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Synthesis and Characterization of Zinc titanates by Solid state reaction

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Abstract: Zinc metatitanate ($ZnTiO_3$), zinc orthotitanate (Zn_2TiO_4) and a metastable zinc titanate ($Zn_2Ti_3O_8$) were synthesized by a simple solid state reaction. Powder XRD, FT-IR, Raman, diffused reflectance and photoluminescence spectroscopy were used to study the phase evolution, crystalline structure and optical properties of samples calcined at different temperatures. Crystalline structure of the titanium dioxide along with calcination temperature influenced the zinc titanate phase formation. A decrease in optical band gap was observed with increase in calcination temperature of the zinc titanates. Zinc orthotitanate showed photolumine scence (PL) properties.
Keywords: Zinc titanates, polymorphs, bandgap, photoluminescence.

Introduction:

Zinc titanate is an interesting ternary oxide system showing different polymorphs like cubic defect spinel $Zn_2Ti_3O_8$, cubic inverse spinel $ZnTiO_3$, hexagonal ilmenite type $ZnTiO_3$, cubic inverse spinel Zn_2TiO_4 and recently reported lithium niobate type $ZnTiO_3$[1,2]. Zinc titanates have been synthesized and phase diagrams are reported by solid state reactions [3,4]. ZnO and TiO_2 are wide bandgap and photoluminescence materials having applications in diverse fields [5,6]. Aim of the present report is to synthesize zinc titanates, to study the diffuse reflectance properties, calculation of optical bandgap and photoluminescence properties of zinc titanates calcined at different temperatures.

Experimental:

ZnO (Sigma Aldrich, 99.999% pure) and anatase TiO_2 (Sigma Aldrich, 99.99% pure) were used for the synthesis of zinc titanates. For the synthesis zinc titanates, stoichiometric amounts of ZnO and TiO_2 were mixed together and grinded for 20 hours and calcined at different temperatures. Experimental conditions were labelled as follows: 1:1 molar ratio ZnO and anatase TiO_2 grinded for 20 hours (ZT1), calcined at 600 °C/10 h (ZT2), 900 °C/5 h (ZT3), 1000 °C/5 h (ZT4), 2:1 molar ratio ZnO and anatase TiO_2 grinded for 20 h and calcined at 900 °C/5h (ZT5), 1:1 molar ratio ZnO and rutile TiO_2 grinded for 20 h and calcined at 1000 °C/5 h (ZT6). Powder XRD was taken using Bruker D8 Advanced powder X-ray diffractometer, FT-IR spectra with Shimadzu using KBr pellets. UV-Vis spectra were recorded in the diffuse reflectance mode (R) on a JASCO UV-Vis NIR V-670 spectrophotometer using $BaSO_4$ as the reference sample. Photoluminescence spectra were taken on HITACHI F-700 FL spectrophotometer in emission mode.

Results and discussion:

XRD patterns of the synthesized zinc titanates were shown in Fig.1. The relative phase compositions, lattice parameters and unit cell volume were calculated using Rietveld like refinement program Powder Cell 2.4. JCPDS cards no. 00-036-1451, 00-021-1272, 00-021-1276, 00-025-1164, 00-026-1500 and 00-039-0190 were used as reference patterns for wurtzite ZnO, anatase TiO_2, rutile TiO_2, cubic inverse spinel Zn_2TiO_4, hexagonal ilmenite type $ZnTiO_3$, and cubic inverse spinel $ZnTiO_3$ respectively. No significant amount of zinc titanates were formed on grinding ZnO and anatase TiO_2 for 20 h.
The amount of c-$ZnTiO_3$ (a=8.3963 Å, unit cell volume = 591.92 Å) and h-$ZnTiO_3$ (a=5.0748 Å, c=13.9267 Å, unit cell volume =310.62 Å) increased from 12 % and 10% on calcination at 600 °C for 10 h and to 53 % and 22 % at 900 °C respectively.

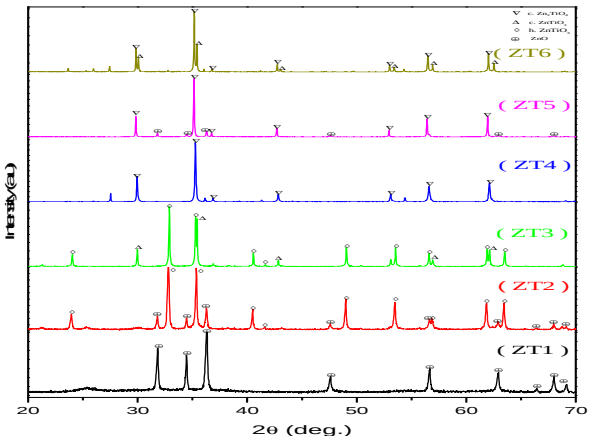

Fig. 1. Powder XRD of zinc titanates.

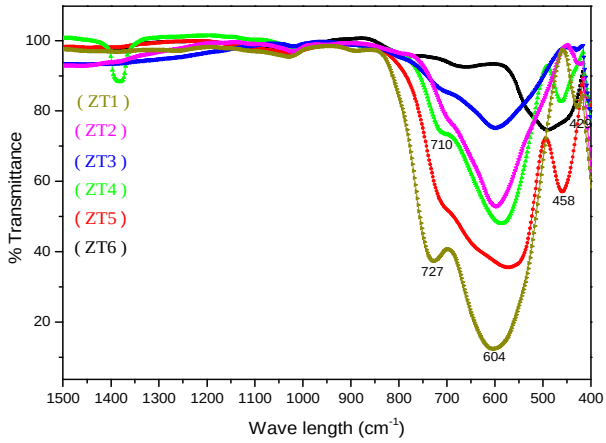

Fig. 2. FT-IR spectra of zinc titanates.

