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Comparison on electrical properties of pure Y_2O_3, bismuth doped Y_2O_3, zinc doped Y_2O_3, bismuth and zinc codoped Y_2O_3 prepared by sol-gel method

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Abstract: Yttrium oxide is widely studied nowadays as a substitute for SiO_2 which is a well-known dielectric material. The uniqueness of yttrium oxide is that it has a high melting point (2430 °C) which is higher than other host materials like alumina, zirconia and yttrium aluminium garnet. Hence an attempt was made to add the dopants, bismuth and zinc simultaneously to the yttrium oxide lattice and to study their properties as a dielectric material. Also the dependence of their electrical properties on structure, particle size and morphology is analysed. Pure Yttrium oxide, bismuth doped yttrium oxide, zinc doped yttrium oxide and bismuth and zinc codoped yttrium oxide samples of 0.5 weight percentage of yttrium precursor as dopant concentration are synthesized by simple precipitation technique, sol-gel method. Electrical properties of the samples are studied and a comparative study is done on the doped and codoped samples and it was found that codoped samples show better electrical properties compared with single dopant samples.

Keywords: Codoped, FTIR, dielectric, loss tangent

1. INTRODUCTION

SiO_2 is the gate oxide/dielectric material in metal oxide semiconductors (MOS) in very large-scale-integrated (VLSI) circuits. By decreasing the thickness of the SiO_2 layer, an increase in charge-storage capacity and transconductance is achieved. However, the smallest thickness of the SiO_2-gated dielectric layer is being approached in modern silicon devices. Further improvement needs materials of higher dielectric constants as the gate material. Y_2O_3thin films are excellent substitutes for gate materials. They can be made very thin (25 nm), and the dielectric constant is approximately four times higher than that of SiO_2 [1]. In addition, they have lower leakage current for a given gate voltage, and higher breakdown strength. In our previous papers [2,3], pure yttrium oxide, bismuth doped yttrium oxide, zinc doped yttrium oxide and bismuth and zinc codoped yttrium oxide samples are synthesized and their electrical properties are analysed. However it was found that for yttrium oxide, zinc is better dopant than bismuth because of its electrical properties, when they are applied as single dopants. A comparison study has been done on the structural and optical properties of bismuth doped yttrium oxide, zinc doped yttrium oxide and bismuth and zinc codoped yttrium oxide samples prepared by sol-gel, solvothermal and wet chemical method.

2. EXPERIMENTAL STUDIES

To prepare pure sample, A Pure, 1 g of Yttrium nitrate hexahydrate ($Y(NO_3)_3.6H_2O$)was dissolved in 10 ml of distilled water and stirred for long time to dissolve the salt completely, followed by ammonium hydroxide, the precipitating agent, added in drops to get a clear solution. Continuous stirring lead to precipitation and the precipitate was left for 15 hours to settle. Then the obtained precipitate was washed with water and dried in an oven at 373 K for 3 hours. After drying, the powder was finely ground. Calcination was done by heating the sample at 623 K in a muffle furnace for 15 hours to obtain pure yttrium oxide[4]. To prepare doped yttrium oxide powders, 1 g of Yttrium nitrate hexahydrate was dissolved in 10 ml of distilled water and stirred for long time to dissolve the salt completely. Then dopant precursor of 0.25, 0.5 and 1 weight percentage of yttrium precursor respectively were added to the solution followed by the addition of 50 ml of ammonium hydroxide. Continuous stirring lead to precipitation and the precipitate was left for 15 hours to settle. Then the obtained precipitate was washed with water and dried in an oven at 373 K for 3 hours. After drying, the powder was finely ground. Calcination is done by heating the sample at 623 K in a muffle furnace for 15 hours to obtain doped yttrium oxide powder [4].To prepare bismuth doped yttrium oxide sampleY_2O_3: Bi(AB2) 0.005g of bismuth nitrate is used. To prepare zinc doped yttrium oxide sampleY_2O_3: Zn(AZ2) 0.005g of zinc acetate dihydrate is used. To prepare bismuth and zinc codoped yttrium oxide sample Y_2O_3: Bi, Zn (ABZ2) 0.005g (0.0025 g of bismuth nitrate, 0.0025g of zinc acetate dihydrate) are used. Flow chart of the method followed for preparation is shown in figure 1.Jasco-FTIR 4100 /japan make is used to take FTIR studies in the range of 500 - 4000 cm^{-1}. Impedance analysis is done by HIOKI 3532 LCR impedance analyser interfaced with a computer in the frequency range of 42 Hz to 1 MHz at room temperature.

