Finally, the Zr-Ti complex sol was added drop wise to barium acetate solution at room temperature through continuous stirring to get the desired composition. The compositions were diluted to a concentration of 0 35 mol/lit with the addition of acetic acid. Thin films were prepared on platinised silicon wafer by spin coating technique using a Milman spin coater The films were deposited at spinning speed of 3000 rpm for 5 min Just after deposition the films were fired at 600°C for 5 min for organic removal and crystallization in to perovskite phase The coating and fairing sequence was repeated 20 times to attain films approximately 800 nm thick Finally, these were annealed at 1100°C for 2 h for perovskite phase formation and improvement in crystallinity The phase formation behavior and surface morphology of these films were analyzed by X-ray diffraction The surface morphology and film thickness were studied by SEM For electrical measurement a gold electrode of 400 μm square were deposited on the top of the film by d c sputtering The substrate platinum was used as bottom electrode The room temperature frequency dependence of permittivity and loss tangent was studied by HP 9142A low frequency impedance analyzer

3. Results and discussion

Figure 1 shows the XRD patterns of Zr substituted $BaTiO_3$ thin films at room temperature The XRD patterns were indexed considering the cubic structure of $BaTiO_3$ It is evident from the plot that all the films were crystallized in to single phase cubic perovskite structure Substitution of Ti^{4+} (0 61 Å) by higher radii Zr^{4+} (0 72 Å) increases the *d* spacing, which shift of diffraction peaks towards lower angle This is a clear indication that Zr is systematically dissolved in $BaTiO_3$ lattice in the studied composition range

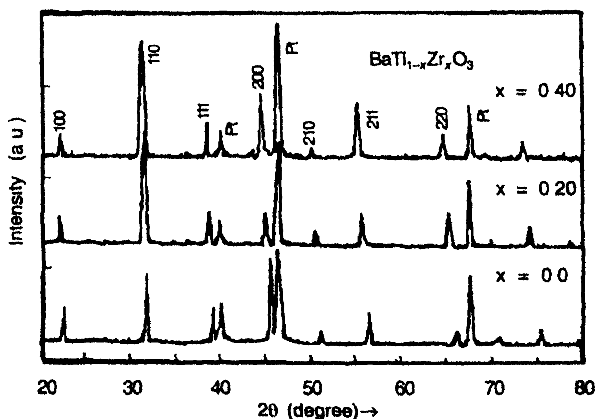

Figure 1. X-ray diffraction pattern of Zr modified $BaTiO_3$ thin films at room temperature.

Figure 2 shows SEM micrograph of sol gel derived BTZ thin film on platinised silicon wafer. All the films have subjected to a final anneal to 1100°C. The addition of Zr to the $BaTiO_3$ lattice decreased the grain size of the crystallized films. The decreasing grain size with increasing zirconium may be attributable to lower grain growth rates from the more slowly diffusion of the Zr^{4+} ion, which has a bigger ionic

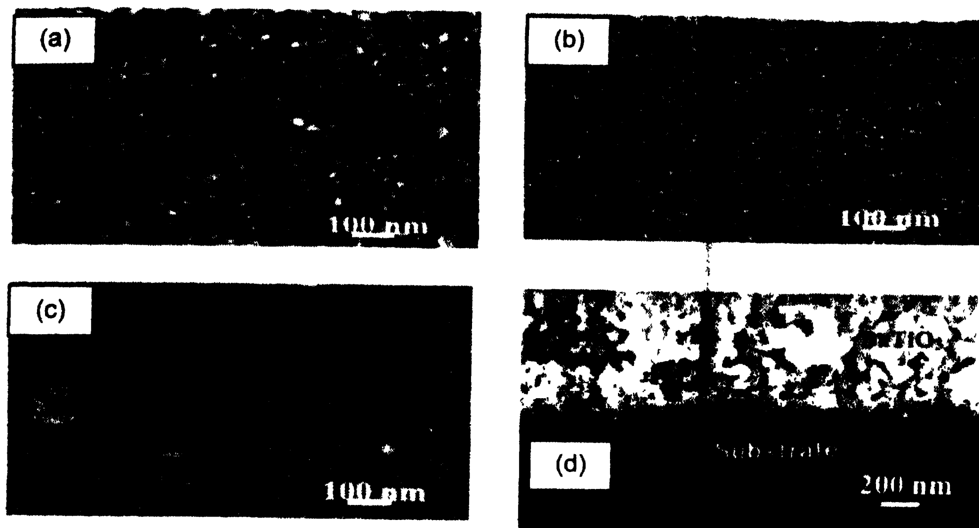

Figure 2. SEM micrographs of sol-gel derived thin film (a) $BaTiO_3$, (b) $BaTi_{0.8}Zr_{0.2}O_3$, (c) $BaTi_{0.6}Zr_{0.4}O_3$ and (d) $BaTiO_3$ (cross sectional view) annealed at 1100°C.

radius than Ti^{4+}. Zirconium content may be attributed to lower grain growth for the same heat treatment [3].

