Zinc Titanate Nanopowders. Synthesis and Characterization

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Research Article

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Zinc titanate nanopowders. Synthesis and characterization

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Abstract:

Zinc titanates nanopowders viz.; Zn$_2$TiO$_4$, ZnTi$_3$O$_8$ and ZnTiO$_3$ were synthesized through the thermal decomposition course of ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ precursor (1:1 mole ratio), prepared via a new co-precipitation method up to 900°C. Thermogravimetric measurement (TG) was utilized to characterize the precursor decomposition while X-ray diffraction (XRD), Fourier transform infra-red (FT-IR) were used to characterize the decomposition products as well as the phase transitions at different temperatures. XRD revealed the starting of titanates formation at 700°C via detecting Zn$_2$TiO$_4$ along with ZnO and TiO$_2$ (anatase) diffraction peaks. By increasing the calcination temperature to 800°C, the ZnO content vanished with the appearing of Zn$_2$Ti$_3$O$_8$ besides ZnTi$_2$O$_4$ and impurities of TiO$_2$ (anatase). Finally at 900°C, the Zn$_2$Ti$_3$O$_8$ content was decomposed into ZnTiO$_3$. Nitrogen adsorption-desorption isotherm of the calcined precursor at 900°C indicated low specific surface area of 7.1 m$^2$ g$^{-1}$ in accordance with the agglomeration nature estimated via transmission electron microscopy (TEM) study. The conductivity measurements showed semiconducting behavior of the prepared titanates with ferroelectric transition in the range 200-308°C. The obtained low dielectric value suggests the uses of present titanates as a co-fired ceramic or resonator ceramics.

Keywords: Zinc titanates; TG; surface are; decomposition; conductivity; dielectric.
1. Introduction

Perovskite oxides; MTiO$_3$ titanates (M = Zn, Sr, Fe, Cd, Ba, Pb, etc.) have been regarded as materials having various applications in solid-oxide fuel cells electrodes; SOFCs [1], metal–barriers [2], sensors [3], electronics [4] and catalysts [5]. As a well-known member of this family, Zinc titanate (ZnTiO$_3$) was already used as pigment [6], dye adsorbent [7], sensor for NO and CO gases [8], microwave resonator materials [9], heat reflective pigment [10] and photocatalyst [11].

Based on the literature [6,12,13], there are three phases existing in the system of ZnO-TiO$_2$: zinc orthotitanate; Zn$_2$TiO$_4$ having cubic spinel structure, Zn$_2$Ti$_3$O$_8$ having defect cubic structure and metatitanate; ZnTiO$_3$ with ilmenite rhombohedral structure. Zn$_2$TiO$_4$ could be easily prepared using conventional ceramic technique using 2:1 mole ratio of ZnO:TiO$_2$ and is considered to be stable up to 1418°C. On the other hand, metastable Zn$_2$Ti$_3$O$_8$ is considered as the low temperature form of ZnTiO$_3$ up to 820°C. Finally, the ilmenite form; ZnTiO$_3$ is very hard to obtain since it decomposes into orthotitanates; Zn$_2$TiO$_4$ and TiO$_2$ (rutile) at 945°C.

The different preparation methods for all zinc titanate phases are reviewed [6]. Co-precipitation method can be considered as the most successful one for obtaining ultrafine powder with narrow size distribution. Using this method, the more complex steps could be avoided besides less time consumption and high purity compared to other methods.

In the present manuscript, a simple coprecipitation technique will be followed to synthesize nano-crystalline zinc titanate powders. In this technique, a stoichiometric co-precipitated mixture of ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ (1:1 mole ratio) will be thermally decomposed up to the titanate formation. To our best knowledge, this is the first report on the synthesis of zinc titanate nanopowder by this method in the literature. The titanate phase’s formation as well as their structure characterization, morphology and phase transitions will be investigated via TG-
DTG, XRD, FT-IR, TEM and BET measurements. The different electrical properties viz. ac-
conductivity as well as dielectric property will also be evaluated.

