

Self-Supported Flexible Magnetic Silica-Titania Based Sol-gel Glasses: a Forth-Coming Material for Sensing Applications

Daniel Alves Barcelos^{1,2,4*}, *Laura C. J. Pereira*^{3,4}, *David Ortiz de Zárate*⁵, *Amadeu Griol*⁵, *M. Clara Gonçalves*^{1,2}

¹ *Chemistry Engineering Department, Institute Superior Technical, University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

² *Center of Structural Chemistry, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

³ *Department of Engineering and Nuclear Science, Institute Superior Technical, University of Lisbon, Estrada Nacional 10, 2685-066 Bobadela LRS, Portugal*

⁴ *Center of Science and Nuclear Technology, Institute Superior Technical, University of Lisbon, 2685-066 Bobadela LRS, Portugal*

⁵ *Nanophotonics Technology Center, Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain*

danielbarcelos@tecnico.ulisboa.pt

Summary:

The objective of this study is to pioneer the fabrication of self-supported flexible silica-titania based glass with magnetic properties through low-temperature synthetic routes. In this regard, superparamagnetic iron oxide nanoparticles (SPIONs) were incorporated in the glass matrices (hybrid sol-gel silica precursors). Across the studied compositions, Young's modulus below 370 MPa demonstrate mechanical flexibility comparable to recognized flexible materials such as PET. Notably, the superparamagnetic behavior of SPIONs persisted at 300K even after their integration in the self-supported flexible glass matrices.

Keywords: flexible glasses, SPIONs, sol-gel process, inorganic glasses, low-temperature synthesis.

Background

Corning® Willow® Glass produced by (high temperature) roll-to-roll process represents a pioneering advancement in glass technology due to its exceptional mechanical performance and versatility. This innovative glass combines the inherent advantages of traditional inorganic glass with a remarkable degree of mechanical flexibility, rendering it applicable across a diverse array of domains, including semiconductor and solar cell technologies [1]. Metallic magnetic glasses, typically derived from the fusion of metallic components, find utility across a broad spectrum of industries encompassing catalysis, chemical processes, and biomedical sensor development. However, it is imperative to acknowledge that both Corning® Willow® Glass and metallic magnetic glasses demand high-temperature fabrication processes, thereby incurring substantial production costs and high ecological footprint. In respect of these drawbacks, there arises a compelling impetus to explore alternative materials that offer comparable functionalities while circumventing the challenges associated with high temperature synthesis. Among such alternatives, Superparamagnetic Iron Oxide Nanoparti-

cles (SPIONs) emerge as a particularly noteworthy candidate. SPIONs exhibit superparamagnetic behavior at ambient temperatures, affording them the unique ability to magnetize and demagnetize rapidly in response to external magnetic fields [1]. Regarding the fabrication of self-supported flexible inorganic glass, a strategic approach is adopted, centered on the utilization of hybrid sol-gel silica precursors characterized by the presence of non-hydrolysable organic groups, which persist within the final glass molecular structure. Consequently, this 3D molecular architecture engenders a heightened degree of mechanical flexibility, akin to that of plastic materials, in the resultant products.

Motivation and objectives

This study is primarily focused on the fabrication of self-supported flexible magnetic silica-titania-based glasses with ambient temperature techniques, to achieve environmentally sustainable and economically feasible materials. The integration of SPIONs within the inorganic glass matrices enables the magnetic performance. The sol-gel synthesis of hybrid glass matrices and the co-precipitation method to produce SPIONs were the room temperature methodologies chosen.

Methods

A (80/20) SiO₂/TiO₂ molar ratio glass composition was settled. The sol-gel synthesis uses 3-Glycidyloxypropyl-trimethoxysilane (GPTMS), triethoxymethylsilane (MTES) and triethoxyvinylsilane (VTES) (SiO₂ precursors); Titanium (IV) propoxide (TPOT) (TiO₂ precursor). For the SPI-ONS, a co-precipitation synthesis is based on the reduction of iron (III) chloride hexahydrate. SPI-ONS were covered with dextran T10 before incorporation in the glass matrix [2].

Results

This investigation marks a significant milestone by synthesizing self-supported flexible glassy materials with magnetic properties using low-temperature synthesis pathways, representing a novel contribution to the field. To the best of our knowledge, this represents the first instance of such materials being produced via these methodologies. Illustrative evidence of the attained outcomes is presented in Figure 1, wherein the bending capability of the self-supported flexible glass (Figure 1a) and the integration of Superparamagnetic Iron Oxide Nanoparticles (SPI-ONS) into a similar matrix (Figure 1b) are depicted.