Figure 3 shows the frequency dependency permittivity and dielectric loss of $BaTi_{1-x}Zr_xO_3$ compositions. Permittivity of all the compositions was very stable in the whole frequency range. In general, permittivity (ε) decreases with the increase in Zr-substitution due to; (i). decrease in concentration of high permittivity material $BaTiO_3$, (ii) decrease in grain size resulting to the decrease in polarizability of the atoms in the structure. At very low frequency (Figure 3(b)), high dielectric loss is observed, which may be due to presence of all type of polarization. That also quickly decreases up to about 1 MHz due to the decrease in space charge polarization. The dielectric loss of all the compositions was very stable in the frequency range 1 MHz to about 8 MHz and this loss is very minimum indicating the good quality of the materials as well as the thin film. At high frequency a dielectric loss peak is observed. Several possible

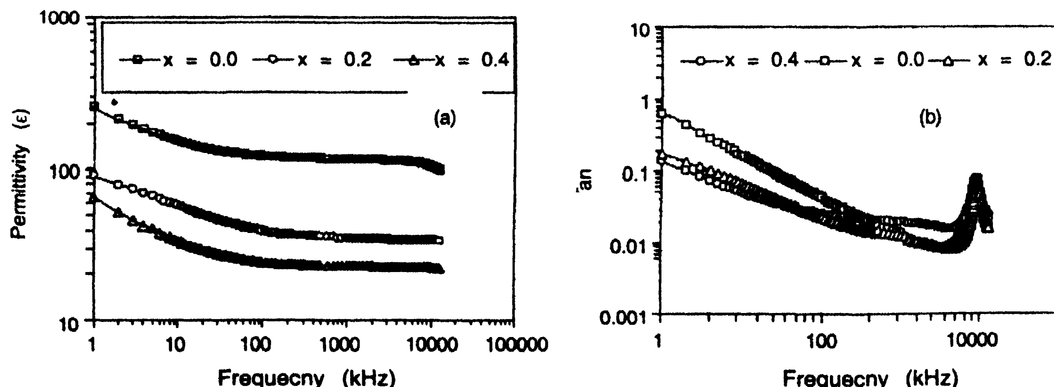

Figure 3. Frequency dependency of (a) permittivity and (b) dielectric loss of different $Ba(Ti_{1-x}Zr_x)O_3$ compositions.

causes exist for such dispersion including the hypothesis of the influence of the contact resistance between the probe and electrode, resonance due to high dielectric constant. Similar frequency dispersion behavior was also reported for other ferroelectric thin film [4,5].

AC conductivity (σ) of the samples was calculated using the formula $\sigma = 2\pi fC(d/A)\tan\delta$, here symbols have there usual meaning. The variation of ac conductivity with Zr-content is plotted in the Figure 4. The conductivity was found to

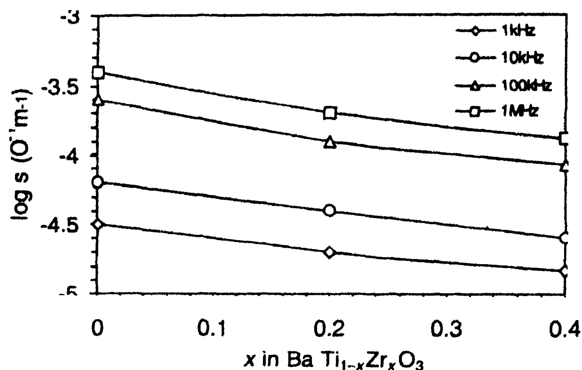

Figure 4. Variation of ac conductivity $Ba(Ti_{1-x}Zr_x)O_3$ thin films with Zr-content (x) at different frequencies

decrease with increase in Zr-concentration and increase with frequency. As a notion impurities and defects are considered to have major effect in titanate ceramics. *i.e.* higher the defect higher will be the conductivity. Here, as Zr-addition reduces the defect in the ceramic, that may be the reason of decrease in conductivity with substitution. As the grain size decreases, the number of grain boundary per unit thickness increases. It is well known [6,7] that in titanate ceramic, grain boundary are highly resistive than the grain. The decrease in conductivity is due to decrease in grain size.

4. Conclusions

From the above study, it may be concluded that

(i) Zr is systematically dissolves in $BaTiO_3$ lattice in the studied composition range.

(ii) Diffusion of Zr is relatively slower than Ti due to its higher ionic radii, resulting lower grain growth.

(iii) Permittivity of all the compositions was very stable in the frequency range 1 kHz to about 8 MHz. In general permittivity (ε) decreases with the increase in Zr substitution due the decrease in polarizability of the atoms in the structure.

(iv) In general tan δ decreases with Zr-substitution.

(v) Dielectric conductivity decreases with Zr-substitution due to increase in number of grain boundary per unit thickness resulted from decrease in grain size.

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