2. Experimental procedures

2.a. Materials

Basic zinc carbonate monohydrate; ZnCO$_3$.2Zn(OH)$_2$.H$_2$O, unhydrous oxalic acid;
H$_2$C$_2$O$_4$ and titanium dioxide (anatase); TiO$_2$ all are of analytical grade (BDH) and utilized as
received.

2.b. Synthesis process

The entire titanates were prepared in the present study via the thermal decomposition of
oxalate-titania precursor; ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ (1:1 mole ratio). A new innovative route for the
preparation of this precursor was utilized in which, a stoichiometric amount of oxalic acid
solution equivalent to precipitate zinc oxalate was added drop wisely to the calculated amount
of basic zinc carbonate and titania suspension under vigorous stirring at about 60°C. after
complete precipitation, the zinc oxalate is expected to precipitate on TiO$_2$ surface through
heterogeneous nucleation [14]. The prepared precursor was filtered, washed with distilled
water, dried then given the name; as-prepared precursor. To characterize the precursor
decomposition route until titanate formation, different samples were calcined in a muffle
furnace at 400°C for 30 min, 500 and 600°C for 1h and for 2h at 700, 800 and 900°C.

2.c. Characterization

Thermogravimetric analysis (TG) of the prepared precursor was conducted in air by a
Perkin Elmer thermal analyzer (STA 6000) at heating rate of 5°C/min up to 1100°C. The
crystal phases were estimated by X-ray diffraction (Bruker AXS) with Cu Kα radiation (λ =
1.5418 Å). The titanates sample were morphologically characterized using transmission electron micrograph (JEOL-2010) with 100 kV accelerating voltage. FT-IR spectra were measured using a JASCO FT-IR 310 spectrophotometer. Specific surface area was measured using BET adsorption and ASAP 2010 analyzer. In electrical measurements, the calcined powders were pressed into pellets (1 cm diameter and 1mm thickness) using 2 ton.cm\(^{-2}\) pressure. The two probe method was then used for measuring the temperature dependence of conductivity and dielectric constant at different frequencies (1-1000 kHz), using a Hioki LCR bridge model 3531.

3. Results and discussion

3.a. Thermal decomposition of ZnC\(_2\)O\(_4\).2H\(_2\)O-TiO\(_2\) precursor

The full decomposition course of ZnC\(_2\)O\(_4\).2H\(_2\)O-TiO\(_2\) precursor (Fig. 1), up to 1000°C in air, consists of three well-defined TG steps. According to the calculated weight losses, the first two steps could be attributed to the loss of water with the formation of anhydrous ZnC\(_2\)O\(_4\)-TiO\(_2\) mixture. The calculated weight loss (14.0 %) for the dehydration process agreed well with that experimentally obtained (13.9 %) up to about 240°C. The dehydration process was found to occur through two separated TG steps in the temperature ranges; 100-125 and 215-240°C, respectively which are characterized by two differential thermogravimetric (DTG) peaks at 116 and 226°C. According to Diefallah [15], the water lost at low temperature range can be considered as crystal water while that lost at higher temperatures as coordinately bounded.

In the third TG step appeared in the range from 306 to 387°C (with DTG peak at 362°C), the observed weight loss (25.5 %) agreed well with the calculated one of 26.5 % attributed to the decomposition of the oxalate content with the formation of ZnO-TiO\(_2\) mixture and evolution of Co and CO\(_2\) as decomposition products [16]. No further weight changes could be observed up to 1000°C.
3.3. X-ray diffraction and titanates formation

The thermal decomposition course of the studied precursor as well as the titanates formation was successfully followed using XRD measurements of calcined precursor samples at temperatures ranging between 400 and 900°C. Fig. 2 illustrates XRD patterns of the different calcined samples along with the different phases formed during calcination process. XRD pattern of the as-prepared precursor indicated the characteristic individual diffraction peaks of both monoclinic ZnC$_2$O$_4$.2H$_2$O and tetragonal TiO$_2$ (anatase) according to the JCPDS file Nos. (25-1029) and (78-2486), respectively. This confirmed well the complete reaction between basic zinc carbonate and oxalic acid without any indication for the presence of any side products.

