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Zinc Titanates Sintered from ZnO and TiO_2 Nanowires Prepared by Hydrothermal Process

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2. Virtual Journal of Nanoscale Science & Technology, vol. 18, iss. 20.(4 November 2008)

Oxide nanowires are promising materials for vacuum emitters, sensors, charge storage elements, light emitters, photodetectors and solar cells. Particularly, ZnO and TiO_2 nanostructures, including nanoparticles, nanorods, nanotubes and nanowires, have recently attracted much attention because of their unique optical, electrical and physical properties. However, the hybrid application of these two nano-structures has not been explored. Nano-size powders have also been proven to benefit the fabrication of ceramics. An intuitive application of ZnO and TiO_2 nano-structures is to synthesize the zinc titanate alloys, in which process, lowering the sintering temperature to less than the melting points of the inner electrode metals such as Ag (~960℃), for use in low-temperature co-fired ceramics (LTCCs) is still challenging.

ZnO and TiO_2 nanowires were prepared separately by hydrothermal processes: (1) ZnO: An aqueous solution of zinc nitrate (0.054M) was prepared by mixing and stirring the $Zn(NO_3)_2$•$6H_2O$ (Showa chemical; purity>99%), polyethylene glycol (PEG) (Showa chemical; 0.15 g), ammonia (1 M), and deionized water in a Teflon vessel until equilibrium. Then, the solution was heated to 80℃ at which temperature it was maintained for 24 h. After it was cooled to room-temperature, the ZnO precipitate was collected, washed using deionized water, and dried at 60℃ in air. (2) TiO_2¬: Five milligrams of commercial TiO_2 powder (Showa chemical; purity>99%) was added into (180 ml, 1M) aqueous NaOH in a Teflon vessel, which was placed inside a sealed stainless vessel. The solution was heated to 130℃ and held for 24 h. The cooled precipitates were collected, washed in deionized water, and then washed using nitric acid solution until the value of pH was below 7. Steps (1) and (2) were repeated until the amounts of powders were enough for sintering of ceramic compacts.

Figures 1 (a) and (b) show SEM images of hydrothermally synthesized TiO_2 and ZnO nanowires. The average diameters of TiO_2 and ZnO nanowires were measured to be ~15nm and ~400 nm, respectively. The BET surface area of the nano-TiO_2 ¬was measured to be 210 m^2/g, which markedly exceeded the commercially available TiO_2 nano-powders (~tens m^2/g).

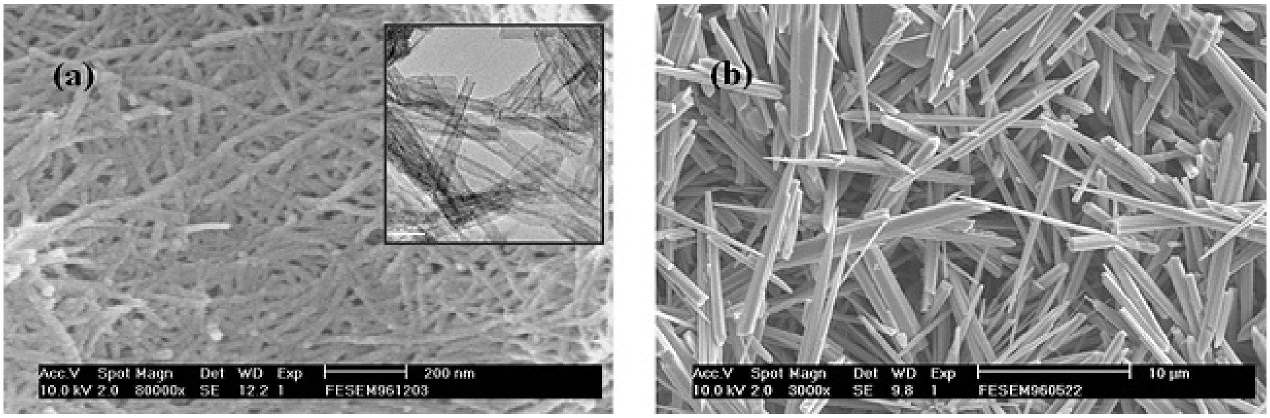


Fig. 1 FE-SEM images of (a) TiO_2 nanowires (b) ZnO nanowires. Inset of (a) shows the transmission electron microscopic image of TiO_2 nanowires.

Samples of (I) ZnO nanowires and conventional spherical TiO_2 powder with micrometer diameters, and (II) ZnO nanowires and TiO_2 nanowires were prepared for DTA measurement to study their thermal stability (Fig. 2). The DTA curve of sample I is explained well by the known TiO_2-ZnO phase diagram. That is, c-$Zn_2Ti_3O_8$ transformed to h-$ZnTiO_3$ at ~800℃, decomposing to rutile and c-Zn_2TiO_4 at ~930℃. The use of ZnO nanostructures reduced the decomposition temperature of h-$ZnTiO_3$ only by ~15℃. In contrast, the endothermic valley of h-$ZnTiO_3$ in sample II shifted downward to a lower temperature below 800℃. This effect is attributed to the use TiO_2 with a high specific surface area. The X-ray diffraction (XRD) patterns of samples II agreed significantly with the DTA observations (Fig. 3).

