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Structural and electrical properties of sintered Fe_2O_3/TiO_2 nanopowder mixtures

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Abstract

Starting nanopowders of TiO_2 (anatase 99.7%) and α-Fe_2O_3 (hematite) were mixed in the weight ratios 60:40 and 40:60. Green samples were sintered in the temperature range 750–1250 °C in air. Structural, morphological and electrical studies were carried out using XRD, SEM and EDS analysis, Hall measurements and electrical conductivity measurements. The aim was analyzing the influence of the starting nanopowder structure on the resulting sample composition, density, grain size and electrical resistivity in view of tailoring properties for developing different applications such as anodes for photoelectrochemical cells, photocatalysts and gas sensors. Compared to pure anatase samples, the presence of hematite lowered the temperature of completion of the anatase to rutile phase transformation to 850 °C. Formation of pseudobrookite was also noted at this temperature. Higher sintering temperatures lead to increased sample density, changes in grain size (grain growth and inhomogenous microstructure) and decreased electric resistivity.

Keywords: A. Grain growth; A. Sintering; C. Dielectric properties; C. Electrical conductivity; Pseudobrookite

1. Introduction

Interest in nanostructured materials has increased rapidly due to some outstanding properties presented by solid materials at the nanoscale [1]. Nanomaterials have been studied in the form of single nanoparticles, individual monodimensional nanostructures (nanorods and nanotubes) or thin films. However, limited attention has been paid to the role that the nanostructure plays in altering the physical properties of materials in bulk form. In some cases the nanostructure enhances characteristics already present in the material, making them more evident, while in others the nanostructure can produce significant modifications in the physical properties. The size effects of the small grain size of the starting powder are in the much larger fraction of atoms localized at interfaces or close to them. Zhang and Banfield studied the impact of particle size on phase stability and phase transformation during the growth of nanocrystalline aggregates of TiO_2 anatase [2] and anatase/brookite [3]. The small grain size of the starting powder will have an influence on the physical properties of ceramics in bulk form both in the case of nanostructured bulk materials and bulk materials with a larger grain size.

Both iron oxide ceramics and titanium oxide ceramics are widely utilized for electronic devices. Iron oxide has a low band gap (2.2 eV), low cost, chemical stability and is environmentally friendly. As a photocatalyst it could absorb most of the visible light, but this is inhibited by poor electrical conductivity [4]. Poor conductivity of bulk hematite inhibits its possible application as a gas sensor [5–7] or photoanode for solar fuel production [8]. Much work has been done to improve the photoelectric and gas sensing properties of hematite including controlling the morphology and size, or

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doping. Recent research has focused on Fe_2O_3/TiO_2 heterogeneous photocatalysts with different mass ratio of Fe_2O_3 and TiO_2 [4]. TiO_2 substituted Fe_2O_3 nanoparticles have been investigated as promising materials for gas sensors (ethanol [9], hydrogen [7]) and other applications. Substitution of TiO_2 in α-Fe_2O_3 above the solubility limit leads to the formation of Fe_2TiO_5 (pseudobrookite). Yu et al. [5] synthesized nanocomposite hollow spheres of Fe_2TiO_5/α-Fe_2O_3. The formation of pseudobrookite created new boundaries between grains of different compositions. This further increased the sample conductivity and coupled with the porous nanostructure improved ethanol gas sensing properties. Courtin et al. [10] investigated improved visible light photoresponses in nanoheterostructured mesoporous photoanodes containing anatase, pseudobrookite and hematite. Pseudobrookite is a rare mineral present in ingenous and metamorphic rocks [11]. It can be produced during the processing of ilmenite ores [12,13]. Pseudobrookite Fe_2TiO_5 with the orthorhombic structure has typically been synthesized through solid-state reactions between Fe_2O_3 and TiO_2 or sol–gel methods [14–17]. Min et al. [18] recently obtained phase-pure pseudobrookite powders by ball milling and hydrothermal processes followed by thermal calcination. Solid state deoxidation of Fe_2O_3/TiO_2 oxide pellets with the purpose of obtaining FeTi for reversible hydrogen storage was studied by Tan et al. [19]. Pseudobrookite exhibits anisotropic spin-glass behavior [20]. Pseudobrookite has a favorable band gap of around 2.0 eV, good solar spectrum absorbing properties, stability in aqueous solutions and has potential to be applied as a photoanode in photoelectrochemical cells [8]. Pandey et al. [21,22] investigated the resistance of pseudobrookite to radiation in view of possible application in radiation hard electronics, microelectronics and spintronics.