XRD pattern of the sample calcined at 400°C showed, in agreement with the decomposition course (Fig. 1), the presence of hexagonal ZnO and tetragonal TiO$_2$ (anatase). The obtained diffraction peaks agree well with those presented in the JCPDS file Nos. (79-0206) and (78-2486), respectively. The no indication for the presence of any peaks characteristic for titanates at this calcination temperature confirmed the inability of any interaction between the decomposition products. The only observed change in the diffraction patterns for samples calcined at 500 and 600°C (Fig. 2) is the obvious improvement in the samples crystallinity without the indication for the appearing of any new phase.

For the sample calcined at 700°C, the obvious appearance of new XRD peaks characteristic for face-centered cubic Zn$_2$TiO$_4$ (JCPDS file No. 73-0578) besides the still exist of ZnO and TiO$_2$ (anatase) peaks indicated the just initiation of the interaction between mixed oxides and titanates formation. In literature, lot of investigations [17-19] were reported on the inability of pure ZnTiO$_3$ formation from 1:1 mole ratios of ZnO and TiO$_2$ mixture. Others [20-22] succeeded to prepare pure ZnTiO$_3$ phase using sol-gel methods. On the other hand, many researchers [19, 23-26] obtained a mixture of titanates such as ZnTiO$_3$, Zn$_2$Ti$_3$O$_8$ and Zn$_2$TiO$_4$
with $\text{Zn}_2\text{TiO}_4$ as major phase. Ivanova et al. [27] and Yan et al. [28] prepared $\text{Zn}_2\text{TiO}_4$, $\text{TiO}_2$ and $\text{ZnO}$ via sol-gel and hydrothermal routes, respectively using 1:1 mole ratio of $\text{Zn}:\text{Ti}$ mixture. Siriwong and Phanichphant [29] prepared $\text{Zn}_2\text{TiO}_4$ single-phase using 1:1 mole ratio of zinc naphthenate and titanium tetra isopropoxide precursors by the flame spray pyrolysis technique.

The precursor calcined at 800°C showed the complete vanishing of $\text{ZnO}$ diffraction peaks with the appearance of diffraction peaks characteristic for the presence of $\text{Zn}_2\text{TiO}_4$ and $\text{Zn}_2\text{Ti}_3\text{O}_8$ (JCPDS file No. 87-1781) phases indicating the complete titanates formation. The $\text{Zn}_2\text{Ti}_3\text{O}_8$ with a defect cubic spinel structure, was first discovered by Yamaguchi et al. [17] and is considered as the low temperature phase of $\text{ZnTiO}_3$. The presence of very weak peaks attributed to the presence of $\text{TiO}_2$ (anatase) could be ascribed to the reduction of very few amount of $\text{ZnO}$ to volatile elemental $\text{Zn}$ [21].

Liu et al. [26] reported that the formation of $\text{Zn}_2\text{TiO}_4$ and $\text{Zn}_2\text{Ti}_3\text{O}_8$ phases could only happen in the presence of anatase whereas $\text{ZnTiO}_3$ formation is limited only in the presence of rutile. They also reported that, when anatase grains are small enough then, it could be completely utilized in the formation of $\text{Zn}_2\text{TiO}_4$ and $\text{Zn}_2\text{Ti}_3\text{O}_8$ while if they are large enough, an anatase to rutile transition would be took place with increasing probability for $\text{ZnTiO}_3$ formation. In this context, the estimated grain size of the anatase phase (for the sample calcined at 700°C) using the strongest peak (101) and Scherrer’s equation [30] amounts to 67 nm which is expected to be small enough to form $\text{Zn}_2\text{TiO}_4$ and $\text{Zn}_2\text{Ti}_3\text{O}_8$ mixture.

