Data collection was performed in the 2θ ranging from 20°-60° of a step scan with a step size of 0.02° and counting time of 0.5 s per step. SiO_2 powder sieved using 100 mesh sieve were added to the sintered PZT powder. Calculated amounts of SiO_2 powders were added to the prepared ceramic (i.e. 5, 10, 15, 20, 25 and 30% by weight of PZT) and ball milled for 4 hrs. The mixture now forms the raw material for Ceramic Glass composite. The ball milled powder is again sieved and compacted in a hardened steel die. An isostatic pressure of 150 MPa is applied to make a pellet of 12 mm diameter. The green pellets are then loaded into a furnace and heated to about 800°C and maintained at that temperature for an hour after which it is cooled down to normal temperature within 2 hours. It is presumed that sintering of the samples have not taken place while vitrification of the glass phase might has resulted. It is important that no solid state reaction between PZT and Glass (SiO_2) should take place. A surface sheen on the pellets implies the composite has been formed. The composite pellets are now ready for characterisation.

The X-ray diffractograms of the different samples were recorded and the peaks were indexed accordingly. ASTM data on PZT and SiO_2 were also used to index the peaks. The diffractograms of all the series of composite samples were plotted elucidated and the peaks were identified from standard data.

Results and Discussions

The x-ray diffractograms of the different samples are shown below in fig. 3 – fig.10. It can be seen from the XRD peaks at around 45^0 that the doublet which is a characteristic of tetragonal PZT lattice[13] merges to one single peak at 30% i.e. (200) and (002) peaks which characterises c/a ratio gradually diminishes at 30% silica content, implying decreasing tetragonality of the lattice. Tetragonality of the lattice is a measure of pyroelectric coefficient[14], and therefore piezoelectric coefficient. So even without measuring the piezoelectric and pyroelectric coefficients, one can, foresee the decrease in the coefficients, with the increasing silica percent. Also from the XRD one can also observe that the sharpness of the lines, which is the characteristics of crystalline nature of a material, gradually keeps on decreasing with the increase in silica percentage. This implies the formation of silica glass, since glasses are amorphous. It produces a hazy background on which the crystalline PZT peaks are superimposed. The broadening of the peaks are also visible in the XRD. The broadening of the peaks in the XRD, implies a decrease in the grain size of the crystalline PZT phase. Although a decrease of grain size cannot be explained in a straightforward manner, the authors could only attribute it to the strains incorporated into it by the silica phase during the vitrification process. The broadening of XRD peaks due to induced strain on a lattice is well known fact. The induced strain here may be due to the abrupt change in lattice constants at the interface between the two phases of the composites.

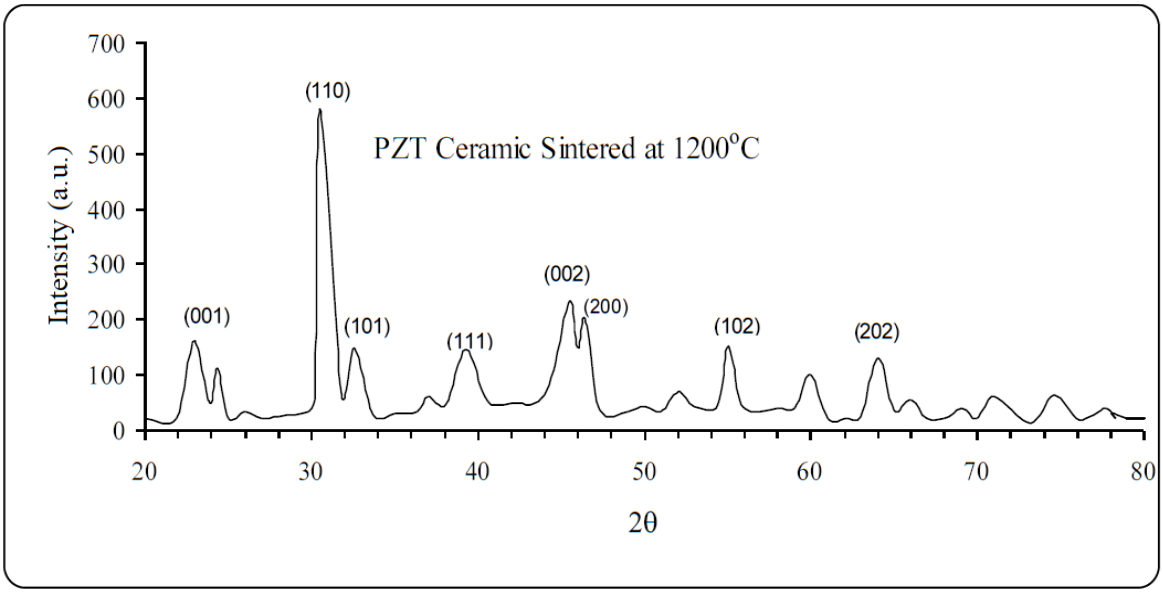

Fig. 3 X-ray Diffractogram of PZT Ceramic with Peaks Identified according to ASTM Data