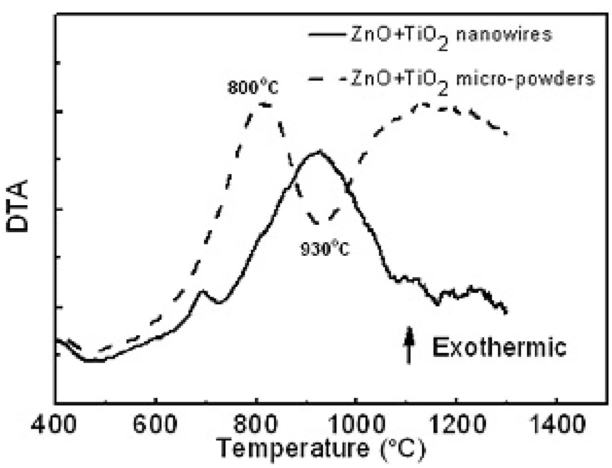


Fig. 2 DTA curves for ZnO nanowires mixed with (I) TiO_2 micro-powders (dashed line) and (II) TiO_2 nanowires (solid line).

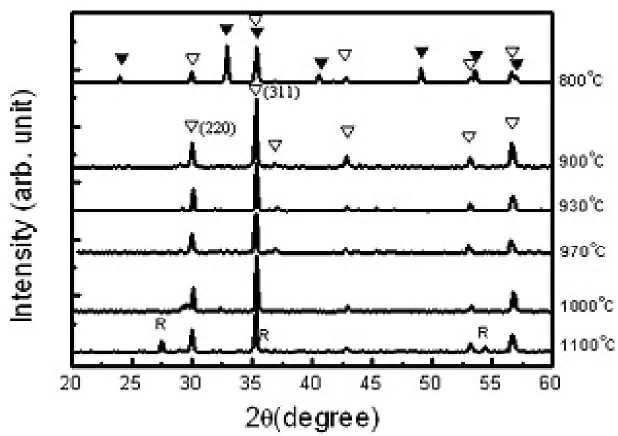
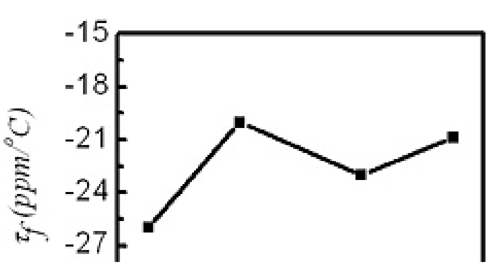


Fig. 3 XRD patterns for samples II.

TiO_2：ZnO (1：1 molar ratio) nanowires were sintered by solid-state sintering without calcination. The dielectric properties were measured at microwave frequency. The value of quality factor multiples the resonant frequency (Q×f) achieved ~22000 when sintered at 1000℃, indicating a potential application in microwave devices. The



temperature coefficient of resonant frequency (τ_f) changed slightly from -26 to -20 as the temperature increased from 900 to 930℃, and then remained constant (-20 ppm/℃) as the temperature increased to 1000℃ (Fig. 4). Furthermore, the relative dielectric constants (ε_r) increased monotonically from 15 to 21 as the temperature increased from 900 to 1000℃. Because of the high τ_f (+450 ppm/℃) and ε_r (105) of rutile, the sign of τ_f of the zinc titanates depends on the amount of rutile. Contrary to works of the dielectric properties of the zinc titanates, no obvious variation between τ_f values over a large range of temperatures were detected. Furthermore, a zero τ_f was expected to be easily achieved by sintering at a temperature of over 1000℃ or by co-firing with very small amount of TiO_2 or other ceramic with positive τ_f. The attempt of adding some TiO_2 is going to be published elsewhere. The shift of the decomposition temperature (from 945℃ to <800℃) suggest that the use of nanosized starting materials for sintering ceramics effectively lowers the sintering temperature.

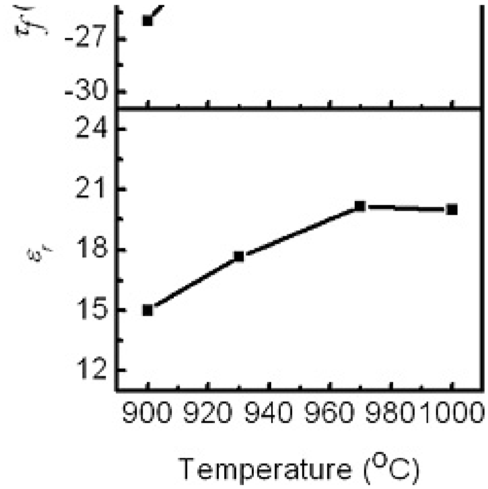


Fig. 4 τ_f and ε_r of the zinc titanates sintered at different temperatures.

In conclusion, this paper presented a calcine-free solid-state sintering process of zinc titanates sintered by hydrothermally synthesized ZnO and TiO_2 nanowires. Unique phase transformation and microwave dielectric properties were found. This attempt is expected to be applied to future development of ceramics with a low sintering temperature and a low-cost process. The thermodynamics and kinetics of the nanowire sintering is a new research topic.