The calculated grain size of the very few amount of anatase in the sample calcined at 800°C (using the strongest peak 101) is about 104 nm which is large enough for anatase-rutile transition and $\text{ZnTiO}_3$ formation. This why the XRD pattern of the sample calcined at 900°C indicated the presence of hexagonal $\text{ZnTiO}_3$ (JCPDS file No. 25-0671). The decomposition of metastable $\text{Zn}_2\text{Ti}_3\text{O}_8$ into $\text{ZnTiO}_3$ and $\text{TiO}_2$ (anatase) by increasing calcination temperature to
900°C illustrates the increasing amount of ZnTiO₃. Again, the presence of weak diffraction peaks characteristic of rutile phase (JCPDS file No. 21-1276) confirmed the anatase-rutile transition and ZnTiO₃ formation.

Really, the reason for selecting the (1:1) mole ratio of ZnC₂O₄:TiO₂ in the present preparation was that this ratio would correspond to the stoichiometric ZnTiO₃. Instead, the above XRD study indicated the formation of different zinc titanate phases including: ZnTiO₃, Zn₂TiO₄ and Zn₂Ti₃O₈. Accordingly, the phase transitions along the present decomposition could be represented as:

\[
\begin{align*}
ZnC₂O₄·2H₂O·TiO₂ & \rightarrow ZnC₂O₄·TiO₂ \rightarrow ZnO·TiO₂ \rightarrow ZnO + \text{anatase} + Zn₂TiO₄ \\
Zn₂TiO₄ + Zn₂Ti₃O₈ + \text{anatase} & \rightarrow Zn₂TiO₄ + Zn₂Ti₃O₈ + \text{anatase} + \text{rutile}
\end{align*}
\]

3.c. FT-IR spectroscopic study

The thermal decomposition course of the entire precursor as well as the titanates formation was also characterized using FT-IR spectroscopy. The characteristic bands obtained for the as-prepared precursor and samples calcined at different temperatures are exhibited in Fig. 3. The precursor sample showed a very broad FT-IR bands around 3441 and 1652 cm⁻¹ assigned to the stretching vibration of O-H bond of water in hydrated zinc oxalate molecule. The vibration band at about 1302 cm⁻¹ could be attributed to the symmetric mode of oxalate ion’s carbonyl group [14]. The observed bands at 773 and 506 cm⁻¹ are attributed to the out-of-plane and in-plane bending modes of water and O–C–O of oxalate, respectively while the band at 348 cm⁻¹ could be assigned to the metal ion vibration [31]. Finally, the bands at 680 and 2924 cm⁻¹ are attributed to TiO₂ [32].

The calcined precursor at 400°C showed a decrease in the band intensities due to the carbonyl group as a result of oxalate content’s decomposition with the formation of metal oxides as discussed above in TG and XRD results. Thus, the broad band appeared at 525 cm⁻¹
can be assigned to the metal-oxygen (M-O). The further appearance of the bands characteristic of water at 3441 and 1652 cm\(^{-1}\) could be attributed to the presence of adsorbed water formed during sample preparation. The samples calcined at 500 and 600\(^\circ\)C indicated nearly the same bands indicated same composition without any chance for titanate formation.

The calcined samples at 700, 800 and 900\(^\circ\)C indicated alike patterns with an apparent absorption band at 583 cm\(^{-1}\) ascribed to Ti–O stretching vibration due to [TiO\(_6\)] octahedron group existing in all titanates forms of Zn\(_2\)TiO\(_4\), Zn\(_2\)Ti\(_3\)O\(_8\) and ZnTiO\(_3\) as previously reported [20,21].

3.d. Morphological study

XRD pattern of the sample calcined at 900\(^\circ\)C (Fig. 2), as previously described, indicated two types of particles including Zn\(_2\)TiO\(_4\) and ZnTiO\(_3\) besides traces of TiO\(_2\). In agreement with this result, TEM image of the calcined precursor at 900\(^\circ\)C (Fig. 4) exhibited two distinct types of particles having different sizes. Generally, the particles are nearly spherical with particle sizes of about 60 and 130 nm and exhibited a dense aggregation. A similar result was obtained by Arin et al. [33] for zinc titanates synthesized via hydrothermal method.