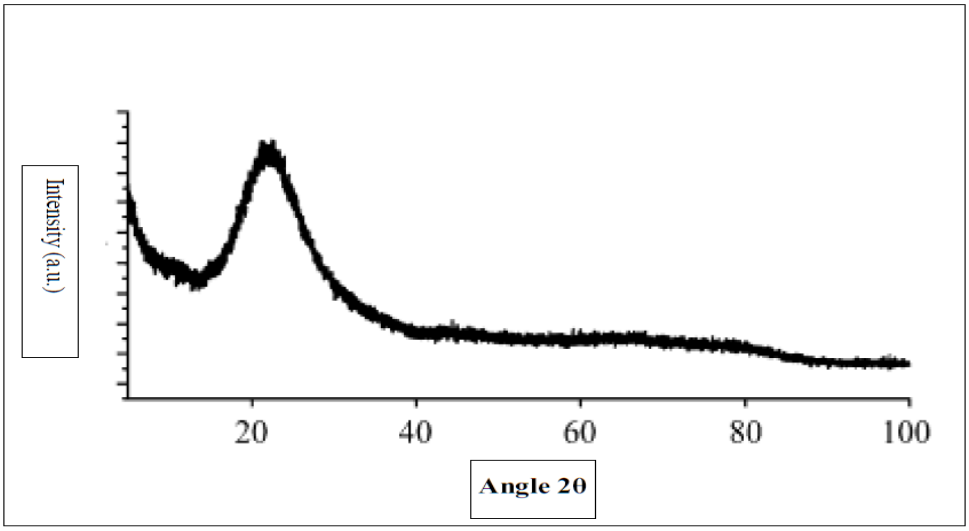

Fig. 4 X Ray diffractogram of Silica Powder (Glassy State)