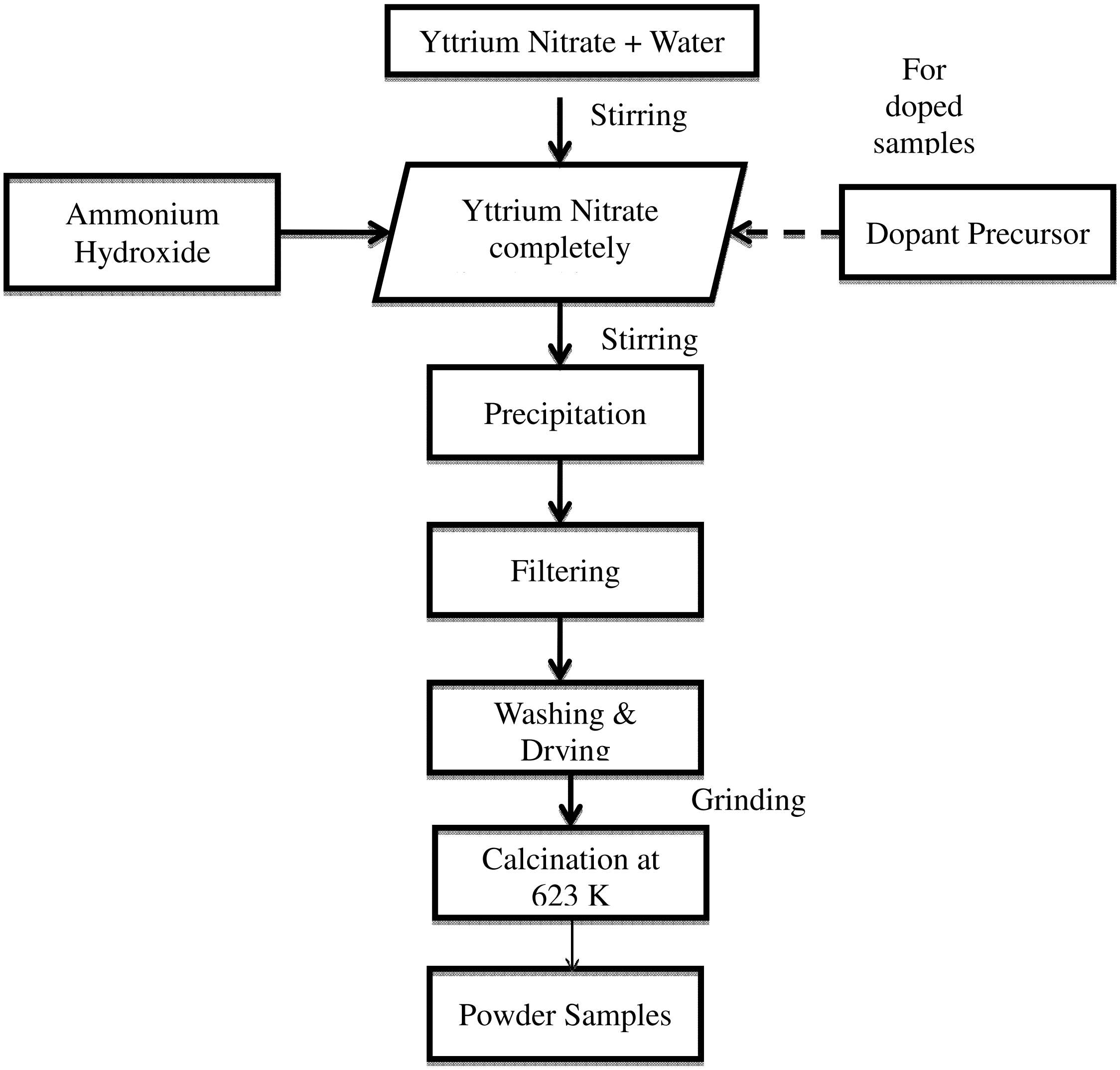

Figure1. Flow chart for sol-gel method

3. RESULTS AND DISCUSSION

3.1 FTIR Studies

FTIR analysis of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by three methods was done for comparison.