On further calcination at 1000 °C, the amount of c-$ZnTiO_3$ and h-$ZnTiO_3$ gradually declined due to their decomposition to form c-Zn_2TiO_4 (a=8.4555 Å, unit cell volume = 604.53 Å) and rutile TiO_2 (a=4.5939 Å, c=2.9587 Å, unit cell volume= 62.44 Å). With 2:1 molar ratio ZnO and anatase TiO_2 at 900 °C, almost pure phase cubic Zn_2TiO_4 (a=8.4556 Å, unit cell volume = 604.55 Å) with traces of ZnO formed. All zinc titanates decomposed to c-Zn_2TiO_4 and rutile TiO_2 at calcination temperature ≥ 1000 °C.

FT-IR spectra:

FT-IR spectra of the zinc titanates were shown in the Fig.2. [TiO_6] and Zn-O-Ti groups existing in different phases of zinc titanates are observed at 650 - 550 cm^{-1} and 735 cm^{-1} respectively. The wave number for Ti-O octahedral absorption increased with decrease in Zn:Ti molar ratio. (ZnO_4) stretching vibrations are observed at 500 - 400 cm^{-1}[7].

Diffused reflectance spectra:

Diffuse reflectance spectra of the zinc titanates were shown in Fig. 3. Bandgap of the zinc titanates were calculated using Tauc's relationship [1]. The minimum and maximum bandgap energy values of 3.24 eV and

3.87 eV were observed in ZnO and TiO_2 composite (ZT1) and cubic $ZnTiO_3$ and hexagonal ilmenite $ZnTiO_3$ composite (ZT3).

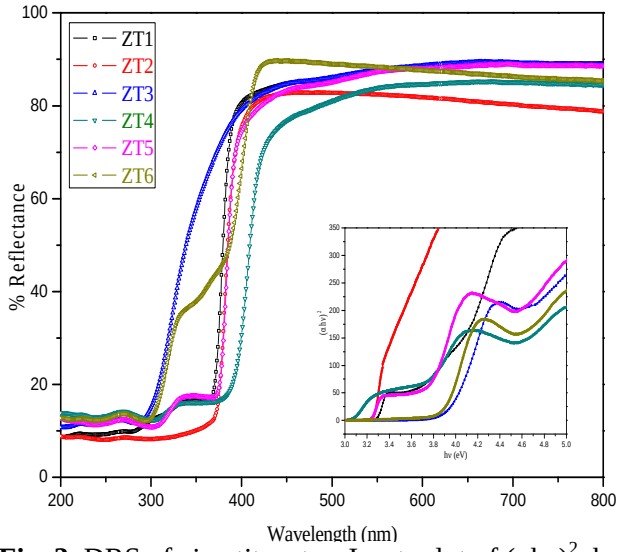

Fig. 3. DRS of zinc titanates. Inset: plot of $(\alpha h\nu)^2$ hν.

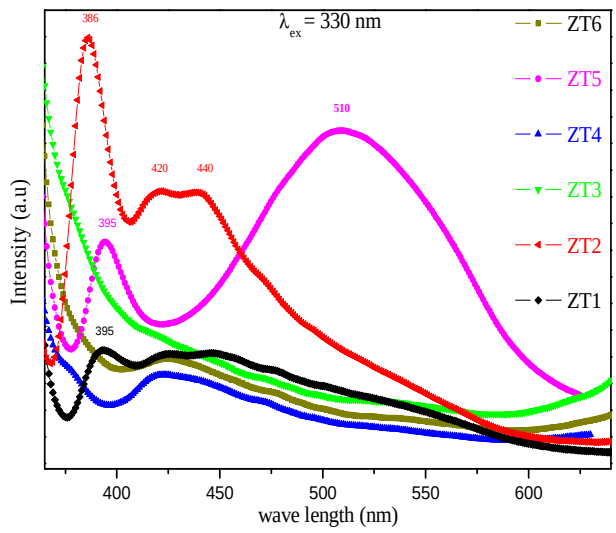

Fig. 4. PL spectra of zinc titanates.

Photoluminescence (PL) spectra:

Photoluminescence spectra of the zinc titanates taken with an excitation wavelength of 330 nm were shown in the fig. 4. Sample ZT1 containing ZnO and TiO_2 showed a strong PL band at 386 nm and two weak PL bands at 420 nm and 440 nm in the violet region. A weak violet emission was observed in sample ZT2 at 393 nm, 420 nm and 440 nm. No PL emission was observed in ZT3 in which cubic inverse spinel $ZnTiO_3$ and hexagonal ilmenite type $ZnTiO_3$ were present. A very weak blue emission was observed in samples ZT4 and ZT5 which contain traces of rutile TiO_2 along with cubic Zn_2TiO_4. A strong green emission band centred at 510 nm and a sharp ultra-violet band centred at 395 nm were observed in ZT containing Zn_2TiO_4 and traces of ZnO. From this we can say that photoluminescence in zinc titanates is due to the presence of traces of either ZnO or TiO_2.

Conclusion:

Zinc titanates were synthesized by solid state reaction using ZnO and TiO_2. Cubic inverse spinel Zn_2TiO_4 was the major product on calcination at 1000 °C irrespective of the phase of the TiO_2 used. Cubic inverse spinel $ZnTiO_3$ and hexagonal ilmenite type $ZnTiO_3$ were formed on calcination of 1:1 mole ratio ZnO and anatase TiO_2 at 900 °C. Samples containing traces of ZnO were photoluminescent. Zn_2TiO_4 containing traces of ZnO showed a strong PL band at 510 nm and a small PL band at 395 nm in the green and violet regions respectively.

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