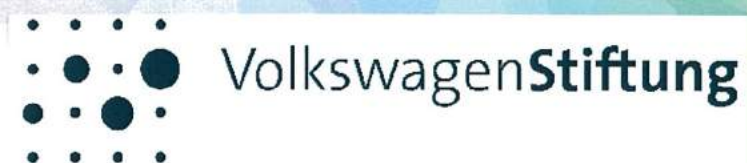


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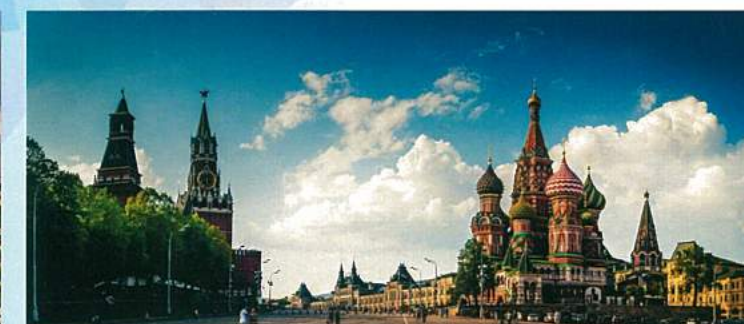


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Synthesis, Theoretical Examination and
Experimental Investigation of Emergent Materials

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The microstructure and optical properties of the Licurgus cup glass

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Licurgus cup probably made in Alexandria in the IVth century is one of the most prominent artifacts of the Roman glass. It is a diatreta cut from an elaborately pressed blank of typical NCS glass with a low magnesium and potassium content. The glass is dichroic, appearing jade green in reflected daylight and wine red in transmitted light. The dichroism of the Licurgus cup glass is usually derived from the presence of mixed Ag-Au nanoparticles (AuAgNPs). To study the optical properties of Licurgus cup the glass was prepared starting from the batch calculated using the glass composition published [1]. The glass was molten at 1500°C in alundum crucible in an electric furnace with MoSi₂ heating elements. The melt was poured and quenched into 7-10 mm thick disks with further annealing in a muffle furnace. The material obtained is a transparent green glass without visible dichroism and phase separation. The colour is caused by the Fe(+2) and Fe(+3) ions in its composition (total Fe content 1,14%, ICP MS). During striking initially at 550 - 560°C the glass at first changes colour to yellowish-green and then becomes dichroic and semiopaque. It is well-known that gold and silver nanoparticles exhibit unusual optical properties such as resonant absorption and scattering of light. This fact was used to explain the unique dichroic character of the Licurgus cup glass. However, this contradicts the fact that the gold ruby glass also containing gold particles of similar form and size is not dichroic, being pink-rose in both transmitted and reflected light. The reason for the Licurgus glass to be dichroic derives from its microstructure. As it was shown in [1] and confirmed by our studies, during striking the process of secondary phase separation occurs. The resulted multiphase structure (Fig. 1) consists of discrete pseudo-spherical particles of phosphate glass in a continuous silicate matrix. The prolonged heat-treatment of the sample results in devitrification of a phosphate phase that crystallizes giving ferric-sodium ortho-diphosphate Na₇(FeP₂O₄)₄PO₄ (P-42(1)c, confirmed XRD). This fact proves the importance of iron as a glass micro component. The experiments to obtain dichroic glass starting from glass batch free of iron failed. The iron-free glass of the same composition as glass of Licurgus cup during striking becomes yellowish-red due to the presence of AuAgNP. The light reflection under different angles was studied. At small glancing angles (large angles of incidence) the penetration depth of light diminishes. The number of AuAgNPs that absorb light declines but the light scattering on the surfaces of iron-phosphate glass droplets enhances. Both AuAgNPs and phosphate glass reflect green light but the amount of light scattered by the former is negligible with respect to that of the latter. To summarize, the red colour of the Licurgus cup glass in transmitted light is due to the light absorption of AuAgNPs while the green colour in reflected light is caused by scattering on sodium-iron-phosphate glass droplets.

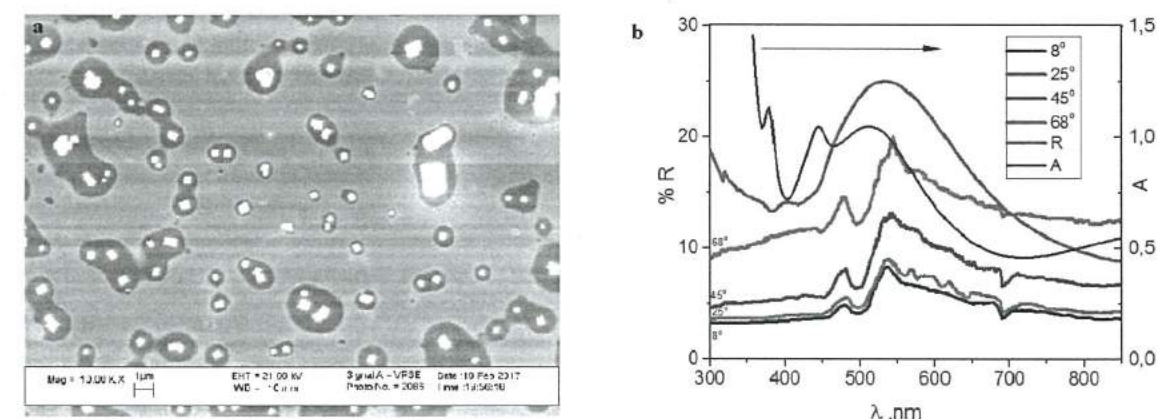


Fig.1. (a) The microstructure of the Licurgus cup glass after prolonged heating (SEM image), (b) Optical absorption (A), reflection spectra of the Licurgus cup glass under different angles (°) of incidence and diffuse reflection (R) spectrum

References:

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