Zinc titanates 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$_2$ precursors mixture (1:1 mole ratio), prepared via a new co-precipitation method up to 900 °C. Thermogravimetric measurement (TG) was utilized to characterize the precursors mixture 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 Zn$_2$TiO$_4$ 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 precursors mixture 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 °C–308 °C. The obtained low dielectric value suggests the uses of present titanates as a co-fired ceramic or resonator ceramics.

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-state 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.

In literature, lot of investigations [14–17] were reported on the inability of pure ZnTiO$_3$ phase using sol-gel methods. On the other hand, many researchers [14, 17, 21–23] obtained a mixture of titanates such as ZnTiO$_3$, Zn$_2$Ti$_3$O$_8$ and Zn$_2$TiO$_4$ with Zn$_2$Ti$_3$O$_8$ as major phase. Ivanova et al [24] and Yan et al [25] prepared Zn$_2$TiO$_4$, TiO$_2$ and ZnO via sol-gel and hydrothermal routes, respectively using 1:1 mole ratio of Zn:Ti mixture. Siriwong and Phanichphant [26] prepared Zn$_2$TiO$_4$ single-phase using 1:1 mole ratio of zinc naphthenate and titanium tetra isopropoxide precursors by the flame spray pyrolysis technique.
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.

Nanocrystalline zinc titanates could be considered as promising candidates for low-temperature sintering dielectrics, which is a desirable property for microwave dielectrics [14]. The dielectric properties reported by Bobowska et al [27] for zinc titanate, prepared via chemical deposition process of a layered titanate colloid with ZnO nanocrystals, suggested its use as a ceramic resonator or a co-fired ceramic. Obrodovic et al [28] reported that the mechanical activation (via ball mill) improved well the electrical properties of zinc titanates. Chang et al [29] reported a transition point in the electrical resistivity and dielectric constant versus temperature for zinc titanates prepared via conventional ceramic method.

In the present manuscript, a simple co-precipitation technique has been followed to synthesize nanocrystalline zinc titanate powders. In this technique, a stoichiometric co-precipitated mixture of ZnC₂O₄.2H₂O-TiO₂ (1:1 mole ratio) has been thermally decomposed up to the titanate formation. To our best knowledge, this is the first report on the synthesis of zinc titanates nanopowders by this method in the literature. The titanate phase’s formation as well as their structure characterization, morphology and phase transitions have been investigated via TG-DTG, XRD, FT-IR, TEM and BET measurements. The different electrical properties viz. ac-conductivity as well as dielectric property have also been evaluated.

2. Experimental procedures

2.1. Materials
Basic zinc carbonate monohydrate; ZnCO₃.2Zn(C₂O₄)₂.H₂O, unhydrous oxalic acid; H₂C₂O₄ and titanium dioxide (anatase); TiO₂ all were of analytical grade (BDH) and utilized as received.

2.2. Synthesis process
The entire titanates were prepared in the present study via the thermal decomposition of oxalate-titania precursors mixture; ZnC₂O₄.2H₂O-TiO₂ (1:1 mole ratio). A new innovative route for the preparation of this precursors mixture was utilized in which, a stoichiometric amount of oxalic acid solution equivalent to precipitate zinc oxalate was added drop wise 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 TiO₂ surface through heterogeneous nucleation [30]. The prepared precursors mixture was filtered, washed with distilled water, dried then given the name; as-prepared precursors mixture. To characterize the precursors’ mixture 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.

2.3. Characterization
Thermogravimetric analysis (TG) of the prepared precursors’ mixture was conducted in air by a Perkin Elmer thermal analyzer (STA 6000) at a heating rate of 5 °C min⁻¹ 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 recorded 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 a die and 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

3.1. Thermal decomposition of ZnC₂O₄.2H₂O-TiO₂ precursors mixture
The full decomposition course of ZnC₂O₄.2H₂O-TiO₂ precursors’ mixture (figure 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 ZnC₂O₄-TiO₂ 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 [31], the water lost at low temperature range can be considered as crystal water while that lost at higher temperatures as coordinately bounded.
The third TG step appearing 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-TiO₂ mixture and evolution of CO and CO₂ as decomposition products \[32\]. No further weight changes could be observed up to 1000 °C.

