

SYNTHESIS CHARACTERIZATION AND PHOTOPROTECTION PROPERTIES OF $ZnTiO_3$ POWDER PREPARED BY CO- PRECIPITATION METHOD

Sirajudheen P^{1*}, gireesh V², Sanoop K B³

^{1,3}Department of Chemistry, WMO Imam Gazzali Arts and Science College,
Kerala, India

²The Kerala Minerals and Metals Ltd (KMML), Kollam, Kerala, India

Abstract:

Zinc titanate ($ZnTiO_3$) powders were synthesized by a simple co-precipitation peroxide method. Zinc chloride and titanium (IV) isopropoxide were used as the starting materials with the ratio of Zn:Ti was 1:1. The prepared powder was calcined at 800°C for 3 hours using the X-ray diffraction the calcined zinc titanate powder crystalline phase formation was found to be cubic. FTIR was taken for confirming the bonding characteristics of ZnO and TiO_2 . Decomposition temperature was analyzed by using TGA. The optical and photoprotection activity of the synthesized powder was evaluated by Lead carbonate test by using Hunter lab color difference meter. Colour difference is determined using a white medium and strength is determined using black medium. The prepared $ZnTiO_3$ powder shows better photoprotection activity.

Keywords:

$ZnTiO_3$, XRD, FTIR, Photoprotection activity

1. INTRODUCTION

Fundamental studies concerning the phase diagram and the characterization of the Zn-TiO₂ system have been continuing since 1960s. This structure is still attracting the attention of researchers. Since, its importance in practical applications with the recent progress of microwave applications, including mobile telephones and satellite communication system, high-quality microwave dielectric resonators, capacitors and filters have been developed promising candidates as dielectric materials for microwave devices and more preferably for low-temperature cofired ceramics (LTCCs).^[1]

Mainly, there are three compounds exist in the Zn-TiO₂ system, including, $ZnTiO_3$ (hexagonal), Zn_2TiO_4 (cubic) and $Zn_2Ti_3O_8$ (cubic). Zinc titanate ($ZnTiO_3$) has an ordered corundum structure, lattice parameters of *a*- and *c*-axis are 5.50787 and 13.9271 Å, respectively^[2,3]. Zinc titanates are generally synthesized by characteristic solid state reactions at high temperatures^[4]. Due to some

limitations of solid-state synthesis, such as large grain size and uncontrolled and irregular morphologies, several alternative methods have been elaborated including mechanochemical activation^[5,6], molten salt synthesis^[7], a semichemical route combined with vigorous microbeads milling^[8,9] and sol-gel method. But the sol-gel processes are generally complicated and the reagents used are expensive. In wet chemical processes for preparing highly quality of powders, better homogeneity, control morphology and smaller particle size are preferred.

The co-precipitation peroxide method was considered to be a promising way to prepare powder for the ferroelectric materials. In this work, ZnTiO₃ powder was prepared by the co-precipitation peroxide method. The phase transformation was studied by X-ray diffraction (XRD). The chemical characterization of zinc titanate involves analysis of elements using AAS. Here the zinc titanate used for the estimation of traces elements and evaluation of optical properties. The optical and photoprotection efficiency of the prepared zinc titanate were evaluated using color difference meter.

The work has a wide range of scope due to the similarity in some characteristics and applications of ZnO and TiO₂. For example the band gap of TiO₂ (rutile ~ 3.0 eV and anatase ~ 3.2 eV) and ZnO (~ 3.3 eV) are almost similar and in the field of application both oxides are used in paints and ceramic industries^[10]. Its application not only limited in the above fields, but ZnO and TiO₂ are used as semiconductors and in new generation of devices such as light emitting diodes, gas sensors, solar cells etc.

