Journal of Alloys and Compounds 677 (2016) 185–189

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Solid state synthesis and structural characterization of zinc titanates

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ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form
19 March 2016
Accepted 28 March 2016
Available online 30 March 2016

Keywords:
Zinc titanates
Sintering
IR spectroscopy
Raman spectroscopy

ABSTRACT

Zinc titanate composite materials were synthesized via solid state sintering process using high-purity metal oxide powders (purity ~99.99%). The titanium incorporation into ZnO matrix was investigated by X-ray diffraction which revealed the coexistence of spinel Zn_2TiO_4 and hexagonal $ZnTiO_3$ with the ZnO wurtzite structures. No reflection peaks of rutile TiO_2 phase were detected. The IR spectroscopy and Raman scattering spectroscopy were used to characterize the structural and chemical properties of the ZnO/TiO_2 composites. The IR bands and vibrational modes of all crystalline phases were detected. The effect of TiO_2 doping rates (x = 3, 5 and 7 wt%) on bands shifting, Raman intensity and structural quality was discussed.

1. Introduction

Zinc titanates are interesting and technologically important materials that attracted great deals of research. They have been extensively investigated for many applications such as catalytic sorbents for the desulfurization of hot coal gases, white color pigments [1] and most importantly as dielectric materials for microwave devices [2–4]. As suggested by Levy [5,6], there are five compounds in ZnO/TiO_2 system. However, only three compounds were confirmed to exist at high temperatures Zn_2TiO_4, $ZnTiO_3$ and $Zn_2Ti_3O_8$. Among these compounds, ilmenite-type hexagonal $ZnTiO_3$ has been reported to possess superior electrical properties. It has a rhombohedra structure which can be decomposed into Zn_2TiO_4 and rutile TiO_2 at $T \geq 945$ °C during the solid state reaction process. So, it is considered to be a metastable phase above this temperature [7].

Synthesis and characterization of ZnO/TiO_2 system have been reported by many authors [7–11]. Zinc titanates still catch the attention of the researchers. M.R. Vaezi and al. [10] synthesized $Zn_2TiO_4/ZnTiO_3$ via CBD (Chemical Bath Deposition) method and reported the temperature effect on morphologies and compositions of the compounds. They found that the appropriate temperature of synthesis $ZnO/Zn_2TiO_4/ZnTiO_3$ nanocomposite powders is in the range between 25 °C and 55 °C. Lei Hou and al. [11] have obtained ilmenite $ZnTiO_3$ using sol gel process. The thermal behavior and phase transformation of the gels revealed that complete crystallization of hexagonal $ZnTiO_3$ is obtained at about 800 °C. P. Vlazan and al. [12] have prepared TiO_2/ZnO core-shell nanoparticles by hydrothermal method in two stages. They observed the agglomeration of nanoparticles, the decrease of the resistivity and the increase of the electrical conductivity with temperature. Yamaguchi and al. [13] elucidated that $Zn_2Ti_3O_8$ is a low temperature form of $ZnTiO_3$. Zn_2TiO_4 can be easily obtained by conventional solid state reaction between 2ZnO and $1TiO_2$. However, pure $ZnTiO_3$ preparation from a mixture of 1ZnO and $1TiO_2$ has not been successful due to its decomposition at about 945 °C. A. Stoyanova and al. [14] proved that the synthesized ZnO/TiO_2 nanocomposites via non-hydrolitic method can be good inorganic antimicrobial agents. B.C. Yadav and al. [15] prepared nanocrystalline zinc titanate via simple physicochemical process and demonstrated the sensing behavior of $ZnTiO_3$ to liquefied petroleum gas. A. Shalaby and al. [16] applied a sol gel method due to obtain a nanocomposite material containing several active phases and possessing a powerful bactericidal effect. Actually, there are several methods to prepare zinc titanates ceramic materials but we chose to adopt conventional solid state reaction in our research paper because it is simpler to operate and uses cheap and easily available oxides as starting materials. In addition to this method of synthesis, we picked low TiO_2 concentrations in order to avoid the segregation of rutile TiO_2 secondary phase as occurred in our previous team work with high MgO concentrations [17].

The aim of the current work is to investigate the effect of the

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http://dx.doi.org/10.1016/j.jallcom.2016.03.244
0925-8388/

TiO_2 incorporation into ZnO matrix via XRD analysis, infra red and Raman spectroscopy measurements, using high-purity raw materials.