In this work we have investigated the influence of the sintering temperature (750–1250 °C) on the phase composition, phase transition temperature, morphology and electrical properties of bulk sintered powder mixtures composed of starting anatase and hematite nanopowders. We have followed how the evolution of the phase content and morphology with increase in the sintering temperature correlated with changes in electrical properties.

2. Experimental

Homogenization of the mixture of hematite (Alfa Aesar, 99%, grain size 20–60 nm) and anatase (Alfa Aesar, 99.7% anatase, grain size 15 nm) powders in the weight ratio 60:40 and 40:60 was performed in a planetary ball mill (Fritsch Pulversisette 5) in stainless steel bowls with stainless steel balls for 60 min. Green samples 10 mm in diameter of the two mixtures and also of pure anatase and hematite were sintered in air in the temperature range 750–1250 °C for two hours. Green samples 8 mm in diameter and 2 mm thick of all four powders were also sintered in a Bähr Gerätebau Type 802s dillatometer with a tube furnace to 1200 °C with a heating rate of 10°/min. Sample density was determined from weight and volume (dimension) measurements.

XRD patterns were recorded on a RIGAKU RINT2000 diffractometer, CuK_α=1.54178 Å. The Sherrer equation was used to estimate the average crystallite size:

$$D = 0.9\lambda/(\beta \cdot \cos\ \theta) \qquad (1)$$

where λ is the X-ray wavelength, θ is the Bragg angle and β the pure full width of the diffraction line at half of the maximum intensity.

SEM analysis was performed on a TESCAN Electron Microscope VEGA TS 5130MM device, while EDS analysis was performed on a INCA Penta FETX3 energy dispersive system. Images were observed on freshly fractured samples. The average grain size was estimated from SEM images by averaging at least 100 grains on the analyzed SEM micrograph.

Hall measurements were performed at room temperature on a Hall effect measurement system (Ecopia HMS-3000) with an applied field of 0.37 T.

Samples used for electrical conductivity measurements were prepared in the form of a sandwich electrode structure. Silver coatings were used as electrodes (ohmic contact). Samples with silver electrodes deposited on both sides were prepared in the capacitor form and can be considered electrically equivalent to a capacitance C_p in parallel with a resistance R_p. These parameters were measured at room temperature in the frequency range 100 Hz–10 MHz on a HP-4194A impedance/gain-phase analyzer with a HP-16047A test fixture. A personal computer with in-house built software was used for acquisition of measured data.

3. Results and discussion

3.1. Structural characterization

Analysis of XRD diagrams of samples of TiO_2 (99.7% anatase) nanopowder sintered in the temperature interval 750–1250 °C (Fig. 1) showed that besides anatase (JCPDS 89-4921) a small

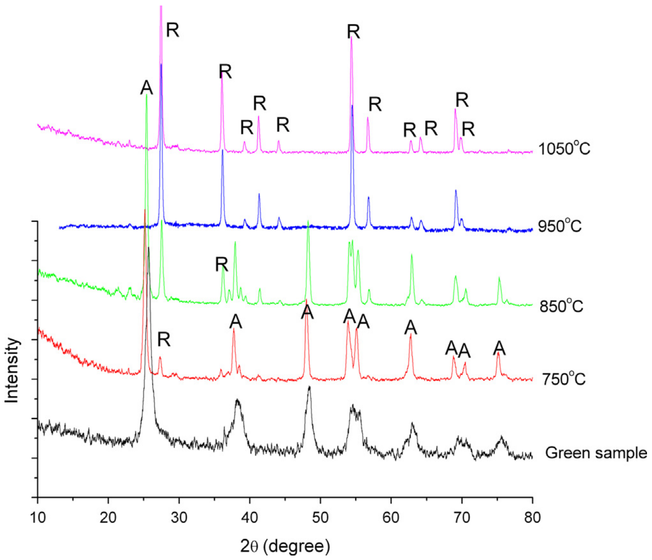

Fig. 1. XRD patterns of TiO_2 sintered 750–1250 °C.