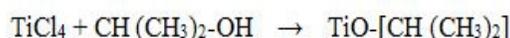
2. MATERIALS AND METHODS

2.1. Materials

Zinc chloride and titanium tetrachloride were used as starting materials. Hydrogen peroxide, ammonia solutions and isopropyl alcohol from Merck are also used. All the chemicals were used without further purification. The optical and photoprotection activity of the synthesized powder was evaluated by Lead carbonate test by using Hunter lab color difference meter. Colour difference is determined using a white medium and strength is determined using black medium.

2.2. Preparation of the sample

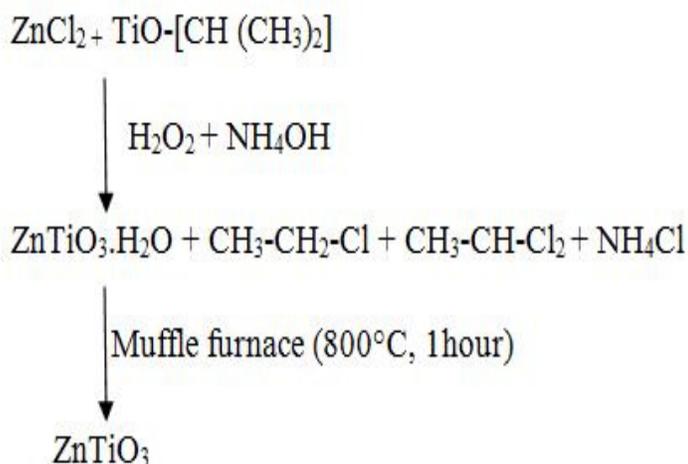
About 0.2mol (0.273 g in 100 ml) zinc chloride was dissolved in 100 ml of water. Then 0.2 mol of titanium tetra chloride in isopropanol was also made up to 100 ml. The two solutions are mixed together to get a homogenous solution. Then about 15 ml of hydrogen peroxide and 20 ml of ammonia solutions are mixed and about 165 ml of water is added to it.



Scheme 1. Synthesis of Titanium iso- propoxide

The homogeneous solution containing zinc chloride and titanium tetra chloride are added to the second solution drop by drop by using a burette. A precipitate is formed in the beaker it is allowed to settle for some time and filtered. The residue obtained is washed with water dried by using Owen and calcined in Muffle furnace at 800° c about half an hour in a silica crucible. The

zinc titanate formed (Scheme- 2) is powdered and used for further experiments. The chemical reactions involved in the preparation of zinc titanate are given in scheme 2.



Scheme 2. Steps involved in the synthesis of ZnTiO₃

2.3. Optical activity experiments

The optical activity of the synthesized powder is evaluated by Lead carbonate test. The instrument used for the test is Hunter lab color difference meter of model DP-9000. This instrument is used to determine^[99] the strength and color difference of the paints and pigments. The principle used in this experiment is the reflection of light. Color difference is determined using a white medium and strength is determined using black medium.

2.4. Photoprotection Capacity

Sunscreens remain an important part of dermatology, with new developments creating longer lasting, more aesthetic photoprotection. Current sunscreen research is aimed at creating better polymers to increase the length of time the sunscreen film remains in place on the skin, despite the presence of sebum and perspiration. Polymers also can suspend particulates, such as zinc oxide and titanium dioxide, allowing the film to be invisible on the skin. Expectantly, the incorporation of new standard actives in the sunscreen monograph will further broaden skin photoprotection^[88].

Lead carbonate test is one of the monitoring tests used to find out the photoprotection activity. In this test, a mixture of lead carbonate, titanium dioxide, and glycerin is illuminated with UV- light. Different moisture contents and the presence of traces of oxygen influence the measurements.^[96]

3. RESULT AND DISCUSSION

3.1. Results of structural and thermal analyses

The X-ray diffraction patterns of prepared $ZnTiO_3$ calcinated at different temperatures are shown in Figure. 1

