ABSTRACT

We report in this study the preparation of gels of a nominal composition \(50\text{TiO}_2-25\text{TeO}_2-25\text{M}_n\text{O}_m\) (\(M = \text{Zn, B}\)) and our attempt to verify the oxide components behaviour using Ti butoxide, Te (VI) acid, Zn acetate and boric acid as precursors. The phase and structural transformations of the prepared gels upon heat treatment in the temperature range of 200 °C - 700 °C are thoroughly studied. The powdered samples still contain organics at 200 °C as verified by XRD. Composites containing an amorphous phase along with different crystalline phases (elementary Te, \(\alpha\)-TeO\(_2\), TiO\(_2\) (anatase), ZnTeO\(_3\), and TiTe\(_3\)O\(_8\)) are formed with temperature increase (above 300 °C). The IR results obtained show that the amorphous phases (300 °C - 400 °C) of the composite materials consist of TiO\(_6\), TeO\(_4\), ZnO\(_4\), BO\(_3\) and BO\(_4\) units in different ratio depending on the composition. The UV-Vis spectra of the gels prepared exhibit a red shift of the cut-off compared to pure Ti butoxide gel behavior.

Keywords: sol-gel, phase transformations, UV-Vis spectra, structure.

INTRODUCTION

It is well known that the sol-gel technology is a widespread method for synthesis of glasses, ceramics, powders, thin films, fibers, and membranes and its major peculiarities and possibilities are discussed in some excellent reviews [1 - 5]. Sol-gel derived materials attract the scientists’ attention due to such advantages as good homogeneities, ease of the composition control, lower melting or sintering temperature and better control of the microstructure. It is of scientific and technical interest to study the structural evolution in the course of the various stages of sol-gel transition and glass or ceramics production as well as the factors which determine the structure and properties of the materials obtained. Up to now, mainly silicate, titanate, zirconate and niobate gels are studied [2, 6 - 9]. Irrespective of the fact that B\(_2\)O\(_3\) is a well known classical glass former, the sol-gel method is not very often used to synthesize amorphous borate materials. Various gel-derived borosilicate glasses of a more homogeneous network compared to that obtained along the traditional melting route are prepared [10 - 13]. It is worth adding that until now boro-titanate glasses are not obtained from melts. It is reported that TiO\(_2\)-B\(_2\)O\(_3\) catalysts photoactivity is improved by boron content increase [14, 15]. Glasses are obtained in the binary system of TeO\(_2\)-B\(_2\)O\(_3\) containing less than 25 mol % of B\(_2\)O\(_3\) due to the presence of a wide region of stable and metastable phase separation [16-19]. The binary TiO\(_2\)-TeO\(_2\) system is of special interest and sol-gel preparation of powders and films is reported in several papers irrespective of the high hydrolysis rate of Te (VI) alkoxides [20 - 22].
On the other hand, glasses are obtained in the same system when TeO₂ content is higher than 75 % [23 - 25]. The structural investigations show that TiO₂ inhibits Te polyhedra structural changes and maintains a continuous glass network [23, 25].

ZnO is an intermediate oxide which was preferred in the past years in preparing transparent glass-ceramics by the conventional melt-quenching method. The materials obtained combine the unique properties of ZnO as well as its good network formation ability. A large number of investigations report sol-gel preparation of composite materials on the ground of the binary TiO₂-ZnO system. Numerous investigations are devoted to the coupled semiconductor TiO₂/ZnO photocatalyst aiming to improve its photodegradation efficiency [26, 27]. The glass forming tendency as well as different structural and optical properties of the binary ZnO-TeO₂ system is investigated [28 - 38] with the application of IR, Raman, EXAFS.

We may conclude, considering the literature data pointed above, that melt quenched glasses of high TeO₂ content (above 60 mol %) and microheterogeneous structures formation is observed in a wide concentration range [16, 39] of the ternary TiO₂-TeO₂-B₂O₃ system. The thermal, optical and structural properties of glasses in the ternary TiO₂-TeO₂-ZnO system are studied by Kabalci et al. [40] and N. Ghribi et al. [41]. Recently, we defined the gel formation regions in these systems and published the results obtained [25, 42].