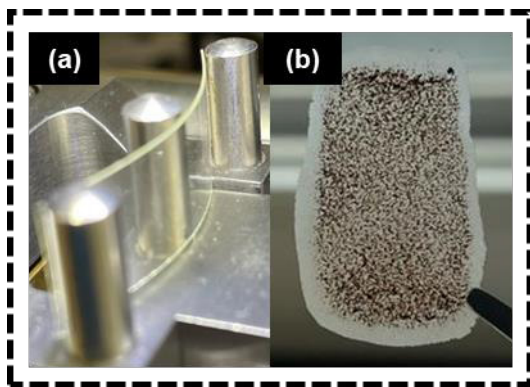


Fig. 1. (a) Self-supported flexible glass; (b) Self-supported magnetic flexible glass.

Additionally, Table 1 provides a comprehensive overview of the obtained results pertaining to the Young's Modulus of the synthesized samples denoted as A1 (GPTMS/TPOT), A2 (GPTMS-MTES/TPOT), and A3 (GPTMS-VTES/TPOT). These values, falling within a range comparable to that of Polyvinyl Chloride (PVC) (200-800 MPa), signify a level of flexibility surpassing that of high-density polyethylene (700 MPa) while exhibiting greater rigidity than low-density polyethylene (200 MPa) [3].

Tab. 1: Young's Modulus Self-Supported flexible glasses.

Sample	Young's Modulus (MPa)
A1	234 ± 12.4
A2	363 ± 20.7
A3	311 ± 17.3

The addition of Superparamagnetic Iron Oxide Nanoparticles (SPI-ONS) did not visibly affect the magnetic characteristics of the synthesized materials. This claim is supported by the consistent observation of superparamagnetic behavior, as depicted in Figure 2.

Moreover, the saturation magnetization closely aligns with the results obtained for unbound SPI-ONS. Furthermore, it is noteworthy that the remanent magnetization underwent an anticipated alteration after the successful integration of SPI-ONS. This phenomenon can be attributed to the cessation of relaxation via Brownian motion, a characteristic feature inherent to SPI-ONS post-incorporation.

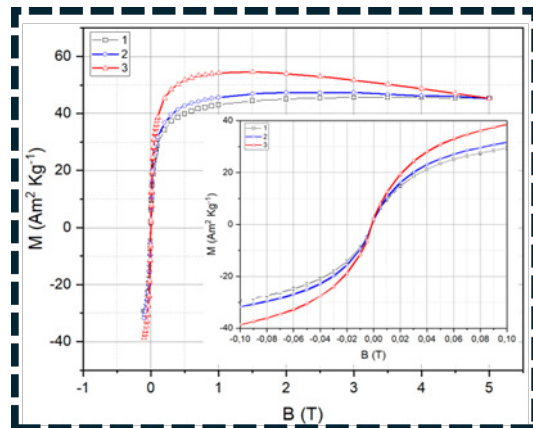


Fig. 2. Self-supported magnetic flexible glass $M(H)$ at 300K (A1).

Furthermore, preliminary assessments concerning the sensing capabilities of the material were conducted, focusing on variations in ethanol concentrations (10%, 5%, and 2.5% v/v). Notably, these tests were conducted without the incorporation of SPI-ONS. The glasses demonstrated discernment among the distinct ethanol concentrations and exhibited a capacity to effectuate changes of 1,716 nm per unit of refractive index. These findings prefigure different utilization across diverse sensing applications, particularly within medical and environmental contexts.

References

- [1] D.A. Barcelos, D.C. Leitao, L.C.J. Pereira, M.C. Gonçalves, *Materials* 14 (2021) 2926; doi: 10.3390/ma14112926.
- [2] Matos, J.C.; Clara Gonçalves, M.; Pereira, L.C.J.; Vieira, B.J.C.; Waerenborgh, J.C. *Nanomaterials* 2019, 9, doi:10.3390/nano9070943
- [3] D.R.H. Jones, M.F. Ashby, Elastic Moduli, in: *Engineering Materials 1*, Elsevier, 2019: pp. 31–47; doi: 10.1016/b978-0-08-102051-7.00003-8.

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