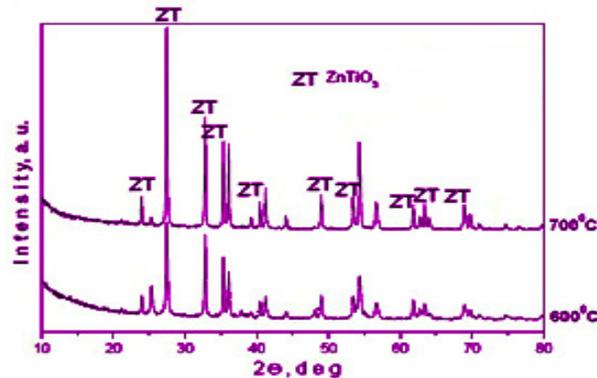


Figure 1. XRD of $ZnTiO_3$

sample amorphous at 600°C is seen and the strongest peaks of cubic $ZnTiO_3$ appeared at 700°C. As per the Hosono et al. [20] occurred the same phase at below 600°C using zinc acetylacetonate and titanium tetraisopropoxide as main precursors by sol-gel method is similar. Alternatively when using the same precursors [21] that at 800°C several peaks related to the hexagonal $ZnTiO_3$ appears, but the cubic crystals are still dominant. In contrast to the above mentioned Golovchansky et al [22] as precursors using titanium tetraisopropoxide and zinc nitrate hexahydrate prepared single-phase hexagonal $ZnTiO_3$ at 500°C followed by cubic phase and rutile has shown above 600°C which are closer to those obtained by Aubert et al. [23] and they point up that after the additional heat treatment at 550°C the peaks intensity increase. In Sherrer's equation the average crystalline size as seemed at 500°C $ZnTiO_3$ particles calculated from the broadening of the diffraction lines.

The Differential Thermal Analysis (DTA) curve of the formerly heat treated at 400°C sample (Figure. 2) elucidates two endothermic (120 and 380°C) and two exothermic peaks at 450 and 540°C.

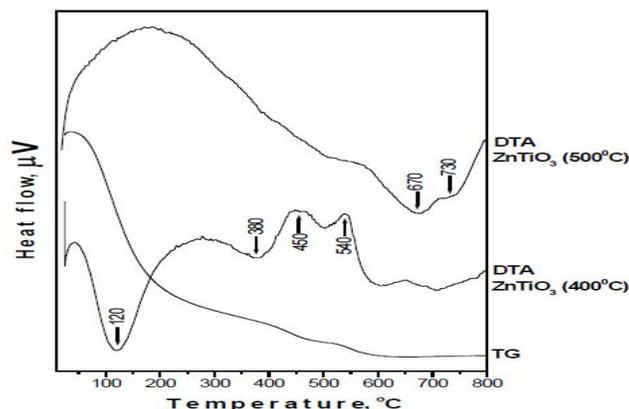


Figure 2. DTA curve of ZnTiO₃

The exothermic lines might related to the combustion of the organic residues and crystallization of the amorphous sample with development of ZnTiO₃ phase (540^oC) and the endothermic effects can be attributed to the dehydration of the sample. Both exothermic peaks (at 450 and 540^oC) are not observed in the DTA curve of the formerly heat treated sample at 500^oC. This shows that the last exothermic effect is related to the crystallization process which is in good agreement with the X-ray diffraction results (Fig. 1). The results are well-matched to those obtained by Wang et al^[10].

The Fourier Transform Infrared Spectra (FTIR) of the prepared zinc titanate (ZnTiO₃) samples are shown in Figure. 3.

