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Structural and Electrical Characterization of High-Knano Crystalline Erbium Oxide

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ABSTRACT

The effect of different annealing temperatures on the crystalline structure, average crystallite size, por specific surface area, dislocation density and strain are studied through x-ray diffraction at room temperature The morphology and the composition of the specimen were checked through the Scanning Electron Micro (SEM) and EDX respectively. The dielectric constant, loss factor are measured in the frequency range of 20 3MHz at room temperature. The ac conductivity in this frequency was determined using the diel parameters.Er_2O_3 may be useful as a gate dielectric.

Keywords: *Ac conductivity, X-ray diffraction, Dielectrics, Specific surface area, Dielectric parameters.*

INTRODUCTION

Nano sized materials have become very important at present, because of its applications in modern technology, fuel cells [1], agriculture [2], medical devices [3], electronics [4] and food industry [5]. The rare earth elements are nontoxic [6] and have unique properties because of $4f^n$electronic structure. They play an important role in the optical fibers and lasers [7] because of their emission spectrum that lies in ultra violet and near infrared region [8]. Integrated circuits are used in almost every device in our daily life. Electronic industry is trying to scale down devices according to Moor's Law [9]. Materials with high dielectric constants ($\acute{\varepsilon}$) are required for the scaling of the devices at the current rate. Rare-earth oxides appear to be a good replacement.Er_2O_3 has a cubic bcc structure up to 2320 ˚C and a hexagonal close packed structure above 2320 ˚C [10]. Its melting temperature is 2430 ˚C[11]. Each unit cell of Er_2O_3contains 80 atoms, 32 of which are Er-atoms which are located on 86b and 24d Wyckoff positions, and 48 oxygen atoms sit in 48e (x = 0.3914, y = 0.1528, z = 0.3819) position [11]. Band gap of $Er_2O_3$is reported to be 5.4eV [11]. This material is used for thermal barrier coatings and structural application [13] because of its extraordinary thermal and chemical stability. Toughness of the Er_2O_3 is comparable to other ceramics such as magnesia and alumina [13].This material is inert to most liquid metals, so it can be useful as corrosion-resistant material [14]. The wide band gap, the unique electrical properties and high dielectric and thermal stability make erbium oxide to replace SiO_2 [15]. This material is also used for thermal barrier coatings in jet engines, because of oxidation resistant. In the present work, Er_2O_3 powder was purchased from the market (sample a).It was annealed at 920 ˚C and 1200 ˚C for three hours respectively and named samples (b) and (c). The characterization of the Er_2O_3 samples for structural analysis by X-ray diffraction; morphology through SEM/ EDX are reported. The study of the dielectric properties over a wide range of frequency (100 Hz-3MHZ) was also carried out to check its potential use as a high-k material.

EXPERIMENTAL

Sample Fabrication

Erbium oxide powder was purchased from the market and its structural information was checked through X-ray diffraction. Afterward it was pressed to measure the dielectric properties of the sample. The pressing of the sample was followed by cold isostatic pressure. Powder of Er_2O_3 was pressed to make thepellets. The pellets of erbium oxide wereinserted in the

rubber mould and sealed the mould in the pressure vessel under the pressure of 2000 bars. Held the pressure on the pellets for 15 minutes and then depressurized it to get the green strength of the pellet. The pellets were annealed at temperatures of 920°C and 1200°C for 3 hours. The samples of erbium oxide were passed through the X-ray diffraction to check the effect of the annealing temperature on the structure and dielectric properties of erbium oxide. The surface morphology was observed through scanning electron microscopy with the elemental analysis by EDX.The dielectric parameters of the samples were measured at room temperature and as a function of frequency.

Characterization techniques

The phase identification and structural analysis were done by X-ray diffraction, using CuK_{α}(λ = 1.5418Å) as the diffraction radiation. The average crystallite size of the powders was determined using Schererformula [16-17].

$$t = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where λ = wave length of X-rays, t = average crystallite size; θ = Bragg's angle; β = Full Width at Half Maxima of the recordedθ, taken in radians.

