

Dielectric Properties and A.C. Conductivity of Nanocrystalline Titania

Priyanka K P¹, Sunny Joseph¹, Smitha Thankachan², Mohammed E M², Thomas Varghese^{*1}

¹Nanoscience Research Centre (NSRC), Department of Physics, Nirmala College, Muvattupuzha-686 661, Kerala, India

²Department of Physics, Maharajas College, Ernakulam, Kerala, India

^{*1}nanoncm@gmail.com

Abstract- Nanocrystalline TiO₂ with different particle sizes was prepared by a low temperature sol-gel synthesis route. The particle sizes were determined through X-ray diffraction technique. The dielectric properties of nanocrystalline TiO₂ at different frequencies ranging from 20 Hz to 20 MHz have been studied over a temperature range 303 K-383 K. It is observed that the dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of all the samples decrease steeply as the frequency is increased and attains a constant lower value at high frequencies. The a.c. conductivity was derived from dielectric constant and loss tangent data. It has a low value at smaller frequencies, which increases as the frequency is increased.

Keywords- Nanotitania; Dielectric properties; A.c. conductivity

I. INTRODUCTION

Nanocrystalline TiO₂ particles are of great interest due to their unique properties and several potential technological applications such as photocatalysis, sensors, solar cells and memory devices [1-4]. TiO₂ exists in three polymorphic phases: rutile (tetragonal, density = 4.25 g/cm³), anatase (tetragonal, 3.894 g/cm³) and brookite (orthorhombic, 4.12 g/cm³). The low-density solid phases are less stable and undergo transition to rutile in the solid state. The transformation is accelerated by heat treatment and occurs at temperatures between 450 and 1200 °C [5]. This transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration, reaction atmosphere and annealing temperature [6-9].

Control of the size, shape and structure of the colloidal precursor is an important factor in determining the properties of the nanomaterial. Titania powders can be synthesized using various methods such as sulfate process [10], chloride process [10], impregnation [11], coprecipitation [12], hydrothermal method [13-15], direct oxidation of TiCl₄ [16] and metal organic chemical vapor deposition method [17]. Sol-gel method [18-20] is one of the most suitable routes to synthesize various metal oxides due to low cost, ease of fabrication and low reaction temperatures. This method is widely used to fabricate TiO₂ for films, particles or monoliths. In general, the sol gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The homogeneity of the gels depends on the solubility of reagents in the solvent, the sequence of addition of reactants, the temperature and the pH. The optimum fabrication conditions are provided for the narrow size distribution of the nanocrystalline TiO₂. In this paper we report a systematic study of the dielectric properties and a.c.

conductivity of nanophase TiO₂.

II. EXPERIMENTAL

In this work, the precursor solution was a mixture of 5 cc titanium (IV)-n-butoxide (Ti(OBu)₄) (98%, supplied by Alfa Aesar) and 10 cc isopropyl alcohol (99%, supplied by Fisher Scientific). The mixture solution was added drop wise into a solution whose pH value was adjusted to 2.0 by adding HNO₃. The reaction was performed at room temperature while stirring for 2 hours. After complete hydrolysis of Ti(OBu)₄, the solution was refluxed at 70°C for 20 hours and a sol was formed. Finally, the as-prepared sol was vacuum dried at 60°C for 2 hours to obtain TiO₂ powders. The obtained powder samples were calcined for 2 hours in a furnace at temperature ranging from 150 to 800 °C in an ambient atmosphere.

The structural characteristics of the synthesized titania nanoparticles have been studied by X-ray powder diffraction (XRD) using Bruker D8 Advance X-ray diffractometer ($\lambda = 1.5406 \text{ \AA}$). X-ray diffraction analyses were carried out for the identification of the crystal phase and the estimation of the average crystallite size. The crystallite size was estimated from the Debye-Scherrer equation [22-25]. The Debye-Scherrer equation is given by

$$t = 0.9 \lambda / \beta \cos \theta, \quad (1)$$

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the peak and θ is the Bragg's angle.