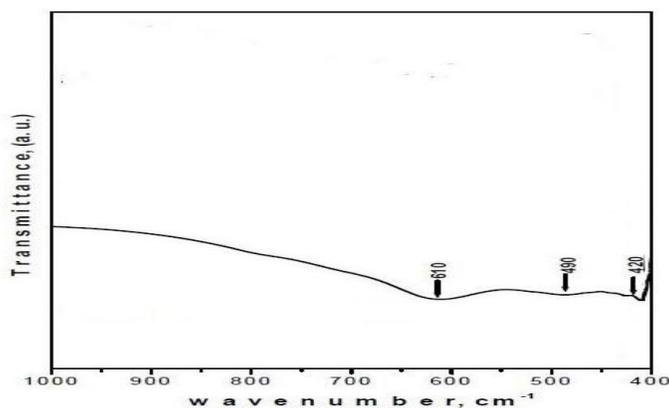


Figure 3. IR spectra of ZnTiO₃

Prevailing bands at 610, 490 cm⁻¹ along with a weak band at 420 cm⁻¹ are found in the spectra of ZnTiO₃. The vibrations of TiO₆ units in ZnTiO₃^[11,12] could be related to that bands in the absorption range 700-400 cm⁻¹. According to the X-ray diffraction data for this sample, only one phase (ZnTiO₃) was noticed. It is also known that bands corresponding to ZnO_n polyhedra are in the same absorption range^[13,14]. The difference of the IR spectrum of another composition (n-aq ZnTiO₃), is connected to the increased intensity of the band centered at 420 cm⁻¹. As it is known

this band is typical for the vibrations of TiO_6 units building up the rutile modification and its existence is in agreement with the X-ray diffraction Results^[15,16]. The weak band near 450 cm^{-1} could be related to the Ti-O stretching vibrations in ZnTiO_3 ^[11, 12].

3.2. Photoprotection Capacity

The photoprotection efficiency of prepared zinc titanate was studied. The photoprotection efficiency is expressed in terms of catalytic activity coefficient (CAC). The result obtained after the study was given in (Table 1). And the graphical representations of the obtained values are given in (figure 4).

Table 1. Photoprotection activity of Zinc titanate

Pigments	Brightness before UV exposure	Brightness after UV exposure	CAC %
ZnTiO_3	91.47	78.48	14.2
TiO_2	93.82	59.58	36.49

The CAC values of TiO_2 were found to be high when compared to the prepared zinc titanate. It shows that the pigment zinc titanate has high photoprotection ability and low photocatalytic activity in UV when compared to that of TiO_2 . It can be further explained by the graph given below.

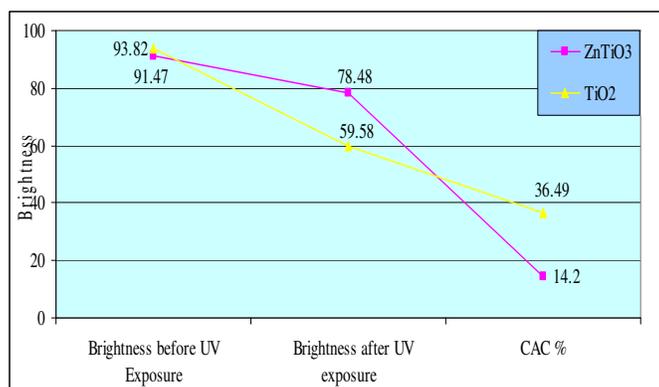


Figure 4. Photoprotection activity of ZnTiO_3 in UV-Light

From the graph it is clear that there is a sharp deviation in the brightness of TiO_2 i.e. before (93.82) and (59.58) after UV exposure, but in the case of zinc titanate, there is no such a sharp deviation before (91.47) and after (78.48) UV exposure. Hence, the catalytic coefficient values of zinc titanate is (14.2) low when compared to that of natural titanium dioxide (36.49). From the values it is clear that the prepared zinc titanate has less photocatalytic activity in UV- light when compared to that of natural titanium dioxide. The study reveals that the prepared zinc titanate had more photoprotection capacity and photodurability than that of the titanium dioxide.

4. CONCLUSION

The ZnTiO₃ powders were synthesized by coprecipitation peroxide method and its physical properties are studied by using XRD, FTIR and TGA. Chemical analysis shows that the prepared zinc titanate contains approximately 40 percentage of zinc and 23.68 percentage of titanium and the compound shows dominant cubic structure. Photoprotection activity of ZnTiO₃ prepared by coprecipitation method was improved in comparison to that of TiO₂. The ZnTiO₃ synthesized by peroxide method possesses better photoprotection properties.

