Optical and microstructural properties of hybrid sol–gel derived $ZrO_2–Al_2O_3–Sm_2O_3$ coatings on glass for photovoltaic applications

Shaban Uzun[1], Stancho Yordanov[1], Mariela Dimitrova[2], Vladimir Petkov[1], Tatyana Ivanova[3], Angel Velikov[1]
[1]Bulgarian Academy of Sciences, Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. Angel Balevski", 67 "Shipchenski prohod" Blvd., 1574 Sofia, Bulgaria,
[2.] Institute of Electrochemistry and Energy Systems "Academician Evgeni Budevski at the Bulgarian Academy of Sciences", 1574 Sofia, Bulgaria
[3.] Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Tzarigradsko chaussee 72, 1784 Sofia, Bulgaria
e-mail: stancho14@abv.bg

Abstract: *This work presents an overview of sol–gel-derived oxide materials and their relevance to optical, photonic and photovoltaic applications, followed by an experimental study of $ZrO_2–Al_2O_3–Sm_2O_3$ thin films deposited on glass substrates. Historical developments of the sol–gel process, beginning with early investigations on silica gels in the 19th century, are outlined together with advancements in optical glasses, anti-reflective coatings, and rare-earth-doped systems. Recent progress in functional materials—including boron-, tellurium- and rare-earth-containing glasses, luminescent oxide systems, and sol–gel-derived zirconia-based coatings—is discussed to highlight their structural, optical and radiation-shielding capabilities.*

In the present study, multilayer $ZrO_2–Al_2O_3–Sm_2O_3$ coatings were prepared via the sol–gel method combined with dip-coating, and subsequently thermally treated at 420 °C. Optical characterization (UV–VIS–NIR) revealed changes in transmittance and reflectance linked to film composition and thickness, while X-ray diffraction confirmed their predominantly amorphous structure at the applied heat-treatment temperature. SEM and EDS analyses provided insight into surface morphology and elemental distribution within the films. The results demonstrate that increasing Al_2O_3 content influences coating porosity and thickness, while Sm_2O_3 contributes luminescent functionality and potential reduction of optical reflection in key solar spectral regions. These findings indicate that $ZrO_2–Al_2O_3–Sm_2O_3$ thin films are promising candidates for protective and functional coatings in photovoltaic applications, where enhanced light harvesting and improved surface properties are essential.

Keywords: SOL-GEL, DIP COATING, $ZrO_2–Al_2O_3–Sm_2O_3$, PHOTOVOLTAIC APPLICATIONS

1. Introduction

The sol–gel method for processing inorganic ceramic and glass materials began to be investigated as early as the mid-19th century with the works of Ebelmen and Graham on silica gels, who discovered that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions forms glass-like SiO_2. The early gels enabled the production of fibers, optical lenses and composites, but the long drying time limited their technological application.

At the end of the 19th and the beginning of the 20th century, gels attracted the attention of chemists due to Liesegang rings and the periodic crystallization phenomena studied by renowned scientists such as Ostwald and Lord Rayleigh [1]. The role of glass in solar energy production and its development for various applications is discussed. The requirements for glass composition to achieve higher solar light transmittance are described. Anti-reflective coatings that improve the efficiency of crystalline silicon photovoltaics are considered. The applications of coated glasses in thin-film photovoltaics are also presented, showing the most intensive emission band at 598 nm, including transparent conductive layers and the benefits of high-resistance transparent coatings. Subsequently, the use of mirror coatings for concentrating solar systems is analyzed, as well as the main manufacturing and technological challenges related to materials and coatings [2,3].

Boron-, tellurium- and rare-earth-based glasses are widely used in optical applications and as shielding materials for γ-rays and neutrons. The addition of SrO modifies the structural and optical properties of these glasses, including density, optical band gap, and absorption characteristics of Sm^{3+} ions, as well as parameters affecting radiation attenuation. Further optimization of SrO content can improve shielding ability by reducing the half-value layer (HVL) and increasing the linear attenuation coefficient, making these glasses suitable for modern optical and radiation-protection applications [4].