The present paper reports comparative studies on the phase and structural evolution upon heating (200 oC - 700 oC) of two gels of a nominal composition 50TiO₂-25TeO₂-25MnOm (mol %, M = Zn, B). A comparison between the gel formation ability of the classical network former B₂O₃ and that of the intermediate oxide ZnO is also attempted.

**EXPERIMENTAL**

**Gelling, drying and heat treatment**

The scheme of sol-gel synthesis of TiO₂/TeO₂/MnOm (M= Zn, B) powders is presented in Fig.1. It is worth noting that the use of more stable and less expensive boric and telluric (VI) acids compared to their alkoxides is found suitable for the preparation procedure [21, 43, 44]. Zn acetate and Zn nitrate are among the various Zn precursors used in the sol-gel technology but the usage of Zn acetate provides more advantages than inorganic Zn nitrate [45] according to the literature data collected.

A combination of Te(VI) acid (Aldrich) along with Ti butoxide (Fluka AG), Zn acetate (Merck), boric acid (H₄BO₄) precursors dissolved in ethylene glycol (C₂H₆O₂) (99 % Aldrich) were used. The initial solutions were subjected to intensive stirring ranging from 5 min to 30 min at room temperature aiming to achieve complete dissolution. The sol-gel hydrolysis reaction proceeded with the participation of absorbed atmospheric moisture only (no water was added to the precursor’s solutions). The pH values measured referred to 4 - 5 depending on composition. The gelation time for the investigated compositions varied from 1 min to 5 min, while the aging was performed in air for several days to complete the process. The gels obtained were subjected to the stepwise heating from 150 oC to 700 oC for one hour exposure time in air. The heat treatment at 200 oC was performed to hydrolyze all OR groups still present, while the further temperature increase (300 oC-700 oC) was applied to determine the phase and structural transformations. Two representative gels of a nominal composition of 50TiO₂.25TeO₂.25ZnO (mol %, sample 1) and 50TiO₂.25TeO₂.25B₂O₃ (mol %, sample 2) were subjected to detailed phase and structural analysis (Figs. 4 and 7, Table 1).

**Samples characterization**

Powder XRD patterns were registered at room temperature with a Bruker D8 Advance diffractometer using Cu-Kα radiation. The morphology of the samples was examined by scanning electron microscopy using a JEOL JSM 6390 electron microscope (Japan) equipped with ultrahigh resolution scanning system (ASID-3D). The optical absorption spectra of the powdered samples were recorded in the wavelength range of 200 nm–1000 nm by a UV-VIS diffused reflectance Spectrophotometer “Evolution 300” using the magnesium oxide reflectance standard as a baseline. The absorption edge and the optical band gap were determined following Dharma et al. instructions [46]. The band gap energies (Eg) of the samples were calculated by the Planck’s equation:

\[ E_g = \frac{h \cdot c}{\lambda} = \frac{1240}{\lambda} \]

where \( E_g \) is the band gap energy (eV), \( h \) is the Planck’s constant, \( c \) is the light velocity (m/s), while \( \lambda \) is the
wavelength (nm). The infrared spectra were registered in the range of 1600 cm⁻¹ - 400 cm⁻¹ using the KBr pellet technique on a Nicolet-320 FTIR spectrometer with 64 scans and a resolution of ±1 cm⁻¹.