It has been observed from the figure 2 of FTIR of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method using ammonium hydroxide as precipitating agent, that the FTIR band around 3400-3500 cm^{-1} caused by O-H stretching of the absorbed water [5] during the storage of the sample in ambient air and is common for all samples which gets broader with respect to dopants.

For Zn-O stretching band appears around 960 cm^{-1} which is present in both doped and codoped samples. And the band around 850 $cm^{-1}$is attributed to the Bi--O stretching vibration [6, 7]. The band around 500 cm^{-1} is attributed to the stretching frequency of Y-O molecule [8]. Shifting of band 1650 cm^{-1} occurs with zinc dopant and its broadening occurs for bismuth dopant. Both splitting and sharpening of bands occur near 1650cm^{-1} for codoped sample and broadening and sharpening occurs near the region 3400 cm^{-1} with addition of all the dopants which is clearly visible in figure 2.

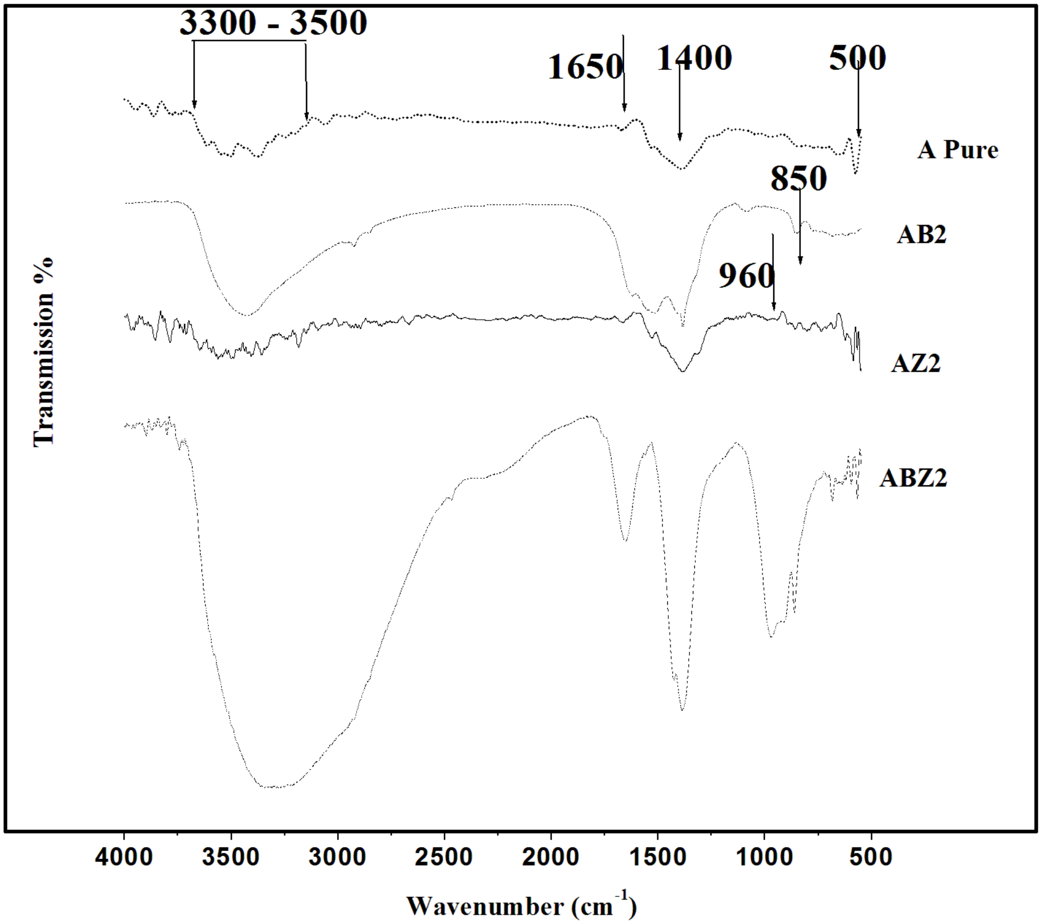

Figure 2 FTIR of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method

3.2 STRUCTURAL STUDIES

Structural analyses of samples were done by XRD and SEM.

