Synthesis and Characterization of Zinc titanates by Solid state reaction

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Abstract: Zinc metatitanate (ZnTiO$_3$), zinc orthotitanate (Zn$_2$TiO$_4$) and a metastable zinc titanate (Zn$_2$Ti$_3$O$_8$) 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 photoluminescence (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$_2$Ti$_3$O$_8$, cubic inverse spinel ZnTiO$_3$, hexagonal ilmenite type ZnTiO$_3$, cubic inverse spinel Zn$_2$TiO$_4$ 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 ground for 20 hours and calcined at different temperatures. Experimental conditions were labelled as follows: 1:1 molar ratio ZnO and anatase TiO$_2$ ground 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$_2$ ground for 20 h and calcined at 900 °C/5h (ZT5), 1:1 molar ratio ZnO and rutile TiO$_2$ ground 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$_2$TiO$_4$, 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$^3$) and h-ZnTiO$_3$ (a=5.0748 Å, c=13.9267 Å, unit cell volume =310.62 Å$^3$) increased from 12 % and 10% on calcination at 600 °C for 10 h and to 53 % and 22 % at 900 °C respectively.

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$_2$TiO$_4$ (a=8.4555 Å, unit cell volume = 604.53 Å$^3$) and rutile TiO$_2$ (a=4.5939 Å, c=2.9587 Å, unit cell volume= 62.44 Å$^3$). With 2:1 molar ratio ZnO and anatase TiO$_2$ at 900 °C, almost pure phase cubic Zn$_2$TiO$_4$ (a=8.4556 Å, unit cell volume = 604.55 Å$^3$) with traces of ZnO formed. All zinc titanates decomposed to c-Zn$_2$TiO$_4$ and rutile TiO$_2$ at calcination temperature $\geq$ 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).

![Graph](image)

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

![Graph](image)

**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$_2$TiO$_4$. 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$_2$TiO$_4$ 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$_2$TiO$_4$ 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$_2$TiO$_4$ 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.
References:


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