Photoluminescence in the UV–VIS region represents a sensitive method for studying the structure and optical properties of glasses and glass-ceramics. Fluoride, phosphate and silicate glasses with high intrinsic UV transparency and chemical purity have been investigated, doped with active luminescent ions with different electronic configurations (s^2: As^{3+}, Sb^{3+}, Sn^{2+}, Pb^{2+}; d^0: Ti^{4+}, Nb^+, Mo^{6+}, Ta^{5+}, W^{6+}; d^{10}: Zn^{2+}, Ag^+ and Cu^+; d^5: Mn^{2+}; f^n such as Sm^{3+}, Eu^{3+}, Eu^{2+}, Tb^{3+}). These ions exhibit diverse photoluminescent activity depending on their electronic structure and the local symmetry of the surrounding environment. The thermal transformation of glass into glass-ceramic changes the coordination and distribution of active centers, leading to variations in the intensity and spectral range of emission, with recorded blue, green and red emissions and lifetimes from 1 µs to 25 ms, confirming the potential of these materials for photonic and optoelectronic applications [5].

Thin $ZrO_2–Y_2O_3$ (YSZ) sol–gel films with 3–12 mol% Y_2O_3 were produced and characterized. All films crystallized in the cubic phase, even at Y_2O_3 contents that do not stabilize this phase in bulk ZrO_2. With increasing Y_2O_3 content, the refractive index slightly increased, while optical absorption, extinction coefficient, hardness and elastic modulus decreased, due to reduced crystallinity and greater lattice distortion in ZrO_2 [6,7].

In the present study, micro-organized multilayer coatings based on $ZrO_2/Y_2O_3/Al_2O_3$ were developed and characterized, obtained by combining the sol–gel method with dip-coating. The influence of Al_2O_3 content (0–20%) on the morphology, structure and physicochemical properties of the coatings was investigated. The optimized procedure developed by the research team enabled the preparation of transparent, stable and coatable solutions even at high concentrations of the aluminum oxide phase. The results show that increasing Al_2O_3 content leads to increased thickness and porosity of the coatings, as well as a higher dimensionless flow parameter (J), indicating a larger amount of deposited material. It was also found that the microstructure and crystallinity of the substrates have a limited influence on film thickness but not on porosity. The obtained data outline the potential of these systems for use as protective or functional oxide coatings with controllable properties [8,9].

In the $ZnO–B_2O_3–SiO_2–Al_2O_3$ system, glasses produced via melt-quenching at different ZnO/SiO_2 ratios (from 5.4 to 1.4) were investigated to determine their effect on glass formation and crystallization behavior. Thermal treatments up to 1050 °C showed sequential crystallization of $Zn_3(BO_3)_2$, β- and α-willemite (Zn_2SiO_4), as well as the formation of gahnite ($ZnAl_2O_4$) at higher temperatures. The resulting materials exhibited bluish-white photoluminescence under λ_{ex} = 254 nm, making them potential candidates for photonic and optoelectronic applications [10].

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1. Experimental procedures

For the synthesis, zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), samarium oxide (Sm_2O_3), nitric acid (HNO_3), acetic acid (CH_3COOH), and distilled water were used. All reagents were of analytical grade and were used without further purification.

A total of 8.048 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 35 mL of absolute ethanol C_2H_5OH (99.9%). The solution was homogenized by magnetic stirring for 1 h and then left to stand for an additional 2 h to ensure complete dissolution and stabilization at room temperature.

Sm_2O_3 (0.527 g) was added to 15 mL of deionized water. A total of 2.5 mL of concentrated HNO_3 was added to the suspension, ensuring its complete dissolution by converting Sm_2O_3 into $Sm(NO_3)_3$, resulting in a clear solution. The obtained transparent solution was used without further processing.

Al_2O_3 (0.255 g) was dispersed in 15 mL of deionized water, followed by the addition of 2.5 mL of HNO_3. The acid treatment improved the surface activity of the particles, facilitating the formation of a stable aqueous dispersion.

The precursors were combined in the following sequence: the $ZrOCl_2$ solution was mixed sequentially with the samarium nitrate solution and the Al_2O_3 dispersion under continuous stirring. To the resulting mixture, 3 mL of acetylacetone (AcAc) was added as a stabilizing agent, along with 2.5 mL of glacial acetic acid (AcOH) to adjust the acidity and stabilize the metal complexes. The final pH of the system was adjusted to 0.5, which prevented hydrolysis and precipitation of the highly charged metal ions and ensured a stable homogeneous precursor. All processes were carried out at room temperature. The resulting homogeneous mixture was left to age for 20 hours before use.

2. Results and Discussion

Optical characterization was performed with UV–VIS–NIR Shimadzu 3600 double-beam spectrophotometer in the spectral region of 280-1800 nm. The transmittance spectra were taken against air. The reflectance spectra were measured by using the specular reflectance attachment (5º incidence angle) and Al coated mirror as reference.

