

Sole-Gel derived $Zn_xTi_yO_z$ Nanocrystals and Coatings for Solar Tech and Photonics

L. Spanhel, J. Mrazek, G. Krylova, A. Brioude[†], G. Chadeyron[‡]

Université de Rennes 1, UMR 6226, Campus Beaulieu, 35420 Rennes, France

[†] Université Claude Bernard Lyon 1, LMI-UMR 5615, 69622 Villeurbanne, France

[‡] Université Blaise Pascal, UMR 6002, 63177 Aubière, France

Ternary $Zn_xTi_yO_z$ oxides are ecologically feasible materials with application potential in catalytic dehydrogenation and desulfurization processes^[1], microwave ceramic dielectrics industries^[2], solar energy research^[3] and the development of novel luminescent phosphors^[4]. Solid state reactions of ZnO and TiO₂ powders at different Zn/Ti atomic ratios offer various microcrystalline phases that is summarized in the following table:

	c-Zn₂TiO₄	c-ZnTiO₃	c-Zn₂Ti₃O₈	h-ZnTiO₃
Structure type	Inverse spinel	inverse defect spinel	inverse defect spinel	Ilmenite
Symmetry Space group	cubic Fd3m	cubic Fd3m	cubic Fd3m/P4 ₃ 32	hexagonal R3
Unit cell	a = 0.846 nm	a = 0.840 nm	a = 0.843 nm	a = 0.507 nm

Our current research is directed towards chemical elaboration of the aforementioned $Zn_xTi_yO_z$ nanostructures in the form of nanopowders and coatings. In our previous studies, ethanol born $Zn_xTi_yO_z$ nanostructures have been successfully used in nitridation process^[3] and in photocatalysis driven by visible light^[5].

More recently, we studied the thermal structural evolution process in $Zn_xTi_yO_z$ xerogel powders isolated from the pre-condensed nanocolloids. Here, a direct heteronucleation process of zinc acetate dihydrate and titanium tetrabutoxide in hot ethanol solution was possible yielding stable concentrated “polymeric” sols of different Zn/Ti ratios ranging between 2 and 0.5, without additional use of additives. The main findings of these studies are:

1. Ternary oxide nanocrystals start to form at around 350°C and depending on the Zn/Ti-ratio, cubic inverse spinel like Zn₂TiO₄ and ZnTiO₃ or hexagonal ilmenite h-ZnTiO₃ could be selectively produced. The appearance of a defect inverse spinel phase Zn₂Ti₃O₈ as repeatedly reported in the past solid state chemistry reports is not confirmed in our study;
2. Dopings with APTES (3-aminopropyltriethoxysilane) or Eu³⁺ block thermal crystal growth and spinel-to-Ilmenite transformations. This allows stabilizing the cubic spinel like c-ZnTiO₃ up to 800°C before it decays into thermodynamically most stable Zn₂TiO₄ and rutile phases^[6]. The red fluorescence of Eu³⁺ exhibits highest intensity in the defect spinel c-ZnTiO₃ nanophase.

Optical studies on $Zn_xTi_yO_z$ sol-gel coatings revealed the presence of indirect gap semiconductors. The band gap energies - E_g of these ternary oxides are in the range between 3.6 eV and 3.8 eV which is significantly larger than in the corresponding binary ZnO and TiO_2 counterparts (E_g around 3.1 - 3.2 eV). The following Figure shows the optical absorption data along with the SEM and AFM microscopic images of nanocrystalline spinel coatings:

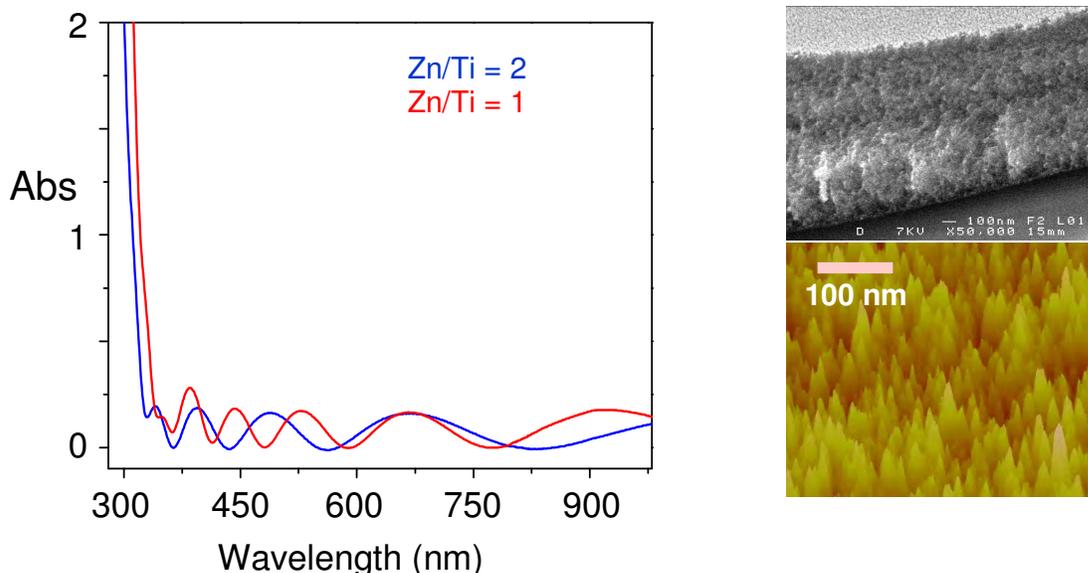


Figure 1 At left: Optical absorption spectra of sol-gel derived nanocrystalline Zn_2TiO_4 and $ZnTiO_3$ spinel coatings; At right: SEM and AFM images of $ZnTiO_3$ coatings on Pyrex glass.

The produced coatings exhibit a natural superhydrophilicity manifested in low water contact angles below 15° . Doping the films with 5% silica improves the morphology and the long term stability of the natural superhydrophilicity. h - $ZnTiO_3$ -ilmenite/ r - TiO_2 rutile nanocomposite coatings have also shown a remarkable activity in the photo-mineralization process of fatty acids. It was possible to monitor this process not only by using the well known FTIR method, but also by analyzing the spectral interference fringe shifts within the frame of the conventional optical absorption spectroscopy. The degradation time profiles of capric-(C10), stearic- (C18) and behenic acid (C22) indicate that it takes longer to mineralize acids carrying longer hydrocarbon chain. The decay follows a first order law of kinetics in all three cases and we additionally note an exponential $k \sim e^N$ relationship between the first order rate constant and the number of methylen groups N ^[7]. Our presentation in the Quantsol 2010 winter workshop will highlight all the above mentioned research activities.

References

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