The as-prepared powder sample was consolidated in the form of cylindrical pellets of diameter 10 mm and thickness 1.2 mm at a pressure of ~ 5 GPa using a hydraulic press. Both the faces of the pellets were coated with air drying silver paste for good electrical contact. The pellets were air dried for 15 minutes and then heat treated at 100 °C for 30 minutes in a hot air oven for electrode curing. Dielectric measurements as a function of frequency in the range of 20Hz - 20 MHz are measured at various selected temperatures from 303 K- 383 K using a four probe impedance analyser (Wayne Kerr H-6500B model) in conjunction with a portable furnace and temperature controller ($\pm 1\text{K}$). The dielectric constant was calculated by using the formula

$$\epsilon' = Cd/\epsilon_0 A. \quad (2)$$

where C is capacitance of pellet in pF, d the thickness of pellet, A the cross-sectional area of the flat surface of the pellet and ϵ_0 the permittivity for free space. The a.c.

conductivity (σ_{ac}) is obtained from the data of dielectric constant (ϵ') and loss $\tan \delta$ using the relation

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta, \quad (3)$$

where $\omega (=2\pi f)$ is the angular frequency. Thus, σ_{ac} depends strongly on the frequency of the applied field.

III. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of as prepared and calcined TiO_2 samples (A - anatase, R - rutile). The XRD pattern of the sample calcinated at 300 °C revealed the presence of the anatase phase. Above 400 °C rutile peaks started to appear and a mixture of both the anatase and rutile phases of TiO_2 existed up to 800 °C. When the calcination temperature is 600 °C, quite sharp peaks of rutile phase are observed. This suggests that there is a phase transition from anatase to rutile at the temperatures lower than 600 °C, which agrees with previous experiments [21]. The residual anatase phase still exists in the samples up to 800°C. At 800°C, the transition to the rutile phase is almost complete. Fig. 1 shows that the diffraction peaks become intense and their FWHM gradually decreases with increasing calcinations temperature, verifying the increase in particle size and increase in pertinent phase.

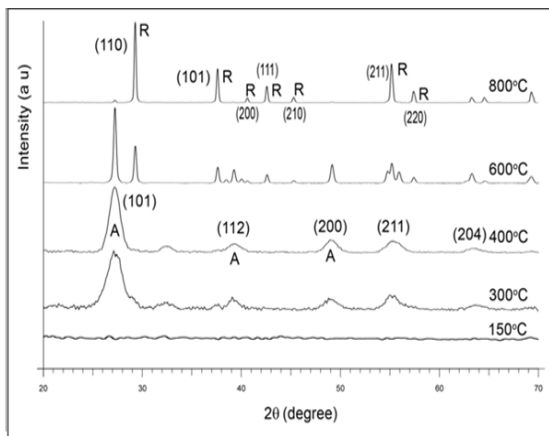


Fig. 1 The XRD spectra of nanocrystalline TiO_2 powder samples treated at different temperatures between 150 °C and 800 °C (A- Anatase; R- Rutile)

The effect of calcinations temperature on the crystallites size is presented in Table 1. At higher calcinations temperatures, the formed crystallites are larger in size, which can be attributed to the thermally promoted crystallite growth. The size of the anatase crystallites increases from 4.6 to 25.8 nm when the calcination temperature is raised to 600 °C. Similar observations have been reported in Literature [22].

TABLE 1 XRD RESULTS FOR TiO_2 CALCINED AT DIFFERENT TEMPERATURES FOR 2 HOURS

Crystallite size (nm)		Calcined temperature (°C)	Sample code
Rutile	Anatase		
--	4.6	300	S ₄
--	5.8	400	S ₃
--	25.8	600	S ₂
33.6	--	800	S ₁