3.e. Surface area characterization

Nitrogen adsorption-desorption isotherm of the calcined precursor at 900\(^\circ\)C (Fig. 5) exhibited, according to the IUPAC classification [34], type II isotherm in which the adsorption is on macroporous adsorbents through strong adsorbate-adsorbent interaction. This type exhibited also a very small hysteresis as appeared in Fig. 5. The specific surface area (SSA) calculated according to BET method is about 7.1 m\(^2\) g\(^{-1}\) which can be considered as the surface area of Zn\(_2\)TiO\(_4\) and ZnTiO\(_3\) main contents. This very low surface area could be attributed in accordance with the TEM image (Fig. 4) to the agglomeration nature of the powder which
lowering porosity. Pore size distributions (BJH) (inset of Fig. 5) showed narrow distribution characterized by three pore size types located around 19, 28 and 42 nm.

3.f. Electrical properties measurements

3.f.i. ac-conductivity

The ac-conductivity measured at different applied frequencies by changing temperature from 30 to 450°C have been studied. The ln\(\sigma\) vs. 1000/\(T\) plot at frequencies ranging between 1 kHz and 1 MHz for the sample calcined at 900°C is shown in Fig. 6(a). The conductivity showed a decreasing behavior by increasing temperature up to about 90°C. During sample’s preparation for conductivity measurements, some water molecules were adsorbed on the titanates surface. This water can be acting as conductor and its removal by increasing temperature could result in decreasing conductivity. Similar behavior was already reported in literature during conductivity measurements [35].

The conductivity showed frequency dependence at low temperatures, in which conductivity increases with increasing frequency, while it indicated frequency independence at higher temperatures. This behavior could be described based on the pumping force of the applied frequency which facilitate the charge carriers’ transfer. By increasing temperature, the generated phonons resist the moving of the charge carriers through phonon-electron collisions and thus canceling the applied frequency effect [36].

The estimated conductivity at 110°C (i.e. temperature at complete adsorbed water evaporation) and frequency of 1 MHz amounts to 6.4x10^{-7} ohm^{-1} cm^{-1}. The conductivity is appeared to be temperature dependent after 110°C and showed a gradual increase with increasing temperature which reflects semiconducting behavior of the present studied titanates. An anomalous behavior was observed in the rising portion of the curve by increasing temperature in the range 200-308°C. By a closer look to Fig. 6(a), this anomalous behavior,
appeared as a transition peak, is clearer at higher frequencies (≥ 500 kHz) and also indicated a gradual change in the peak position to lower temperature by increasing frequency.

Chang et al. [37] reported an anomalous strong decrease (exponential decrease) in conductivity vs. reciprocal temperature close to the ferroelectric Curie temperature ($T_C$) in most perovskite type structure such as ZnTiO$_3$. Such anomalous behavior is well-known as positive temperature coefficient of resistivity (PTCR) [38] and was attributed to electrical potential barrier resulted from the existence of a two-dimensional surface layer of acceptor ions or oxygen adsorbed at grain boundaries [39]. The increase in the applied frequency is expected to decrease the electrical potential barrier and thus shifts the Curie temperature towards lower temperature.

The conduction activation energies ($E_a$), in the high temperature range using Arrhenius equation: $\sigma = \sigma_0 \exp\left(-E_a / K_T\right)$, were calculated as a function of frequencies, using $\ln\sigma$ vs 1000/T plot (Fig. 6(a)), and summarized in Table 1. The estimated values agree well with the obtained semiconducting behavior and suggested that the conduction is through the electron hopping [36]. The reported values showed a gradual decrease with increasing frequency, agreed well with the obvious increase in conductivity, attributed to the effect of applied frequency in facilitating charge carriers transfer.