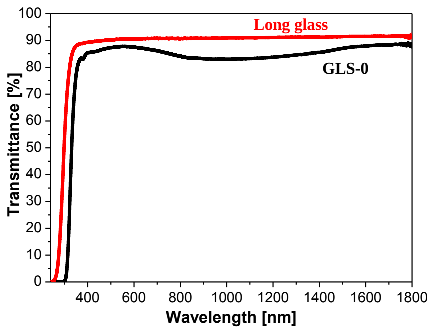

Figure 1. *The figure shows the transmission spectrum of a clean ZSA-0 substrate*

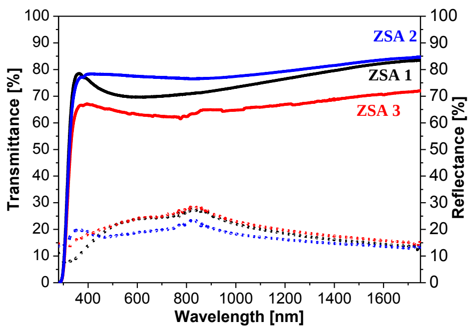

Figure 2. *The figure shows the transmission and reflectance spectrums of a samples: ZSA1, ZSA2, ZSA3*

An X-ray diffractometer with a Bragg-Brentano θ-2θ focusing system was used. The samples were examined at room temperature with Cu-Kα radiation (monochromatic radiation with wavelength λ = 154178Å) in the interval 20º<2θ <65º, at a step of 0.025 2θ for 10 seconds. A graphite monochromator was used for better peak resolution (better signal-to-noise ratio).

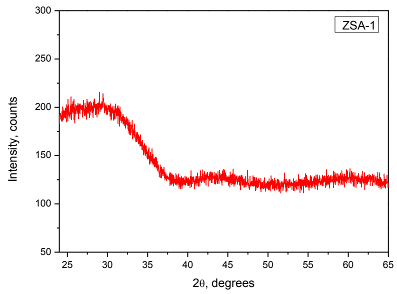

Figure 3. *The figure shows the X-ray diffractometer of ZSA1*

The X-ray diffraction patterns of ZSA1, ZSA2 and ZSA3 are of the same type - they show a typical amorphous state, i.e. at 420°C the temperature is the glass transition temperature.

The surface morphology of the samples was studied with the scanning electron microscopy technique, using the SEM unit Zeiss Evo 10 (Carl Zeiss Microscopy GmbH, Jena, Germany). Images were taken in secondary electrons mode with 25 keV accelerating voltage and no special coating on the samples. The chemical composition was investigated with energy dispersive spectroscopy (EDS) using a Zeiss SmartEDX probe, and the results were compiled with APEX software (version 1.5.0017).

The EDS analysis focused on the functional components of the $ZrO_2–Al_2O_3–Sm_2O_3$ system clearly reveals the presence of zirconium, aluminum, and samarium in the resulting coating. Zirconium is the dominant metallic element, with its content (14.41 wt%) confirming the successful formation and high concentration of the ZrO_2 phase within the sol–gel layer. Aluminum is detected at 0.45 wt%, which corresponds to the expected low Al_2O_3 content under the applied synthesis conditions. Samarium is identified at a mass fraction of 0.31 wt%, indicating uniform incorporation of Sm_2O_3 into the oxide network.

The presence of these three elements and their relative concentrations confirm that the functional $ZrO_2–Al_2O_3–Sm_2O_3$ system is successfully integrated into the sol–gel coating, forming a homogeneous and stable oxide layer.

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The discussion includes: Optical Properties, Structural Analysis (XRD and Morphology and Elemental Composition (SEM/EDS) - shows the following&

1. Optical Properties

- The clean ZSA-0 substrate exhibits high optical transmittance in the 280–1800 nm range, confirming its suitability as a base for subsequent functional coatings.
- The coated samples ZSA1, ZSA2, and ZSA3 show varying degrees of changes in transmittance and reflectance, indicating that the optical properties depend on the composition and concentration of the added oxides (ZrO_2, Sm_2O_3, Al_2O_3).
- The observed decreases in transmittance at specific wavelengths are likely due to the formation of an amorphous oxide network and increased light scattering resulting from the nanostructured surface.

2. Structural Analysis (XRD)

• The diffraction patterns of samples ZSA1, ZSA2, and ZSA3 exhibit a typical amorphous profile, characterized by broad, weakly pronounced maxima and the absence of crystalline peaks.