3.2.1 XRD

From the XRD (figure 3) it has been observed that the pure sample showsamorphous nature with hump around 30° peak and the Y_2O_3:Bi sample showslight crystalline nature with emerging peaks related to Monoclinic (JCPDS391063) structure of yttrium oxideand Y_2O_3:Zn sample shows better crystallinity with diffraction peaks due to planes in cubic (JCPDS 411105)structure of yttrium oxide and the Y_2O_3:Bi, Zn sample shows amorphousnature due to the suppression by the presence of two dopants.

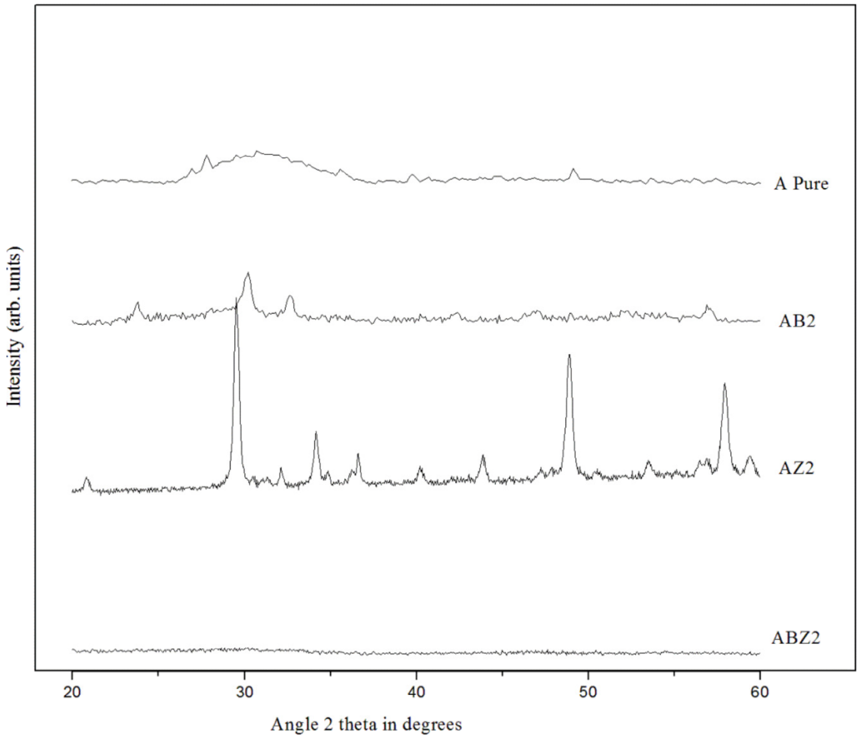

Figure 3. XRD of pureY2O3,, Y2O3: Bi, Y2O3: Zn and Y2O3:Bi, Zn samples of
0.5 weight percentage of yttrium precursoras dopant concentrationprepared by sol-gel method.

3.2.2 SEM

SEM images of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples prepared by sol – gel method of 0.5 weight percentage of yttrium precursor as dopant concentration are shown in figures 4 (a), (b), (c) and (d). From the images it has been observed that pure yttrium oxide shows agglomeration of grains due to dipole interaction and the doped and the codoped samples mostly show triangular or hexagonal morphology due to the presence of dopants[9,10].