The lattice parameter (a) was calculated from the X-ray diffraction data using formula [18]

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (2)$$

where'd' is the d-spacing of the diffraction planes ;h, k and l are the miller indices of the diffraction planes in the XRD pattern. The lattice constants for the samples are tabulated in Table 1. X-ray density $\rho_x$can be calculated from the X-ray data using the relation [19-20].

$$\rho_x = \frac{16M}{N_A a^3} \quad (3)$$

here'M' is the molecular weight of the sample, 'N_A' is Avogadro's number (6.022 x 10^{23}atoms/mole) and 'a'is the lattice constant, 16is the number of molecules per unit cell.

Measured density can be resolved for each sample from the pellets dimensions from the formula [18, 19]

$$\rho_m = \frac{m}{\pi r^2 h} \quad (4)$$

'ρ_m' is the measured density,'m' is the mass of the pellet. 'r'is the radius of the pellet and 'h' is height of the pellet. The porosity of each pellet was calculated with the help of the well-known relation[20].

$$\rho = (\rho_x - \rho_m)/\ \rho_x \quad (5)$$

where'ρ_x'and'ρ_m'are the X-ray and measured densities respectively.

The specific surface (S_s) area (m^2g^{-1})was estimated by the relation [20], using the above mentioned parameters.

$$S_s = 6000/t\,\rho_m \quad (6)$$

The dislocation density (D_d) was estimated from the average crystallite size as

$$D_d = \frac{1}{t^2} \quad (7)$$

Lattice strains of the Er_2O_3 was determined using the Williamson-Hall formula

$$\varepsilon = \frac{ß}{4\tan\theta} \quad (8)$$

All the obtained values of these parameters are given in Table 1. The morphological investigation was done using scanning electron microscopy (SEM) and (EDX). The dielectric constant ($\dot{\varepsilon}$), dielectric loss tangent ($\tan_{\delta}$) and acconductivity (σ_{ac})of the samples were measured in the frequency range of 100Hz to 3MHz at room temperature. Dielectric measurements were carried out using WANE KERR LCR meter 6440B.The digital LCR meter provides information of frequency, series capacitance (C_s), parallel capacitance (C_p), and quality factor (Q). The thickness (l) of our samples was approximately 1.97mm; diameter of pellet≈ 14mm and the area (A) of pellet was calculated using these data. The calculations for dielectric constant ($\dot{\varepsilon}$), imaginary part (ε'')of dielectric constant and dielectric loss tangent ($tan\delta$) are completed using the following standard equations[17, 18].

$$\dot{\varepsilon} = \frac{(C_p l)}{\varepsilon_\circ A} \quad (9)$$

$$\varepsilon'' = (\tan\delta)\dot{\varepsilon} \quad (10)$$

$$\tan\delta = \frac{1}{Q} = \frac{\varepsilon''}{\dot{\varepsilon}} \quad (11)$$

From the values of dielectric constant and loss tangent, the ac electrical conductivity (σ_{ac}) of the samples, was calculated using the relation [20]

$$\sigma_{ac} = \omega\,\varepsilon_0\,\dot{\varepsilon}\tan\delta \quad (12)$$

where $\omega = (2\pi f)$, f is the applied frequency and all other variables are defined already.

RESULTS AND DISCUSSION

Structural Analysis

The X-ray diffraction was performed at room temperature and is shown in Fig.1. The samples were labeled as: powder of erbium oxide as (a) pellet of erbium oxide annealed at 920°C as (b) and pellet of erbium oxide annealed at 1200°C as (c).The XRD results revealed the cubic (bcc) structure of all the erbium oxide samples.