3.2. X-ray diffraction and titanates formation
The thermal decomposition course of the studied precursors’ mixture as well as the titanates formation was successfully followed using XRD measurements of calcined precursors mixture samples at temperatures ranging between 400 and 900 °C. Figure 2 illustrates XRD patterns of the calcined samples along with the different phases formed during calcination process. XRD pattern of the as-prepared precursors mixture indicated the characteristic individual diffraction peaks of both monoclinic ZnC₂O₄.2H₂O and tetragonal TiO₂ (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.

XRD pattern of the sample calcined at 400 °C showed, in agreement with the thermal decomposition course (figure 1), the presence of hexagonal ZnO and tetragonal TiO₂ (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 (figure 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.

The precursors mixture calcined at 800 °C showed the complete vanishing of ZnO diffraction peaks with the appearance of diffraction peaks characteristic for the presence of Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$O$_8$ (JCPDS file No. 87–1781) phases indicating the complete titanates formation. The Zn$_2$Ti$_3$O$_8$ with a defect cubic spinel structure, was first discovered by Yamaguchi et al [15] and is considered as the low temperature phase of ZnTiO$_3$. The presence of very weak peaks attributed to the presence of TiO$_2$ (anatase) could be ascribed to the reduction of very few amount of ZnO to volatile elemental Zn [19].

Liu et al [21] reported that the formation of Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$O$_8$ phases could only happen in the presence of anatase whereas 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 Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$O$_8$ while if they are large enough, an anatase to rutile transition would be took place with increasing probability for 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 [33] amounts to 67 nm which is expected to be small enough to form Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$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 ZnTiO$_3$ formation. This why the XRD pattern of the sample calcined at 900 °C indicated the presence of hexagonal ZnTiO$_3$ (JCPDS file No. 25–0671) besides Zn$_2$TiO$_4$ content. The decomposition of metastable Zn$_2$Ti$_3$O$_8$ into ZnTiO$_3$ and TiO$_2$ (anatase) by increasing calcination temperature to 900 °C illustrates the increasing amount of ZnTiO$_3$. Again, the presence of weak diffraction peaks characteristic of rutile phase (JCPDS file No. 21–1276) confirmed the anatase-rutile transition and ZnTiO$_3$ formation.

Really, the reason for selecting the (1:1) mole ratio of ZnC$_2$O$_4$:TiO$_2$ in the present preparation was that this ratio would correspond to the stoichiometric ZnTiO$_3$. Instead, the above XRD study indicated the formation of different zinc titanate phases including: ZnTiO$_3$, Zn$_2$TiO$_4$ and Zn$_2$Ti$_3$O$_8$. Accordingly, the phase transitions along the present decomposition could be represented as:

\[
\begin{align*}
\text{Zn}_2\text{C}_2\text{O}_4+2\text{H}_2\text{O}\rightarrow &\text{ZnC}_2\text{O}_4.2\text{H}_2\text{O} \\
\text{ZnC}_2\text{O}_4.2\text{H}_2\text{O}+\text{TiO}_2\rightarrow &\text{ZnC}_2\text{O}_4\text{-TiO}_2 \\
\text{ZnC}_2\text{O}_4\text{-TiO}_2\rightarrow &\text{ZnO}\text{-TiO}_2 \\
\text{ZnO}\text{-TiO}_2\rightarrow &\text{ZnO}+\text{anatase}+\text{Zn}_2\text{Ti}_4 \rightarrow \\
\text{Zn}_2\text{Ti}_4+\text{Zn}_2\text{Ti}_3\text{O}_8+\text{anatase}\rightarrow &\text{Zn}_2\text{Ti}_4+\text{Zn}_2\text{Ti}_3\text{O}_8+\text{anatase}+\text{rutile} \\
\text{Zn}_2\text{Ti}_3\text{O}_8\rightarrow &\text{ZnTiO}_3+\text{TiO}_2 \\
\end{align*}
\]

3.3. FT-IR spectroscopic study
The thermal decomposition course of the entire precursors’ mixture as well as the titanates formation was also characterized using FT-IR spectroscopy. The characteristic bands obtained for the as-prepared precursors mixture and samples calcined at different temperatures are exhibited in figure 3. The 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 [30]. 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 [34]. Finally, the bands at 680 and 2924 cm$^{-1}$ are attributed to TiO$_2$ [35].