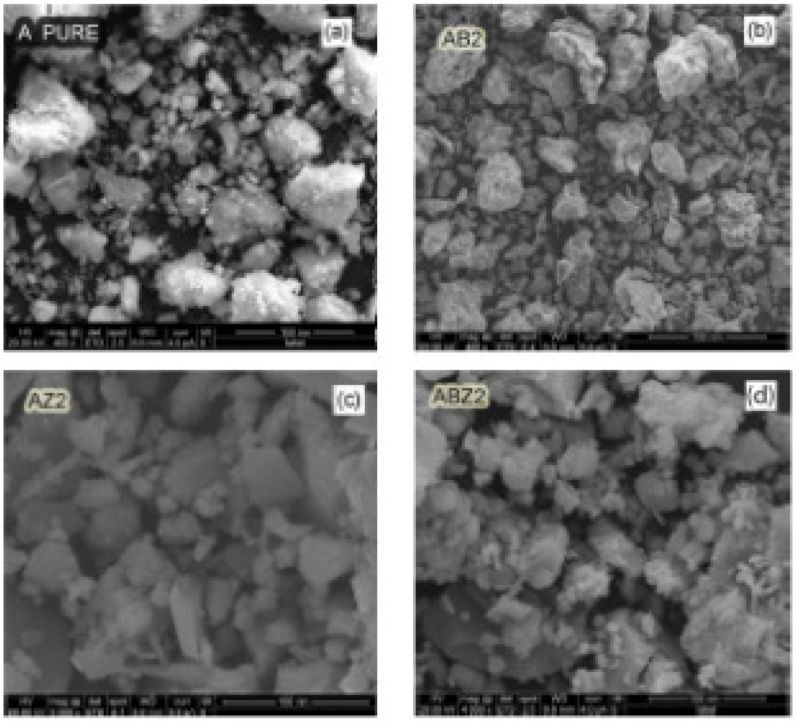

Figure 4 (a), (b), (c) and (d) SEM images of pure yttrium oxide, Y_2O_3:Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples prepared by sol-gel method

3.3 ELECTRICAL STUDIES

The electrochemical impedance spectroscopy is a versatile tool to investigate the conduction mechanism in the pelletized samples. Figure 5 represents Cole - Cole graph, which is drawn between resistive and reactive components of the impedance, of pure yttrium oxide andY_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method by using ammonium hydroxide as precipitating agent. The plot shows a semi-circle in the high frequency range. The semicircle yields information about the properties of the sample. The low frequency intercepts of the semicircle on the real axis yields bulk resistance (R_b) and is extracted from the impedance plots using EQ software developed by Boukamp[11,12]. The bulk resistance and the corresponding relaxation time along with other details of pure yttrium oxide and bismuth and zinc codoped yttrium oxide samples are tabulated in table 1. The presence of the semicircle in impedance plots reveals that there is bulk polarization and ion migration which are physically in parallel [13]. The ionic conductivity of the samples has been evaluated by using the relation ,

$$\sigma = l/R_b A.$$

Where l is the thickness of the pellet, A is its area and $R_b$is the bulk resistance. The maximum ionic conductivity of nearly 3×10^{-7} Scm^{-1} has been obtained for the pellet of bismuth and zinc codoped yttrium oxide, with 0.5 weight percentage of yttrium precursor as dopant concentration and pure sample prepared by sol-gel method. The a.c conductivity obeys Jonscher's Power law [14] and it is found to vary with angular frequency (ω),

$$\sigma(\omega)_{ac} \,\alpha\, A\omega^{n}$$

Where n is the power law exponent, A is temperature dependent parameter. Here in the pure and bismuth and zinc codoped yttrium oxide samples 'n' is found to vary between 0.76 to 0.81, which shows that site relaxation time is more than the backward hopping. From the figure 5 of complex impedance plots of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel, it shows a semi-circle in the high frequency range. And the calculated ionic conductivity appears to be less for Y_2O_3:Zn and Y_2O_3:Bi samples and higher for pure yttrium oxide and Y_2O_3:Bi, Zn samples and it is tabulated in table 1.