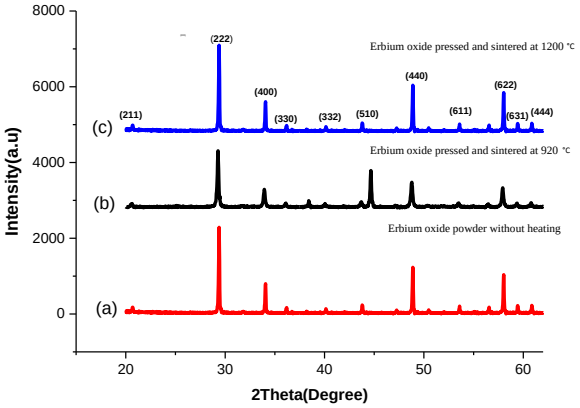

Figure1.*X-ray diffractions patterns of samples (a), (b) and (c)*

The results of XRD showed the nano crystalline sizes of the erbium oxide. The results disclosed that as the annealing temperature increased the average crystallite size also increased. For the most prominent peak (222), the average crystallite size of the samples (a), (b) and (c) was found to be 53.94nm, 65.41nm and 75.45nm respectively. The lattice constant of samples also calculated from the XRD pattern was10.50A, 10.54A and 10.53A corresponding to samples (a), (b) and (c).This agreed with the reported literature [21, 22] within experimental errors. The XRD patterns ofall thesamples were also in agreement with JCPDS card numbers 00-001-0827.As the annealing temperature of the erbium oxide increased the peaks became more intense as intensity of peaks showed the crystallinality of the material.The parameters of the XRD analysis are shown in Table 1.

Table1.*Lattice constant (a), crystallite size ($t_{(222)}$) ,bulk density(p_x), dislocation density(m^{-2}) strain(%), porosity(%), specific surface density(S_s) of erbium oxide*

XRD parameters	sample(a)	sample(b)	sample(c)
Lattice constant (A)	10.50	10.54	10.53
Average crystallite size (nm)	53.94	65.41	75.48
Bulk density(gcm^{-3})	8.78	8.79	8.80
Measured density(gcm^{-3})	-	4.84	5.52
P%	-	45	36.1
Specific Surface area (m^2g^{-1})	-	18.95	14.40
Dislocation density*10^18(m^{-2})	3.436	2.337	1.7552
Strain%	0.006	0.005	0.0045

Scanning Electron Microscopy

The scanning electron microscopy (SEM) was done on powder and pellets of erbium oxide. The micrographs of the SEM confirmed the Nano- sized composites structure of erbium oxide samples (a), (b)and(c). The size of the grainsvaried from 70nm to 350nm, deviating the accepted definition of Nano materials that is 100nm. Another noted point is that the x-ray diffraction gives the average crystallite size while SEM provides the grain/particle sizes. The SEM micrographs of erbium oxides for samples (a), (b) and(c) are shown in Figs. 2 and 3. The shapes of the grains are spherical. The micrographs of pellets which were annealed at temperature of 1200°C showed the homogenous distribution of the grains with less porosity as compared to the powder sample of erbium oxide for sample (a) and (b). Some grains are agglomerated with each other to form cluster with various shapes. As the annealing temperature increased the gain size increased

and the thickness of the grain boundaries decreased as a result of crystal growth.