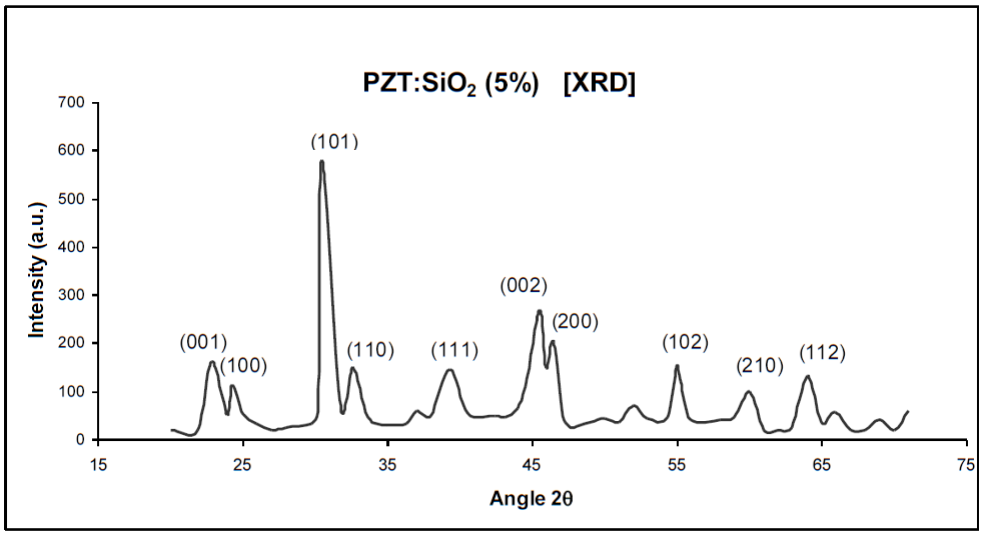

Fig. 5 X Ray diffractogram of PZT : Silica 5% Composite

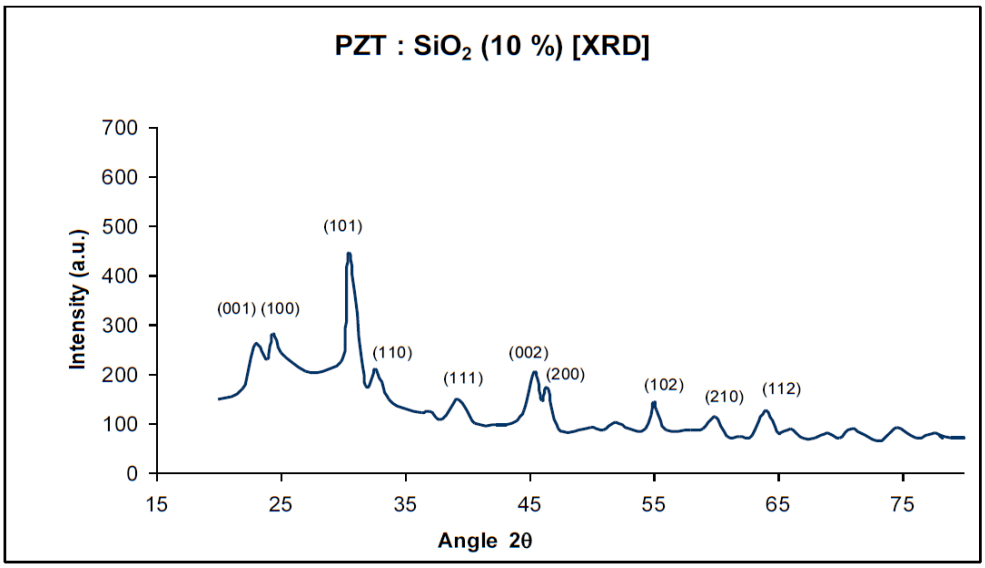

Fig. 6: X Ray diffractogram of PZT : Silica 10% Composite

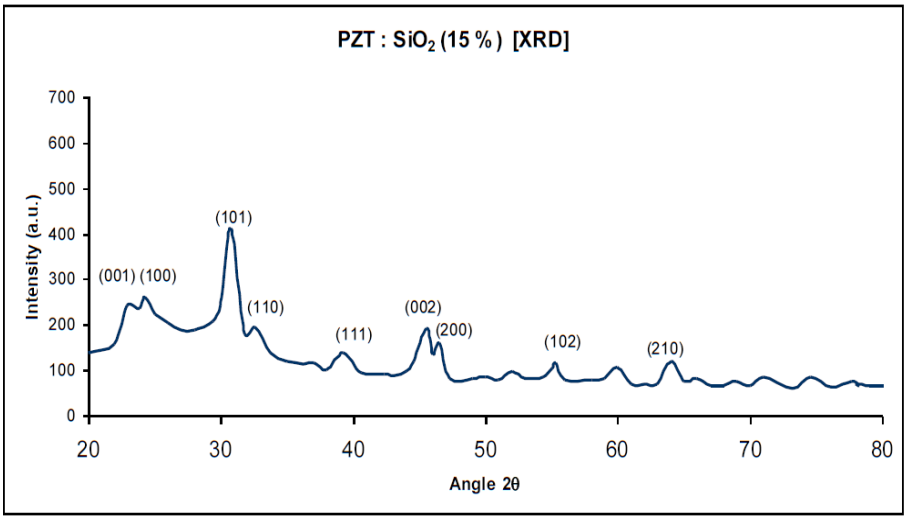

Fig. 7: X Ray diffractogram of PZT : Silica 15% Composite

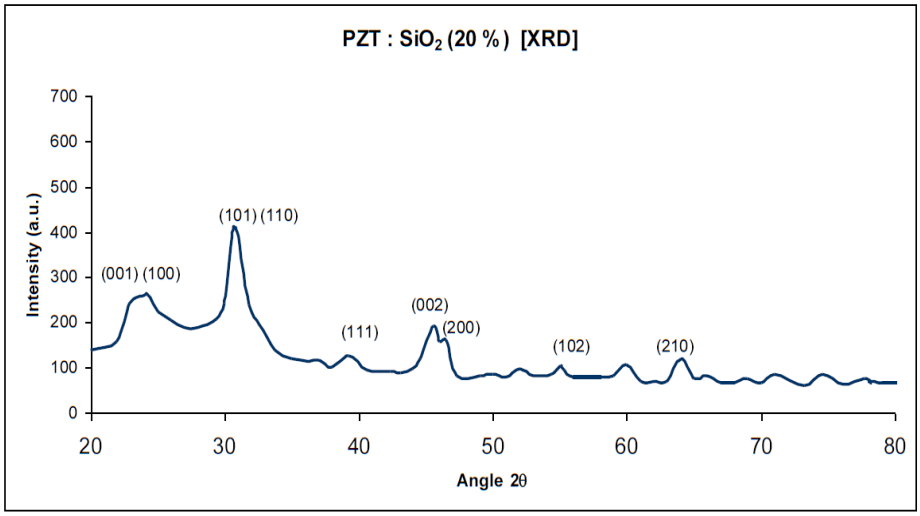

Fig. 8: X Ray diffractogram of PZT : Silica 20% Composite

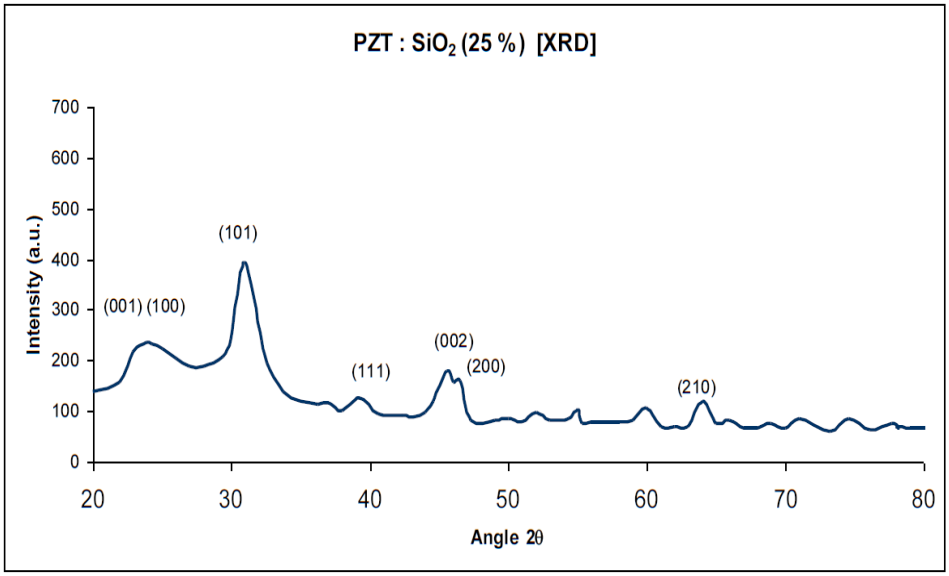

Fig . 9: X Ray diffractogram of PZT : Silica 25% Composite

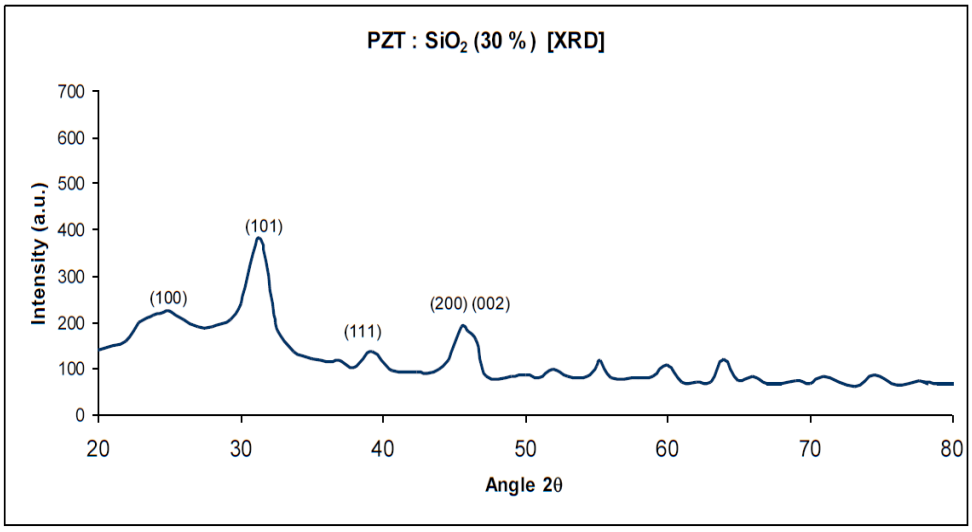

Fig. 10: X Ray diffractogram of PZT : Silica 30% Composite

Conclusions

It can be seen from the X-ray diffractograms that the crystalline character of the composite gets reduced with more and more percentage of silica. It is evident from the X-ray diffractogram of the successive samples as shown in figures 3 to 10. Yet the tetragonal phase of the active material viz. PZT ceramic remains intact as it can be observed by the split of the (200) (002) doublet[15] generally observed in the 2θ value between 40^{o} and 45^{o}. No triplets were observed in the expected region ruling out the presence of an additional phase. Also the presence of SiO_2 as a glassy matrix improves its usability in micro electromechanical devices since this helps in integration with silicon based devices.

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