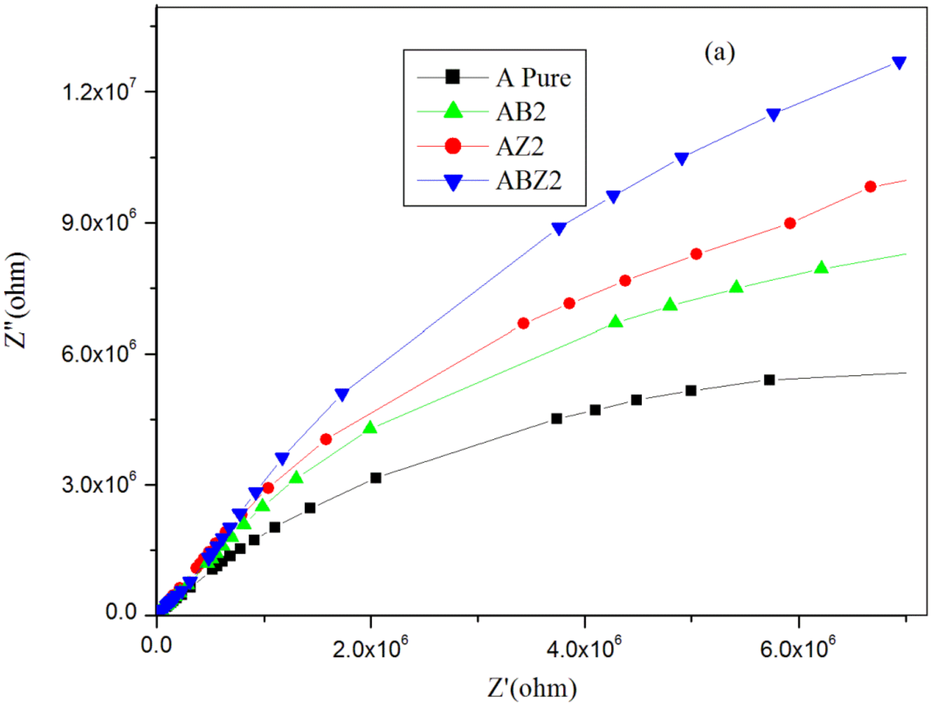

Figure 5 The complex impedance plots of pure and Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method

Table 1 Details of electrical properties of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3: Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration

Sample Name	**Conductivity (Scm^{-1})**	**Bulk Resistance (ohm)**	**Relaxation time (Seconds)**	**n**	**Constant Phase element Cz**
A Pure	3.50×10^{-7}	210400	5.35×10^{-5}	0.780	5.47×10^{-10}
AB2	3.29×10^{-8}	2684200	5.64×10^{-5}	0.787	2.68×10^{-10}
AZ2	5.06×10^{-8}	1455300	5.33×10^{-7}	0.76	1.21×10^{-9}
ABZ2	2.93×10^{-7}	246170	$7.93x10^{-7}$	0.811	4.75×10^{-10}

In general, the dielectric constant study of a nanomaterial gives an outline about the nature of atoms, and ions, and their bonding in the material. Here, the dielectric constant was measured as a function of frequency (40 Hz - 1MHz) at room temperature. The dielectric constant was evaluated by using the following relation,

$$\varepsilon_r = (Cd / \varepsilon_0 A)$$

Where C is the capacitance, d is the thickness of the pellet, and A is its area and ε_0 is the relative permittivity of free space.

It is observed that the dielectric constant decreases with increase in frequency, showing dispersion in low frequency range. All samples show dispersion due to Maxwell-Wagner polarization and are also in agreement with the Koop's phenomenological theory [15, 16].

From the analysis of the dielectric constant and dielectric loss as a function of frequency, the different polarization mechanisms in solids can be understood. At lower frequencies as all the four types of polarization are involved, the dielectric constant and the dielectric loss are very high. From the dielectric constant and the dielectric loss (Figure 3) of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method, it has been observed to decrease gradually due to the increase in the frequency, which is due to the presence of polarizations (interfacial and dipolar) and the disappearance of the other two types. This proves that the dielectric constant and dielectric loss are strongly frequency dependent.

It has been observed from the figure 6 of dielectric study of pure yttrium oxide and Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method, that the dielectric constant is high at low frequency which may be due to the space charge polarization and low at high frequency region. Apart from pure samples, mostly Y_2O_3:Zn samples show high dielectric constant value and dielectric loss value too.