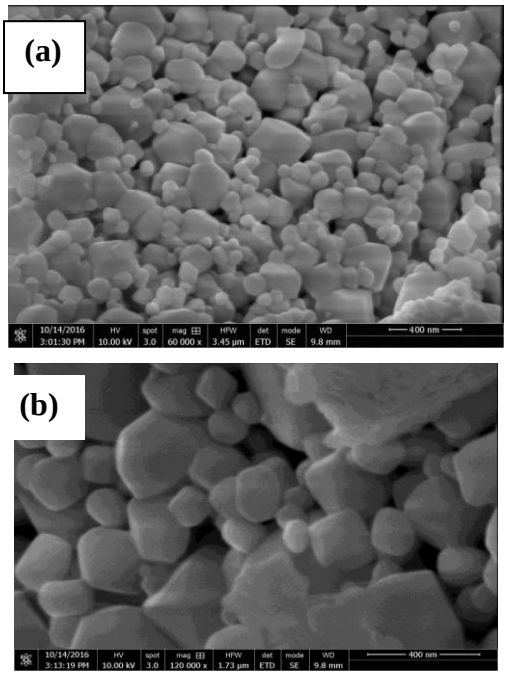

Figure2. *SEM micrographs of erbium oxide samples (a) and (b).*

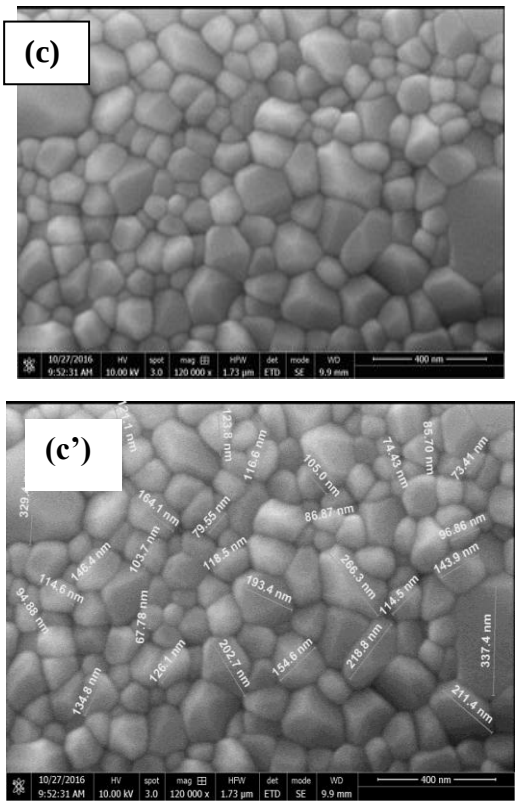

Figure3.*SEM micrographs of erbium oxide sample (c) and its size measurements (c').*

The grain size distribution of the erbium oxide sample annealed at 1200°C is shown in Fig.4. The diameter of the grain varied from 73nm to 340nm.This shows that by heating the sample the grain sizes of erbium oxide increased as compared to the sample without heating(sample a). The EDX revealed the presence of erbium and oxygen elements in all the samples as is shown in Fig.5 for sample (c).

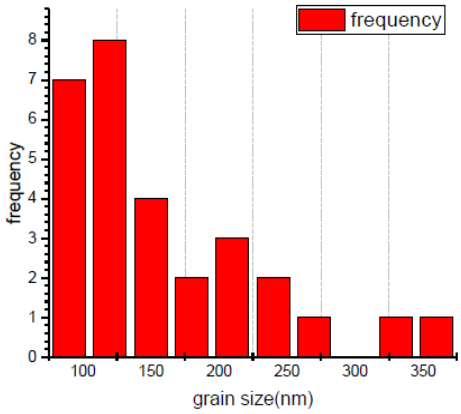

Figure4. *Distribution of grain sizes in erbium oxide for sample (c)*

Dielectric parameters

Dielectric constant

The dielectric constant of the erbium oxide annealed at 920°C and 1200°C weremeasured using LCR meter in the frequency from 100Hz to 3.0 MHz at room temperature. Figs. 6 and7 show the dielectric parameters with respect to frequency. As annealing temperature of material increased, the dielectric constant of the sample(c)also increased. The grain size of the erbium oxide increased andenhanced the dielectric properties of the erbium oxide. The dielectric constant had an inverse dependence on the frequency, as the frequency increased; polarization in erbium oxide samples decreased and became constant at higher frequencies due to material conductivity. The variation of the dielectric constant with frequency obeys the Maxwell Wagner theory.

Loss tangent

Dielectric loss tangent explains the energy loss inside the erbium oxide. It was due to the weak polarization at the higher frequencies. Here polarization lags after the applied ac field.Figs.6 (D_2) and 7(D_2)show the relationship between the loss tangent and frequency at constant room temperature. The graphs show that loss tangents have maximum value at low frequencies and became smaller at higher frequencies because as the polarization becomes constant electrons get mobile. It is also evident from the plot between loss tangent and frequency for sample (b) that Debye relaxation peak occurs at

lowerfrequencies because of the resonance phenomena. It was also noted that the loss factor for sample (c) was higher compared to the loss factor for sample (b) because of the increase in grain sizes due to annealing at higher temperature.