A. Temperature Dependence of ϵ' and $\tan \delta$

Fig. 2(a) presents the variation of dielectric constant ϵ' with frequency at different temperatures, showing that dielectric constant decreases in all temperatures with increase in frequency, which can be considered as a normal dielectric behavior [23]. This behaviour can be explained on the basis of Koops theory [24]. According to Koops theory the dielectric structure is an inhomogeneous medium of two layers of the Maxwell-Wagner type [25]. The dielectric structure is assumed to be composed of a highly conducting grain separated by relatively poor conducting substance called the grain boundaries. This causes the localized accumulation of charges under the influence of electric field, which results in interfacial polarization. The effect of grain interfaces is more obvious at lower frequencies where we observe relatively large values of ϵ' . The space charge polarization occurring at the interfaces at lower frequencies can also be contributed to the dielectric permittivity at lower frequencies [26]. The dielectric constant initially decreases abruptly with increase in frequency. However, it remains almost constant at higher frequencies for all samples (Fig. 2). The reason is that beyond a particular frequency of the applied electric field, the electron exchange does not follow the alternating field [27]. Hence the polarization decreases causing a decrease in dielectric constant ϵ' . Since more dipoles will be oriented as temperature increases, an increase in dipole moment might occur [28]. As a result, the value of ϵ' increases with increase in temperature for fixed frequencies.

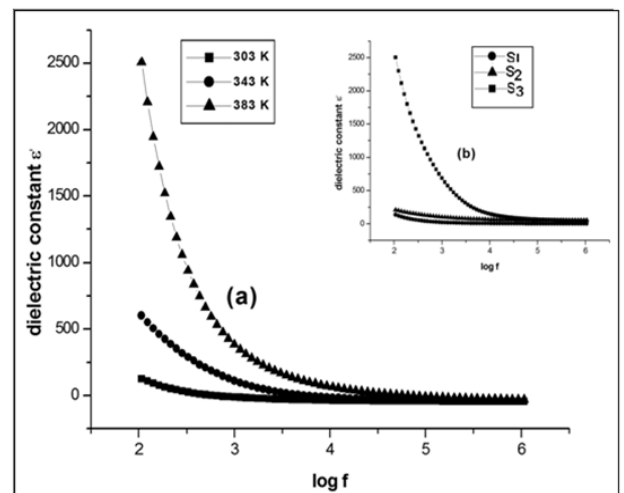


Fig. 2 Variation of dielectric constant (ϵ') with frequency of sample S₃ at different temperatures and (b) samples S₁, S₂ and S₃ at room temperature

Fig. 2(b) shows that at room temperature the values of ϵ' increases with the increases of the calcinations temperature, and the sample (S₁) calcinated at 800 °C has a large value for the dielectric constant, where the rutile phase is predominant. This anomalous behaviour might occur due to the increase of the ratio between the anatase and rutile crystal form. It is known that rutile phase has a dielectric constant higher than that of anatase phase [29]. This kind of anomalous dielectric behaviour can be ascribed to interface polarizations [30]. At lower frequencies the increase in dielectric constant with temperature is mainly due to

polarization of interfacial dipoles which are strongly dependent on temperature [31]. As temperature increases, the accumulation of charges on the grain boundaries increases, which causes an increase in the interfacial polarization at lower frequencies. Therefore the dielectric polarization increases resulting in an increase of ϵ' with temperature at lower frequencies.

There is a correlation between the conductivity and the dielectric behaviour of the material. The conductivity is mainly due to hopping of electrons. When hopping frequency is almost equal to the frequency of the applied electric field, a maximum of loss tangent will occur [32]. The variation of loss tangent ($\tan \delta$) of sample S_3 as a function of frequency and temperatures is shown in Fig. 3(a). In nanomaterials, impurities, defects and space charge formation in the interface layers together produce an absorption current causing a dielectric loss. As the frequency of the applied field increases the absorption current gets reduced, and hence the dielectric loss will be reduced as shown in Fig. 3(a). Since the probability of hopping of electrons per unit time increases with temperature, the loss tangent also increases (Fig. 3(a)). At higher frequency end, the loss factor is caused by the conversion of movement of charges into vibration of the lattices, i.e., phonons [33]. It is found that the values of $\tan \delta$ initially decrease rapidly with frequency and then decrease at a slower rate. The variation of $\tan \delta$ with frequency for different samples is shown in Fig. 3(b). It can be seen that the sample (S_3) with a particle size of 5.8 nm calculated at 400 °C has a large value for the loss tangent ($\tan \delta$) at a temperature of 383 K. It can be seen from the Fig. 3(b) that as particle size decreases the dielectric loss tangent increases. When the particle size reduces, the volume percentage of interface boundaries and the amount of defects that cause various kinds of polarizations might increase. This is the reason why the value of dielectric loss tangents increases with respect to reduction in particle size. The absence of dielectric loss peaks in the frequency versus dielectric loss curves of the

present samples show the wide distribution of relaxation times [34].