RESULTS AND DISCUSSION

Phase transformations

The gel formation regions in both systems [25, 42] are determined at room temperature. Transparent and monolithic gels are obtained applying the scheme shown in Fig. 1. It is noteworthy that the gel formation region in the TiO₂-TeO₂-ZnO system is expanded toward ZnO corner in comparison to that in TiO₂-TeO₂-B₂O₃ (Fig. 2). Probably, the Zn acetate promotes in higher degree the hydrolysis and polycondensation processes compared to the system with H₃BO₃ presence. Moreover, there is data that the acetate groups can act as coordinating or bridging ligands, which is an important premise for better molecular association [47]. The images of the ternary gels (1 and 2) which are under consideration in this paper are given in Fig. 3. It is evident that the gel containing ZnO is more transparent than that containing B₂O₃. The XRD patterns of the gels subjected to heat treatment in the temperature range of 200 oC -700oC are shown in Fig. 4. Those obtained below 200oC are complicated due to the presence of organics and they are not considered in this paper. It is seen that composite materials containing an amorphous phase and different crystalline phases: metallic Te (JCPDS 78-2312), α-TeO₂ (JCPDS 42-1365), anatase (JCPDS 78-2486), rutile (JCPDS 21-1276), ZnTeO₃ (JCPDS 44-0240), and TiTe₃O₈ (JCPDS 50-0250) are formed in the temperature range 200°C - 500°C. The amorphous phase is dominant up to 400°C but decreases gradually with temperature increase and its amount is negligible at ca 500 °C. It is evident that organic constituents still exist at 200°C in both samples (Fig. 4). Presence of elementary tellurium in sample 2 (50TiO₂.25TeO₂.25B₂O₃) is detected between 200°C and 400°C, while it is fully oxidized at ca 500°C. Probably, B₂O₃ retards tellurium oxidation. For a comparison, elementary tellurium is found in a narrow temperature range (~ 300°C) in sample 1 (50TiO₂.25TeO₂.25ZnO). Anatase is observed in both samples at 400°C and a small amount is converted to rutile at this temperature in sample 1 (50TiO₂.25TeO₂.25ZnO). Obviously, the presence of ZnO enhances the crystallization of rutile at lower temperatures (400°C). It appears at 700 °C in the XRD patterns of sample 2 (Fig. 4). The average crystallite size of TiO₂ (anatase) in the powdered sample 1 (calculated with the application of the Sherrer’s equation) is ca 60 nm (Fig. 4) at 400°C. Crystalline phases (anatase, rutile, TiTe₃O₈ and ZnTeO₃) only are found (Fig. 4) in the powders prepared at temperature values higher than 500°C.

SEM observations of the gels treated at 400°C (sam-
ple 1) and 500°C (sample 2) are performed (Fig. 5). It is seen that the morphology results from crashing of the monolithic gels during the heating. Both samples are characterized by a strong tendency to agglomeration with aggregates average size greater than 10 mm. The microprobe analysis shows no presence of carbon in both samples, which in fact indicates that the organic constituents are completely removed at these temperatures. The phase morphology of sample 2 is more interesting. Bright needle- and sphere-like particles rich in TeO$_2$ are observed on the sample surface (Fig. 5, sample 2f).

**Optical properties and structural transformations**

The diffuse reflectance absorption spectra of the investigated gels (aged at room temperature) as well as of pure Ti butoxide gel are illustrated in Fig. 6. The observed absorption edges and calculated optical band gap values are pointed out in Table 1. It is evident that the ternary gels containing TeO$_2$, ZnO and B$_2$O$_3$ exhibit higher absorption in the UV region in comparison to pure Ti butoxide gel. The appearance of two absorption bands below and above 300 nm, the so called charge transfer bands, is another peculiarity of the UV-Vis spectra [25, 42]. Isolated TiO$_4$ groups with absorption band in the region of 200 nm-260 nm are the main building units in the unhydrolyzed Ti butoxide. They are transformed into TiO$_6$ units as a result of the polymerization processes and show absorption above 300 nm [48]. The more intensive absorption peak observed for both gel compositions (samples 1 and 2) at ca 300 nm - 310 nm is associated with an increase of the degree of Ti atoms polymerization when compared to that in pure Ti butoxide gel. Our data is in accordance with that obtained by Klein et al. [48] for TiO$_2$/SiO$_2$ gels. It has to be noted that the broader absorption peak at ca 300 nm in the UV-Vis spectra of 50TiO$_2$.25TeO$_2$.25ZnO (sample 1) is assigned to the exciton absorption peak of bulk ZnO, which normally exists in the 300 nm-360 nm spectral region (Eg $\sim$ 3.24 eV).
Fig. 4. XRD patterns of the investigated compositions.
The overlapping of the exciton absorption peak and the charge transfer bands hampers to obtain more precise information about ZnO effect on Ti polymerization ability. The absorption edge of gels 1 and 2 refers to 493.5 nm and 506.7 nm, respectively. Obviously, TeO₂, ZnO and B₂O₃ shift the absorption edge of pure Ti butoxide gel (445.82 eV) towards a higher wavelength (red shift).