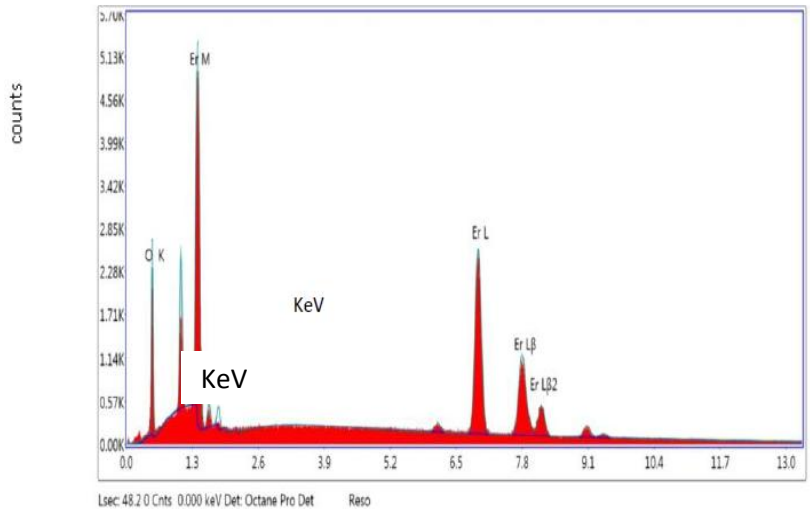

Figure5.*EDX spectrum of erbium oxide powder (sample c)*

Ac- conductivity

The ac-conductivity as a function of frequency is shown in Figs.6 (D_3) and 7(D_3). Ac-conductivity is directly proportional to the frequency as given in equation (12) above. It is also clear from the observations that ac conductivity increased with a rise in frequency. Similar results are reported by Bakhsh and Maqsood [21]. The dielectric behavior can be explained on the basis of Maxwell-Wagner polarization [23] and Koop's Dielectric theory [24]. According to Maxwell-Wagner model, the mobility of charge carriers is impeded by existence of interfaces or grain's boundaries in the material. This causes Maxwell-Wagner polarization at the interfaces and increases the dielectric constant at low frequencies (from mHz to several Hz), at higher frequency mobile ions cannot follow the frequency and Maxwell-Wagner polarization is no more effective. The dielectric loss of both the samples is higher at low frequency, which decreased with the rise in frequency.

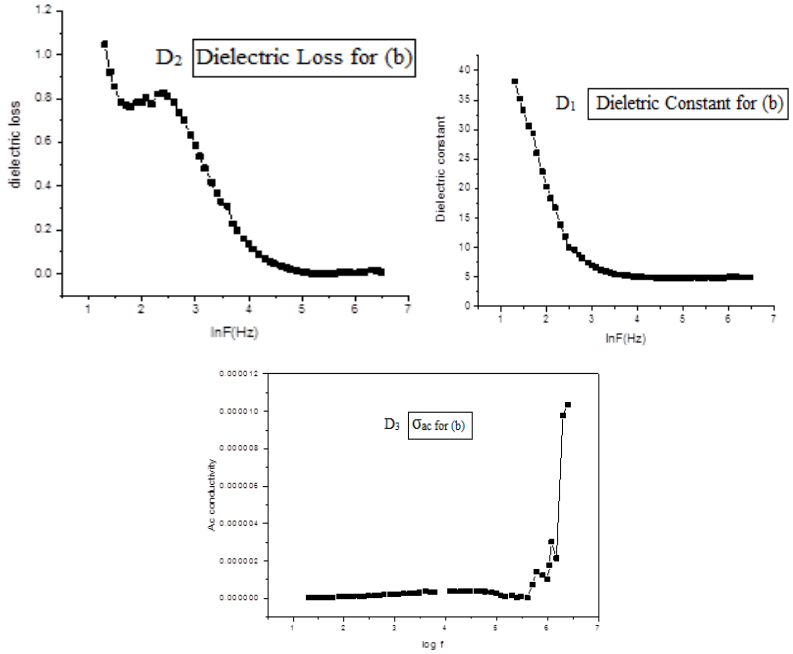

Figure6. *Variation of (D_1) dielectric constant (D_2) loss tangent and (D_3) ac conductivityas a function of frequency for sample (b)*