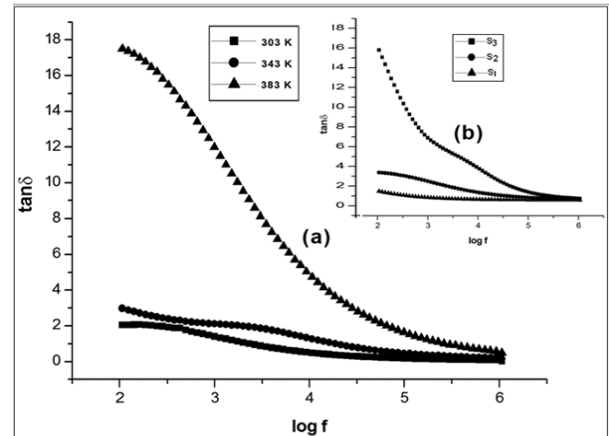


Fig. 3 Variation of loss tangent ($\tan \delta$) with frequency of (a) sample S_3 at different temperatures and (b) samples S_1 , S_2 and S_3 at 383 K

B. Temperature Dependence of a.c. Conductivity

The plot of a.c. conductivity (σ_{ac}) of sample S_3 with frequency and temperature is shown in Fig. 4(a). It is clear from the figure that the conductivity is found to be high for higher frequencies at a given temperature, which confirms small polaron hopping in the present sample [35]. As the frequency of the applied field increases, hopping of charge carriers also increases thereby increasing the conductivity. A similar variation is observed for other temperatures. The increase of ac conductivity with temperature is also evident in Fig. 4(a). The maximum value of σ_{ac} at 303 K is 0.25×10^{-3} while the corresponding value of σ_{ac} at 383 K is 2.4×10^{-3} . The a.c. conductivity is much more sensitive to temperature in the higher temperature regime than the lower temperature regime. The low temperature a.c. conduction can be due to bipolar hopping mechanism whereas the high temperature conduction is due to thermally activated single polaron hopping [36].

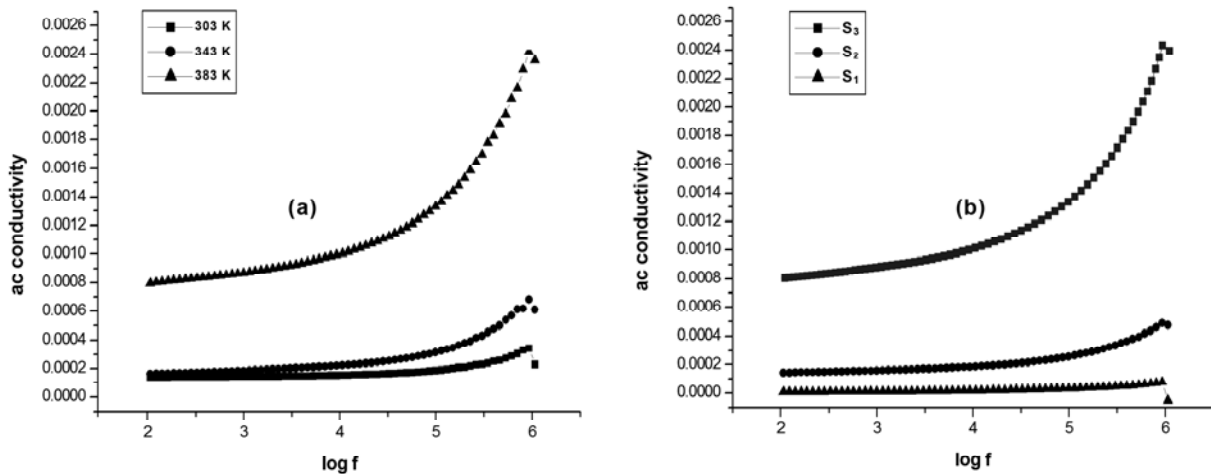


Fig. 4 Variation of a.c. conductivity (σ_{ac}) with frequency of (a) sample S_3 at different temperatures and (b) samples S_1 , S_2 and S_3 at 383 K