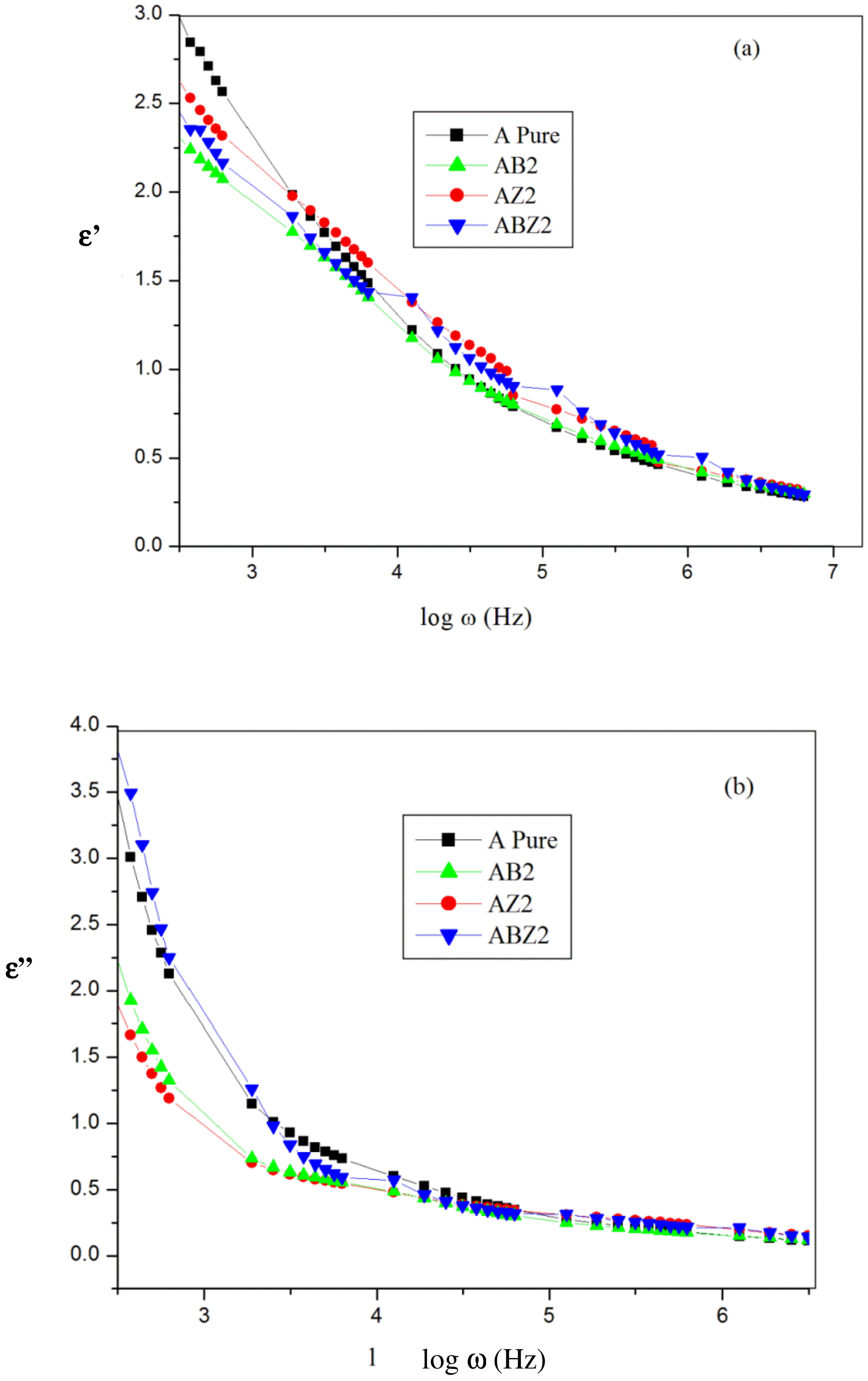

Figure 6 Variation of dielectric constant and loss factor of pure yttrium oxide, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel (a & b), at room temperature.

The measure of ratio of the dielectric loss factor ε'' to the dielectric constant ε' is defined as loss tangent. It is given as

$$\tan \delta = \varepsilon''/\varepsilon'$$

It is useful to obtain relaxation parameters of the samples. From the analysis of variation of loss tangent spectra from the figure 7 of pure Y_2O_3, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method, tan δ increases with frequency and reaches a maximum value and then decreases. The calculated relaxation time is found to be less for the pure Y_2O_3, and Y_2O_3:Bi, Zn samples.