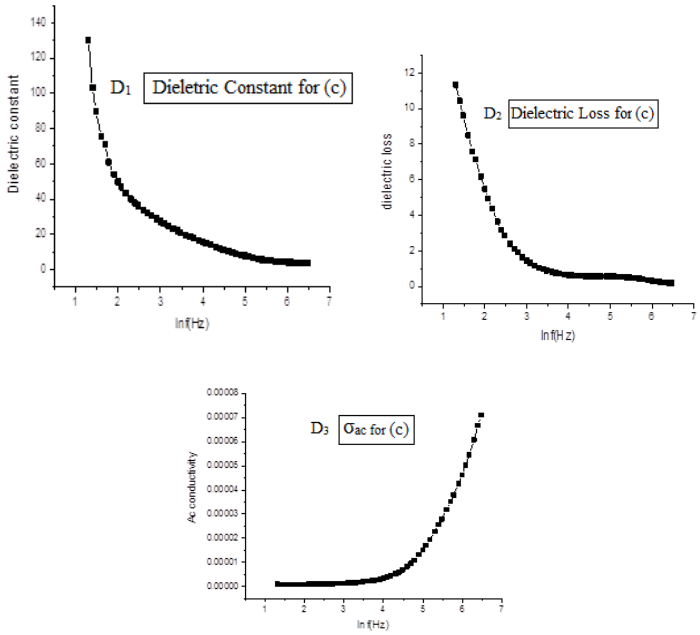

Figure7.*Variation in (D_1) dielectric constant,(D_2) loss tangent and (D_3) ac conductivity as a function of frequency for erbium oxide sample (c)*

The dielectric parameters for samples (b) and (c) at various frequencies are tabulated in table 2.

Table2.*Dielectric constant (ὲ), Dielectric loss tangent (tanδ) and ac conductivity (σ_{ac}) for erbium oxide samples (b) and (c)*

Electrical Properties	**Sample (b)**	**sample (c)**
$\acute{\varepsilon}$ at 1 MHz	5.04768	4.17324
$\acute{\varepsilon}$ at 2MHz	4.96781	3.93903
$\acute{\varepsilon}$ at 3 MHz	4.95184	3.9231
tanδ at 1MHz	0.0373	0.32167
tanδ at 2MHz	0.0175	0.22385
tanδ at 3 MHz	0.0093	0.1749
σ_{ac} at 1MHz (sm^{-1})	$10.460x10^{-6}$	$7.093x10^{-5}$
σ_{ac} at 2MHz(sm^{-1})	$9.6911x10^{-6}$	$6.0762x10^{-5}$
σ_{ac} at 3MHz(sm^{-1})	7.678×10^{-5}	$4.653x10^{-5}$

CONCLUSION

The nano crystalline size of the erbium oxide with cubic (bcc) structure was confirmed from the X-ray diffraction.The effect of the annealing temperature on the erbium oxide showed the growth of crystallite size. The bulk densities of the erbium oxide samples (erbium oxide powder, erbium oxide pressed and sintered at 920°C and 1200°C) were in agreement with the reported density of the erbium oxide. The SEM micrographs showed as the sintering temperature increased, the size of grains increased and the distribution of grains got more homogenous. As the powder of erbium oxide was pressed by a pressure of 2000 bars, SEM showed the agglomerated clusters of grains with spherical shapes. The presence of erbium and oxygen elements in the material was confirmed by energy dispersive analysis. As the frequency increased, the dielectric properties of the erbium oxide decreased. The dielectric constant of the erbium oxide increased as the sintering temperature increased. This study provides useful information and further understanding of erbium oxide as high-k materials. This study is expected to contribute in the future progress of microelectronics industry.

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