The variation of σ_{ac} for samples S_1 , S_2 and S_3 at 383 K is shown in Fig. 4(b). It is found that the a.c. conductivity decreases with increasing calcinations temperature. At higher calcinations temperature, the formed crystallites are larger in size, hence, the hopping distance decreases which might cause the decrease of a.c. conductivity [36]. For sample S_1 , the maximum value of σ_{ac} is 0.15×10^{-3} while the corresponding values for samples S_2 and S_3 are 0.4×10^{-3} and 2.4×10^{-3} respectively. According to Elliot's barrier hopping model, the a.c. conductivity is given as

$$\sigma_{ac} = n\pi^2 NN_p \varepsilon' \omega R_w^6 / 24 \quad (4)$$

where n is the number of polarons involved in the hopping process, NN_p is proportional to the square of the concentration of states and R_w is the hopping distance [36]. If the particle size of the sample is reduced, the hopping distance increases which in turn increases σ_{ac} as is evident from the Equation (4). In the present work, the value of σ_{ac} increases as the particle size of the sample is reduced from 25.8 nm to 5.8 nm, is a direct confirmation of the Elliot's theory.

IV. CONCLUSIONS

The sol-gel synthesis route was employed to fabricate nanotitania powders with an average particle size of 5.8 nm for the anatase phase. Anatase and rutile phases were investigated through a controlled calcinations process. Anatase phase is formed with calcinations temperature above 300 °C, and rutile is the only crystal phase present for temperatures above 800 °C. The dielectric constant decreases in all samples with increase of frequency. The highest dielectric constant value has been observed for the sample calcinated at 800 °C and was assigned to grain-boundary polarization. The dielectric loss tangent decreases with frequency, and the sample with minimum particle size shows large value of $\tan \delta$ at a specific frequency. The a.c. conductivity is found high for higher frequencies at a given temperature and was confirmed small polaron hopping in the present sample.

ACKNOWLEDGMENT

The authors acknowledge their thanks to Nirmala College, Muvattupuzha and Maharajas College, Ernakulam for providing the opportunity to undertake this study. The financial support by KSCSTE, Thiruvananthapuram and University Grants Commission, New Delhi is gratefully acknowledged.