REFERENCE

- [1] P. Pookmanee, J. Yotasing "Chemical Synthesis And Characterization of ZnTiO₃ Powder Prepared by the Coprecipitation Method" Advanced Materials Research Vols. 55-57 (2008) pp 65-68 online at <http://www.scientific.net> © (2008) Trans Tech Publications, Switzerland.
- [2] Dulin FH, Rase DE "Phase equilibria in the system ZnO–TiO₂". J Am Ceram Soc 43:125–131.(1960)
- [3] Bartram SF, Slepetyev RA "Compound formation and crystal structure in the system ZnO–TiO₂". (1961) J Am Ceram Soc. 44:493–499
- [4] Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, T.H. Fang, S. Wu, "Ceramic International", 30, 2183-2189 (2004).
- [5] P. M. Botta, E. F. Aglietti and J. M. Port López," Journal of Materials Science", 39, 5195-5199, (2004).
- [6] N. Labus, N. Obradović, T. Srećković, V. Mitić, M.M. Ristić, "Science of Sintering", 37, 115-122, (2005).
- [7] X. Xing, C. Zhang, L. Qiao, G. Liu, J. Meng, "Journal of the American Ceramic Society", 89 (3), 1150-1152 (2006).
- [8] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Y.H. Kim, "Journal of the American Ceramic Society", 82, 3043–3048 (1999).
- [9] X. Liu, F. Gao, L. Zhao, M. Zhao, C. Tian, "Effects of V₂O₅ addition on the phase- structure and Journal of Electroceramics, 18, 103-109 (2007).
- [10] S.F. Wang, F. Gu, M.K. Lu et al., Mater, Res, dielectric properties of zinc titanate ceramics", 1283-1288 (2003)
- [11] O. Yamaguchi, M. Morimi, H. Kawabata, et al., J. Amer. Ceram. Soc., 70, c97-8 (1987).
- [12] B. G. Shabalin, Mineral. Zh., 4, 54-61 (1982).
- [13] M. Mancheva, R. Iordanova, Y. Dimitriev, J. Alloys Compd, 509(1), 15-20 (2011).
- [14] M. Andres-Verges, M. Martinez-Gailego, J. Mater. Sci., 27, 3756-62 (1992).
- [15] A. Murashkevich, A. Lavitkaya, T. Barannikova et al., „Infrared absorption spectra and of TiO₂-SiO₂ composites“, J. Appl. Spectr., 75 (5), 2008, 730-734.
- [16] E. Yurchenko, G. Kustovarov, S. Bacanov, "Vibrational spectroscopy of inorganic compounds" Nauka 1981 (in Russian).
- [17] C. Srinivasan, N. Somasundaram, Current Science, 85, 1431-38 (2003)
- [18] K. Hirota, M. Sugimoto, M. Kato, K. Tsukagoshi, T. Tanigawa, H. Sugimoto Ceram Intern 36, 497-506 (2010)
- [19] C. Karunakaran, V. Rajeswari, P. Gomathisankar, J Alloys Comp 508, 587-591 (2010)
- [20] E. Hosono, S. Fujihara, M. Onuki, T. Kimura, J. Amer. Cer. Soc., 87(9), 1785-1788 (2004)
- [21] S.F. Wang, F. Gu, M.K. Lu et al., Mater, Res, Bull, 38, 1283-1288 (2003)
- [22] A. Golovchansky, H. Kim, Y. Kim, J. Kor. Phys. Soc., 32, S1167-S1169 (1998)
- [23] T. Aubert, F. Grasset, M. Potel, V. Nazabal, T. Cardinal, St. Pechev, N. Saito et al., Sci. Technol. dv. Mater., 11, 044401-9(2010)