It is well known that, ac conductivity depends on the capacitance and thus on the material’s dielectric property. This behavior may be assigned to the space charge polarization present in the material [40]. Consequently, the observed anomalous observed in the dielectric constant ($\varepsilon'$) vs. temperature relation at different applied frequencies (Fig. 6 (b)), agrees well with that obtained in the conductivity temperature relation (Fi6. 6(a)). At this observed transition, the electric dipoles are disorderly arranged due to the asymmetric shift in the crystal axis’s symmetry with respect to the effective polarization direction. As a result, an abrupt increase in the value of dielectric constant is observed [41,42].
The room temperature dielectric value obtained at applied frequency of 1MHz (Fig. 6(b)) is 43 which is higher than that reported for ZnTiO$_3$ prepared by chemical deposition of 25 [43] and solid-state conventional method of 30 [23]. This obtained dielectric value suggests the uses of present titanates as a co-fired ceramic or resonator ceramics [43].

4. Conclusions

ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ precursor (1:1 mole ratio), synthesized via a new co-precipitation method, was successfully utilized for the preparation of zinc titanate nanopowders. The thermal decomposition of this precursor was resulted in the formation of a mixture of Zn$_2$TiO$_4$, ZnTi$_3$O$_8$ and ZnTiO$_3$ titanates in nanocrystalline form along with very tiny amount of both forms of TiO$_2$ (anatase and rutile). The present decomposition course has not been reported previously in literature and the different phases formed along the decomposition at different temperatures were characterized using TG, XRD, FT-IR and TEM to estimate the different phase’s transitions. The titanates formation started at about 700°C with the formation of Zn$_2$TiO$_4$ along with secondary phases of ZnO and TiO$_2$ (anatase). At 800°C, Zn$_2$Ti$_3$O$_8$ started to appear, besides ZnTi$_2$O$_4$ and impurities of TiO$_2$ (anatase), and at 900°C it showed its decomposition into ZnTiO$_3$. The conductivity measurements showed semiconducting behavior and indicated ferroelectric transition in the range 200-308°C. The obtained dielectric value suggests the uses of present titanates as a co-fired ceramic or resonator ceramics.

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**Figure captions**

**Fig. 1:** TG-DTG curves for the thermal decomposition of ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ (1:1) precursor in air. Heating rate = 5ºC min$^{-1}$.

**Fig. 2.** XRD patterns of ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ (1:1) precursor calcined at different temperatures.

**Fig. 3.** FT-IR spectra of ZnC$_2$O$_4$.2H$_2$O-TiO$_2$ (1:1) precursor calcined at different temperatures.

**Fig. 4.** TEM image of calcined precursor at 900ºC for 2h. Scale bar, 100 nm.

**Fig. 5.** N$_2$ adsorption/desorption isotherm obtained for calcined precursor at 900ºC for 2h.

**Fig. 6.** Electrical properties of calcined precursor at 900ºC for 2h. (a) ln$\sigma$ vs. 1000/T as a function of applied frequency. (b) Dielectric constant vs. absolute temperature as a function of applied frequency.

**Table caption**

**Table 1.** Activation energies calculated from ln$\sigma$ vs. 1000/T plot as a function of frequencies for calcined precursor at 900ºC for 2h.
Fig. 2
Fig. 3

Fig. 4
Fig. 5
Fig. 6
Table 1. Activation energies calculated from ln $\sigma$ vs. 1000/T plot as a function of frequencies for calcined precursor at 900°C for 2h

| Frequency | $E_a$ (eV)  |
|-----------|-------------|
| 1 kHz     | 2.52 ± 0.54 |
| 50 kHz    | 1.40 ± 0.07 |
| 100 kHz   | 1.34 ± 0.06 |
| 300 kHz   | 1.13 ± 0.05 |
| 500 kHz   | 1.11 ± 0.06 |
| 700 kHz   | 1.06 ± 0.07 |
| 1000 kHz  | 1.03 ± 0.05 |