The calcined sample 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 °C indicated nearly the same bands indicated same composition without any chance for titanates formation.

The calcined samples at 700, 800 and 900 °C indicated alike patterns with an apparent absorption band at 583 cm$^{-1}$ ascribed to Ti–O stretching vibration due to [TiO$_4$] octahedron group existing in all titanates forms of Zn$_2$TiO$_4$, Zn$_2$Ti$_3$O$_8$ and ZnTiO$_3$ as previously reported [18, 19].

3.4. Morphological study
TEM image of the calcined precursors mixture at 900 °C (figure 4) exhibited an agglomeration of particles having different sizes and shapes. A similar aggregation behavior was obtained by Arin et al [36] for zinc titanates synthesized via hydrothermal method.
3.5. Surface area characterization

Nitrogen adsorption-desorption isotherm of the calcined precursors mixture at 900 °C (figure 5) exhibited, according to the IUPAC classification [37], type II isotherm in which the adsorption is on macro-porous adsorbents through strong adsorbate-adsorbent interaction. This type exhibited also a very small hysteresis as appeared in figure 5. The specific surface area (SSA) calculated according to BET method is about 7.1 m² g⁻¹ which can be considered as the surface area of Zn₂TiO₄ and ZnTiO₃ main contents. This very low surface area could be attributed in accordance with the TEM image (figure 4) to the agglomeration nature of the powder which lowering porosity. Pore size distributions (BJH) (inset of figure 5) showed narrow distribution characterized by three pore size types located around 19, 28 and 42 nm.

3.6. Electrical properties measurements

3.6.1. ac-conductivity

The ac-conductivity measured at different applied frequencies by changing temperature from 30 to 450 °C have been studied. The lnσ versus 1000/T plot at frequencies ranging between 1 kHz and 1 MHz for the sample calcined at 900 °C is shown in figure 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...
Figure 5. N₂ adsorption/desorption isotherm obtained for calcined precursors mixture at 900 °C for 2h.

Figure 6. Electrical properties of calcined precursors mixture at 900 °C for 2h. (a) lnσ versus 1000/T as a function of applied frequency. (b) Dielectric constant versus absolute temperature as a function of applied frequency.
increasing temperature could result in decreasing conductivity. Similar behavior was already reported in literature during conductivity measurements [29].

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 [38].

The estimated conductivity at 110 °C (i.e. temperature at complete adsorbed water evaporation) and frequency of 1 MHz amounts to $6.4 \times 10^{-7}$ 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 figure 6(a), this anomalous behavior, appeared as a transition peak, is clearer at higher frequencies ($\geq$500 kHz) and also indicated a gradual change in the peak position to lower temperature by increasing frequency.

Chang et al [39] reported an anomalous strong decrease (exponential decrease) in conductivity versus 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) [40] which could be attributed to the electrical potential barrier resulted from the existence of a two-dimensional surface layer of acceptor ions or oxygen adsorbed at grain boundaries [41]. 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:

$$
\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right),
$$

were calculated as a function of frequencies, using ln$\sigma$ versus 1000/T plot (figure 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 [38]. 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 [42]. Consequently, the observed anomalous observed in the dielectric constant ($\varepsilon'$) versus temperature relation at different applied frequencies (figure 6(b)), agrees well with that obtained in the conductivity temperature relation (Figure 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 [43, 44].

The room temperature dielectric value obtained at applied frequency of 1 MHz (figure 6(b)) is 43 which is higher than that reported for ZnTiO$_3$ prepared by chemical deposition of 25 [27] and solid-state conventional method of 30 [22]. This obtained dielectric value suggests the uses of present titanates as a co-fired ceramic or resonator ceramics [27].

### 4. Conclusions

ZnC$_2$O$_4$·2H$_2$O-TiO$_2$ precursors mixture (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 precursors mixture 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

| 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 |
The 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.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

**Declarations**

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**Conflicts of interest/Competing interests (include appropriate disclosures)**

The authors declare no competing interests.

**Availability of data and material (data transparency)**

Data and materials will be available on demand.

**Code availability (software application or custom code)**

Not applicable.

**Consent for publication**

By submitting the manuscript, the authors understand that the material presented in this manuscript has not been published before, nor has it been submitted for publication to another journal. The corresponding author attests that this study has been approved by all the co-authors concerned.

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