2. Experimental details

The zinc titanates materials were prepared by using a conventional solid state sintering process using pure ZnO and TiO_2 powders (purity ~99.99%) as the starting materials. The chosen weight amounts of TiO_2 were (x = 3, 5 and 7 wt%). The mixed components were homogenously milled in an agate and then calcined in air at 300 °C for 3 h. The mixed powders were pressed into pellets (of 1 mm in thickness and 8 mm in diameter) and sintered at high temperature 900 °C for 24 h with heating rate of 20 °C/min. Pellets were then cooled slowly to room temperature. The Optical measurements were examined in our previous study in the wavelength range 200–1000 nm via UV-VIS-NIR spectrophotometer (SHIMADZU UV-3101PC) and were compared with some literature data as shown in Table 1 [14,15,18]. Powder X-ray diffraction (XRD) studies were carried out in the scan range 2θ = 25°–60° using Bruker axs D8 advance diffractometer with Cu-Kα radiation wavelength of 0.15406 nm. IR spectroscopy was performed using Perkin Elmer spectrometer ranging from 400 to 2500 cm^{-1}. Raman spectra were executed by Micro-Raman Horiba HR 800 in the wave number range 50–2000 cm^{-1}. All measurements were taken at room temperature.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of doped ZnO powder with different TiO_2 concentrations. ZnO peaks are typically identified using JCPDS card N° 36-1451. The prominent diffraction peaks attributed to hexagonal wurtzite ZnO are located at 2θ = 31.82°, 34.48°, 36.31°, 47.59° and 56.60° which are respectively assigned to (100), (002), (101), (102) and (110) plane reflections. The TiO_2 incorporation in ZnO matrix is proved by the appearance of some peaks referred to zinc titanates ceramic materials such as spinel Zn_2TiO_4 and ilmenite-type hexagonal $ZnTiO_3$. Nevertheless, no reflection peaks of TiO_2 structure are detected. It shows at 2θ = 29.88°, 36.72° and 42.74°, the Zn_2TiO_4 peaks attributed respectively to (112), (202) and (220) planes according to JCPDS card N° 19-1483. The hexagonal $ZnTiO_3$ peaks are situated at 2θ = 35.16°, 53.00° and 56.66° assigned to (110), (116) and (018) respectively (JCPDS card N° 26-1500). The ionic crystal radii of Zn^{2+} and Ti^{4+} are respectively 0.75 and 0.61 Å which stimulate essentially the slight blue shift followed after that by a red shift for TiO_2 doping rate x = 7 wt% and the notable intensity changes of zinc titanates peaks as observed in the inset. These changes are most likely caused by the existence of uniform and non-uniform strains in doped ZnO [19]. In our case, the alloying is more enhanced with increasing TiO_2 doping concentrations as demonstrated in our previous investigations [18], also, the intensities of $ZnTiO_3$ peaks still rising until an amount x = 5 wt% and decreasing after that.

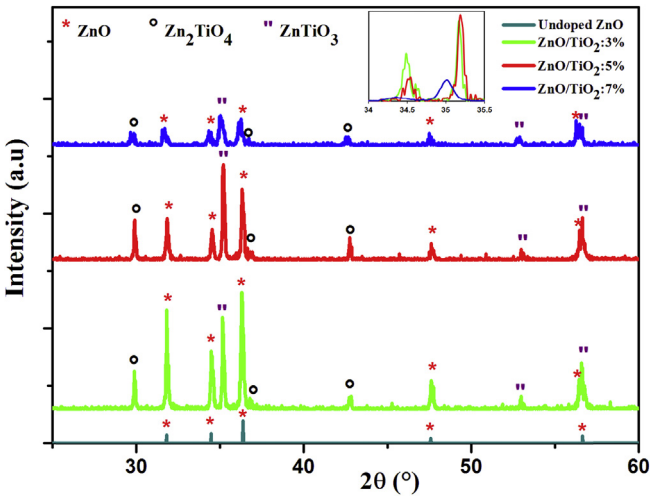

Fig. 1. XRD profiles of ZnO–TiO_2 composites with rutile amounts x = 3, 5 and 7 wt%.

The TiO_2 effect can be viewed also in the structural parameters such as lattice constants ("a" and "c"), grain size and lattice stress calculated respectively from the equations below:

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3}\left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (2)$$

$$\sigma = Y_{hkl}\,\varepsilon \quad (3)$$

where d_{hkl} is the distance between adjacent planes in the Miller indices (hkl), D is the grain size, λ is the wavelength of the used X-ray radiation, k is the constant equal to 0.9, β_{hkl} is the full width at half maximum (FWHM) of the diffraction peak, θ is its Bragg diffraction angle, Y_{hkl} is Young's modulus, ε is the strain constant and σ is the lattice stress. For a hexagonal structure, Young's modulus is calculated as ~127 GPa [20].

Fig. 2 a) illustrates the decrease of lattice parameters just before the TiO_2 doping rate 5 wt%. This decrease should be engendering lattice strain and stress in the bulk of synthesized ZnO/TiO_2 ternaries. Indeed, it is seen in Fig. 2 b the diminishing of lattice stress which can be generated most likely from the existence of impurities, defects and lattice distortion from 50.8 to −38.1 MPa [21]. However the decrease of the grain sizes from 69 to 33 nm can be related to the crystalline segregation effect and the feeble coalescence of nano-grains at 900 °C [19]. Similar results have been reported in literature [21,22]. M. S. Kim and al. [21] have observed the

Table 1
Characteristics of zinc titanates obtained by different TiO_2 concentrations.

Synthesis method	T (°C)	TiO_2 concentration	Grain size (nm)	Eg (eV)	% Sensor response	Field of application	Ref
Solid state sintering method	900	1–7 wt%	73–33	ZnO:3.10–3.18 $ZnTiO_3$:4.75–5.05			[18]
Physicochemical route	450		19	$ZnTiO_3$:4.1	TiO_2:45% ZnO:260%	Liquefied petroleum gas sensor	[15]
Nonhydrolytic route	200–600 and 500	50 mol% and 90 mol%	15–20			Inorganic antimicrobial agents	[14]