REFERENCES

- [1] W. Li, S.I. Shah, C.P. Huang, O. Jung and C. Ni, *Mater. Sci. Eng. B*, 96, 247, 2002.
- [2] J.T. Remillard, J.R. McBride, K.E. Nietering, A.R. Drews and X. Zhang, *J. Phys. Chem. B*, 104, 4440, 2000.
- [3] E. Traversa, *J. Am. Ceram. Soc.* 78, 2625, 1995.
- [4] A.I. Kingon, J.P. Maris and S.K. Steiffer, *Nature (London)*, 406, 1032, 2000.
- [5] A. Tsevis, N. Spanos, P.G. Koutsoukos, Van der Linde and J. Lyklema, *J. Chem. Soc., Faraday Trans.*, 94(2), 295, 1998.
- [6] H.Z. Zhang and J.F. Banfield, *J. Mater. Chem.*, 8, 2073, 1998.
- [7] H.Z. Zhang and J.F. Banfield, *J. Phys. Chem. B*, 104, 3481, 2000.
- [8] M.R. Ranade, A. Navrotsky, H.Z. Zhang, J.F. Banfield, S.H. Elder, A. Zaban, P.H. Borse, S.K. Kulkarni, G.S. Doran and J.H. Whitfield, *PNAS*, 99, 6476, 2002.
- [9] J. Arbiol, J. Cerda, G. Dezanneau, A. Cirera, F. Peiro, A. Cornet and J.R. Morante, *J. Appl. Phys.*, 92, 853, 2002.
- [10] Howe. Grant M (Ed), *Kirk-Othmer Encyclopedia of Chemical Technology*, vol.24, p.225, John Wiley & Sons, Inc, 1997.
- [11] M.I. Litter and J.A. Navio, *J. Photochem. Photobiol. A. Chem.*, 84, 183, 1994.
- [12] L. Palmisano, V. Augugliaro, A. Sclafani and M. Schiavello, *J. Phys. Chem.*, 92, 6710, 1998.
- [13] Y. Wang, H. Cheng, Y. Hao, J. Ma, W. Li and S. Cai, *J. Mater. Sci.*, 34, 3721, 1999.
- [14] H. Cheng, J. Ma, Z. Zhao and L. Qi, *Chem. Mater.* 7, 663, 1995.
- [15] Y. Wang, Y. Hao, H. Cheng, J. Ma, B. Xu, W. Li and S. Cai, *J. Mater. Sci.*, 34, 2773, 1999.
- [16] M.K. Akhtar, Y. Xiong and S.E. Pratsinis, *AIChE J.*, 37, 1561, 1991.
- [17] Z. Ding, X. Hu, G.Q. Lu, P.L. Yue and P.F. Greenfield, *Langmuir*, 166216, 2000.
- [18] C.C. Wang, Z. Zhang and J.Y. Ying, *NanoStructured Mater.*, 9, 583, 1997.
- [19] Thomas Varghese and K.M. Balakrishna, *Nanotechnology: An introduction to synthesis, properties and applications*, New Delhi: Atlantic Publishers, 2011.
- [20] A. Burns, G. Hayes, W. Li, J. Hirvonen, J.D. Demaree and S.I. Shah, *Materials Science and Engineering*, BXXX MSB, 9793, 1-6, 2004.
- [21] S. Mahshid, M.S. Ghamsari, M. Askari, N. Afshar and S. Lahuti, *Semiconductor Physics, Quantum Electronics & Optoelectronics*, V. 9, N 2, P. 65-68, 2006.
- [22] M.P.F. Graca, C.C. Silva, L.C. Coata and M.A. Valente, *Int. J. Nanoelectronics and materials*, 3, 99, 2010.
- [23] M.A. Gabal and Y.M. Angari, *Mat. Chem. & Phys.*, 115, 578-584, 2009.
- [24] C.G. Koops, *Phys. Rev.*, 83, 121, 1951.
- [25] K.W. Wagner, *Am. Phys.*, 40, 317, 1973.
- [26] B. Tareev, *Physics of dielectric materials*, Moscow: Mir Publishers, 1979.
- [27] A.N. Patil, M.G. Paul, K.K. Patankar, V.I. Mathe, R.P. Mahajan and S.A. Patil, *Bull. Mater. Sci.*, 23 (5), 361, 2000.
- [28] K. Tanika, R.N. Choudhary, S. Seema and K.S. Singh, *Indian J. Phys.*, 73 A(4), 453, 1999.
- [29] G.F. Dionne, J.F. Fitzgerald and R.C. Aucoin, *J. Appl. Physics*, 47, 1708, 1976.
- [30] X. Ye, Z. Xiao, D. Lin and S. Huang, *Mater. Sci. Eng.*, B74, 133, 2000.
- [31] H. Fang, B. Chen, K. Jiang, J. Sha, Z. Jiao, Q. Zhang and L. Zhang, *Phys Status Solidi B*, 192, K11, 1995.
- [32] D. Ravinder and K. Vijayakumar, *Bull. Mater. Sci.*, 24(5), 505, 2000.
- [33] J. Hasson, F.M. Yen and M.H. Ashim, *Ionics*, 13, 219-222, 2007.
- [34] W.D. Kingery, *Introduction to ceramics*, New York: John Wiley, 1976.
- [35] S.S. Bellad, S.C. Wattawe and Chougule, *Mater. Rs. Bull.*, 34 (7), 109, 1999.
- [36] S. Rajani, *Indian J. Pure Appl. Phys.*, 31, 894, 1993.