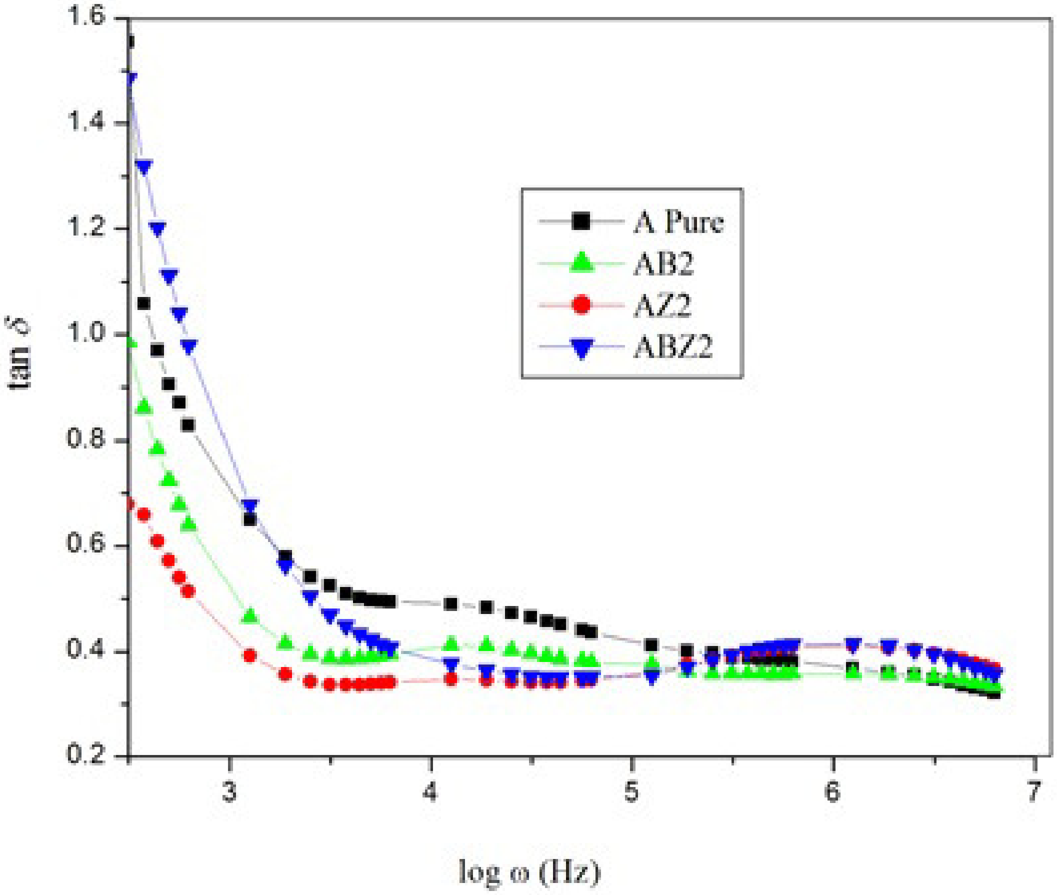

Figure 7 Variation of dielectric loss factor of Y_2O_3, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor dopant concentration prepared by (a) sol-gel method with frequency at room temperature

4. CONCLUSION

In this paper electrical property of pure Y_2O_3, Y_2O_3: Bi, Y_2O_3: Zn and Y_2O_3:Bi, Zn samples of 0.5 weight percentage of yttrium precursor as dopant concentration prepared by sol-gel method are analysed. Presence of functional group is identified by FTIR studies. Structural analysis is done by XRD and SEM, which shows the influence of dopants. It has been observed that pure Y_2O_3 and

Y_2O_3: Bi, Zn samples show good electrical property than other samples. Single dopant samples did not show enhancement in the electrical properties due to doping, on the contrary the conductivity is decreased. However, the codoped samples show better properties compared with single dopant hence paves the way for use of bismuth and zinc codoped yttrium oxide samples for future applications.

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