• This confirms that the temperature of 420°C is below the crystallization threshold of the system and corresponds to the glass-transition region.

• The absence of crystalline phases indicates successful formation of a stable sol-gel amorphous oxide matrix, which is preferred for optical applications due to its low light-scattering properties.

3. Morphology and Elemental Composition (SEM/EDS)

• SEM measurements reveal a smooth and uniform surface without agglomerates or cracks, which is characteristic of well-formed sol-gel coatings.

• The EDS analysis of ZSA1 confirms the presence of all intentionally introduced elements — Zr, Sm, and Al — as well as the main components of the glass matrix (Si, O, Na, Ca, Mg).

• The high relative content of oxygen (≈59 wt%) and silicon (≈10 wt%) corresponds to the formation of a stable Si–O–Zr network.

• Zr (≈14.4 wt%) is the dominant metallic component, confirming the successful incorporation of zirconium into the coating structure.

• The presence of Sm, although in low concentration, demonstrates that the rare-earth element is evenly distributed within the resulting oxide system.

• The low carbon content indicates minimal residual organic material after heat treatment.

3. Conclusions

1. The obtained coatings are amorphous, optically active, and chemically homogeneous, demonstrating the effectiveness of the applied sol-gel procedure.

2.The combination of ZrO_2, Sm_2O_3, and Al_2O_3 results in stable and uniform oxide layers suitable for photovoltaic and photonic applications.

3.The optical analysis, XRD, and EDS results are mutually consistent and confirm the successful synthesis of the desired layers.

4.The coatings on glass substrates were prepared by sol-gel method using dipping technique. The present study characterizes self-cleaning thin films of ZrO_2, Al_2O_3 and Sm_2O_3 for photovoltaic applications.

5.This study investigates the optical and microstructural properties of ZrO_2–Al_2O_3–Sm_2O_3 coatings prepared by the sol–gel method and deposited on glass substrates for photovoltaic applications, as they enhance the efficiency of light-to-electricity conversion. The addition of Al_2O_3 improves the mechanical stability and interface adhesion, while Sm_2O_3 acts as a luminescent additive that modifies the spectral response and can reduce surface reflection at key solar wavelengths.

References:

1.L. L. Hench, J. K. West, The sol-gel process. Chemical Reviews, (1990), 90(1), 33-72.

2.Ganjoo, Ashtosh, et al. "Glass and coatings on glass for solar applications." *Springer Handbook of Glass*. Cham: Springer International Publishing, 2019. 1635-1676.

3.Biswas, Joydeb, et al. "Optical and luminescence properties of Sm_2O_3 doped SrO–PbO–ZnO–P_2O_5–TeO_2 glasses for visible laser applications." *Solid State Sciences* 129 (2022): 106910.

4.AL-GHAMDI, Hanan, et al. Strontium Oxide-Reinforced Borotellurite Glasses: Synthesis, Structure, and Optical Characteristics and γ-Ray and Neutron Attenuation Capability. *Journal of Electronic Materials*, 2024, 53.9.

5.EHRT, Doris. Photoluminescence in glasses and glass ceramics. In: *IOP Conference Series: Materials Science and Engineering*. IOP Publishing, 2009. p. 012001.

6.Diaz-Parralejo, Antonio, et al. "Optical and mechanical characterization of sol-gel thin films of ZrO2 stabilized with different Y_2O_3-doping mol%." *Ceramics International* 49.11 (2023): 19552-19555.

7.Fedorov, Pavel P., and Evgeniya G. Yarotskaya. "Zirconium dioxide. Review." *Конденсированные среды и межфазные границы* 23.2 (eng) (2021): 170-188.

8.Carrasco-Amador, Juan Pablo, et al. "Preparation and characterization of ZrO_2/Y_2O_3/Al_2O_3-based microstructured multilayer sol–gel coatings." *Ceramics International* 43.16 (2017): 14210-14217.

9.Díaz-Parralejo, Antonio, et al. "Mechanical properties and thermal shock in thin ZrO_2–Y_2O_3–Al_2O_3 films obtained by the sol-gel method." *Ceramics international* 47.1 (2021): 80-86.

10. Abdel-Hameed, Salwa AM; MARGHA, Fatma H. Preparation, crystallization and photoluminescence properties of un-doped nano willemite glass ceramics with high ZnO additions. *Optik*, 2020, 206: 164374.