









Stabilization of anatase phase by uncompensated Ga-V co-doping in TiO₂: A structural phase transition, grain growth and optical property study

Nasima Khatun ^a, Saurabh Tiwari ^a, Jayanti Lal ^b, Chuan-Ming Tseng ^c, Shun Wei Liu ^c,
Sajal Biring ^c  , Somaditya Sen ^a  

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<https://doi.org/10.1016/j.ceramint.2018.09.012> 

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Abstract

Uncompensated Ga-V co-doped TiO₂ samples have been prepared by modified sol-gel process. Inhibition of phase transition due to co-doping is confirmed by X-ray diffraction measurement. Activation of phase transition increases from 120 kJ/mol ($x = 0$) to 240 kJ/mol ($x = 0.046$) due to Ga-V incorporation. In anatase phase, lattice constant increases by the effect of Ga³⁺ interstitials. This results in inhibition of phase transition. Anatase phase becomes stable up to ~ 650 °C in co-doped sample whereas for pure TiO₂ phase transition starts in between 450 and 500 °C. High-resolution transmission electron microscope image shows particle size decreases in anatase phase due to co-doping. Increasing strain due to Ga-V incorporation results in reducing crystallite size. Brunauer–Emmett–Teller analysis shows that surface increases from 4.55 m²/g (pure TiO₂) to 96.53 m²/g ($x = 0.046$) by Ga-V incorporation. In rutile phase, grain growth process is enhanced mainly due to the effect of Vanadium and particles show a rod-like structure with majority {110} facets. Bandgap

decreases in both phases and reduced to visible light region. For charge balance in uncompensated Ga-V co-doped sample, structural distortion created in the lattice by combining effect of substitution, interstitials and oxygen vacancies, which results in stabilization of anatase phase and reducing of bandgap.

Introduction

TiO₂ is of continual interest due to its multifunctional properties. Different crystal structure and corresponding electronic band structure facilitate its applications in different fields such as in optoelectronic devices [1], [2], self-cleaning glass coating materials [3], photocatalyst [4], [5], fuel cell [6], dye-sensitized solar cell [7], [8], opacifier and white pigment [9], [10], etc. It facilitates environmentally beneficial reactions through photocatalytic activity by splitting of water to generate hydrogen and treatment of polluted air and water [11]. Low cost, nontoxicity, and high chemical stability add a special importance for application.

TiO₂ has three naturally occurring polymorph [12]. In order of abundance, these are rutile (R), anatase (A), and brookite (B) [13]. At lower temperature anatase is the most stable phase due to its low surface free energy [14], [15]. Pure brookite phase is not available at normal ambient condition due to its complex crystal structure. Both anatase and brookite are metastable phases. With increasing temperature (≥ 750 °C) both the phases are irreversibly transformed into stable rutile phase [16]. Density functional theory (DFT) calculation showed that effective mass of electrons and holes is smaller in anatase phase compared to brookite and rutile phases [17]. This facilitates the migration of carriers and enhances photocatalytic activity. Due to lighter effective mass, smaller particle size (highly stable < 10–15 nm) [12], [18] and longer lifetime of photogenerated charge carriers [17], anatase is an active polymorph for photocatalytic applications than brookite and rutile [19], [20], [21].

In spite of these important properties of anatase TiO₂, there are few restraints. Anatase TiO₂ has lower thermal stability (≤ 450 – 500 °C) and wide bandgap (3.2 eV) [22]. Due to its wide bandgap, it only absorbs ~ 5% radiation of the solar spectrum. The entire visible region (~ 45%) remains unutilized. From a practical application point of view, utilization of visible light is beneficial. Therefore, people have made significant efforts to shift its phase transition temperature to a higher temperature region and tune the bandgap of TiO₂ in visible light range. Different processes have been adapted for this purpose. These include synthesis methods [23], [24], [25], inducing strain [26], [27], doping with different elements (Fe, Mo, V, Ru, Cu, Fe, Cr etc.) [14], [28], [29], [30], [31], etc.

Among all these processes, doping is the easiest way to control phase transition and thereby properties (tune the bandgap). From the literature, it was observed that Ga doping inhibits the phase transition and play a robust role in photocatalytic activity (PCA) in UV region [32], [33]. Vanadium considerably reduces the bandgap but promotes phase transition [16], [34], [35]. Hence, in this context uncompensated gallium and vanadium co-doping have been chosen to overcome both the problem. Here in this work, effect of uncompensated Ga-V co-doping on structural phase transition, grain growth process and optical properties of TiO₂ has been discussed.

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Experimental

Ga and V co-doped TiO₂ (Ti_(1-x)(Ga_{0.8}V_{0.2})_xO₂: TGV) nanoparticles (with $x = 0.00$ (TGV0), 0.015 (TGV1), 0.031 (TGV3) and 0.046 (TGV4)) are prepared by modified sol-gel synthesis. The Ti-solution is prepared by mixing required amount of dihydroxy-bis titanium (TALH: C₆H₁₈N₂O₈Ti) in deionized (DI) water at room temperature. An appropriate amount of Ga(NO₃)₃ is dissolved in DI water in one beaker. In another beaker, V₂O₅ is also dissolved in DI water by adding little amount of ammonium hydroxide (NH₄

Results and discussions

TGA measurement on dry gel powder (TGV0) is performed from room temperature (RT-27 °C) to 800 °C. Weight loss of 1.04%, from RT to ~ 110 °C, is observed in pure TiO₂ (TGV0) (Fig. 1). This is due to elimination of physically adsorbed water [36]. In the temperature regime, ~ 110–315 °C a sharper weight loss of 2.52% is observed. This may be attributed to the rupture of polymeric chain of black powder and removal of ethylene glycol units [37]. A final very sharp weight loss of 5.61% is observed in

Conclusions

Uncompensated Ga-V co-doped TiO₂ samples have been successfully prepared by modified sol-gel process. Anatase phase becomes stable up to ~ 650 °C in co-doped sample whereas in pure TiO₂ phase transition starts ~ 450–500 °C. This inhibition of phase transition due to co-doping is confirmed by XRD patterns. Rietveld refinement at anatase phase shows lattice constants and unit cell volume increases with increasing doping concentration. Ga ions occupy more interstitial sites than substitutional

Acknowledgment

The authors are sincerely thanking Indian Institute of Technology Indore for providing funds and all research related facilities. The authors also thank Sophisticated Instrument Centre (SIC) of IIT Indore for FESEM studies. One of the authors (Dr. Sajal Biring) acknowledges support from Ministry of Science and Technology, Taiwan (MOST 105-2218-E-131-003 and 106-2221-E-131-027).

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