IR spectroscopy is used to monitor the phase transformations in the gels subjected to heat treatment (in the temperature range of 200°C - 700°C) (Fig. 7). The assignments of the vibrational bands of the separate structural units are made on the basis of the well known spectral data for the precursors (Ti (IV) n-butoxide, H₆TeO₆, Zn acetate and boric acid (Fig. 8) and the crystalline phases existing in the TiO₂-TeO₂, TiO₂-ZnO, TeO₂-ZnO systems [25, 50, 51]. The IR spectra of samples heated to 200°C show an absorption band in the region of 1120 cm⁻¹-1040 cm⁻¹ which is due to Ti-O-C stretching vibrations and another one at 890 cm⁻¹-880 cm⁻¹ which is assigned
to C-O or C-H stretching vibrations of the residual solvent ethylene glycol [52]. The band at 620 cm\(^{-1}\) with a shoulder at 640 cm\(^{-1}\) can be related to the overlapping of the vibrations of TiO\(_6\), TiO\(_4\), and TeO\(_4\) units [25, 42, 53, 54]. The lower intensity of both bands in the spectrum of 50TiO\(_2\).25TeO\(_2\).25ZnO (sample 1) indicates a higher degree of hydrolysis and condensation processes probably as a result of ZnO presence. Thus, we can suggest that at lower temperatures (200\(^{\circ}\)C) the amorphous phases consist both of organic and inorganic building units. The bands located in the range of 1500 cm\(^{-1}\)-1300 cm\(^{-1}\) are assigned to the bending vibrations of CH\(_3\) and CH\(_2\) organic groups. They are not visible above 300\(^{\circ}\)C and which is why the spectra recorded at higher temperature values (300\(^{\circ}\)C - 700\(^{\circ}\)C) are mainly characterized by bands below 900 cm\(^{-1}\). The latter are typical for inorganic units. They are broadened up to 500\(^{\circ}\)C but their intensity stays low. This is a peculiarity attributed to disordered systems. The IR and XRD data discussed above provide to suggest that the amorphous phases in the temperature range 300\(^{\circ}\)C - 500\(^{\circ}\)C consist only of inorganic building units TeO\(_2\), TiO\(_2\), and ZnO\(_2\) whose absorption bands are in the range 700 cm\(^{-1}\) - 400 cm\(^{-1}\). It is difficult to distinguish the vibrations of these groups due to their strong overlapping [53 - 60]. The characteristic vibrations of BO\(_3\) and BO\(_4\) groups are not well defined in the IR spectra. It is a well-known fact [61 - 63] that B-O stretching for trigonal BO\(_3\) units is situated in the spectral region of 1500 cm\(^{-1}\)-1200 cm\(^{-1}\), that for tetrahedral BO\(_4\) units is observed at 1200 cm\(^{-1}\)-850 cm\(^{-1}\), while the bending vibrations of various borate segments are outlined in the range of 800 cm\(^{-1}\)-600 cm\(^{-1}\). These bands are not detected in our spectra. Only a weak band centered at ca 970 cm\(^{-1}\), typical for BO\(_4\) units, is observed in the spectrum of sample 2 at 500\(^{\circ}\)C. The formation of BO\(_3\) units in the amorphous phase can not be excluded. Their presence is proved in compositions of higher B\(_2\)O\(_3\) content [25]. The IR spectra of samples heated above 500\(^{\circ}\)C show vibrations characteristic for the inorganic structural units building the crystalline phases (TiO\(_2\) - anatase, rutile, TiTe\(_2\)O\(_6\) and ZnTeO\(_3\)). In fact they verify the phase transitions observed by XRD (Fig. 4).

**CONCLUSIONS**

It is found that the gel formation region in the ternary TiO\(_2\)-TeO\(_2\)-ZnO system is expanded toward ZnO corner in comparison to that in TiO\(_2\)-TeO\(_2\)-B\(_2\)O\(_3\). According to the XRD results referring to samples heated up to 300\(^{\circ}\)C the composites consist mainly of an organic–inorganic amorphous phase which is completely transformed into
inorganic one above 300°C. The simultaneous presence of Te, Zn and B in the ternary gels causes the red-shifting of the cut-off in comparison to pure Ti butoxide gel behavior. The UV-Vis results show that the ternary gels exhibit a higher degree of condensation compared to that of pure Ti butoxide gel. It is suggested, on the ground of the IR results of samples treated at 200°C, that ZnO presence leads to a greater extent of hydrolysis and condensation processes compared to that in presence of B2O3. The latter is a classical network former but obviously, under the experimental conditions provided and the combination of precursors used in this study, ZnO behaves as a better amorphous network former. More experiments are required to explain this interesting result.

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