Investigation of metal-induced crystallization mechanisms on amorphous SiO₂

Florio D.*¹, Cauzzi D. A.¹, Cademartiri L.¹ *dario.florio@unipr.it

1 Dipartimento di Scienze Chimiche della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze, 11/a 43124 Parma

One of the most versatile growth techniques of inorganic materials is represented by sol-gel method, which however produces amorphous forms. To obtain crystalline structures, often with different and more performing physical properties, calcination is most often required. However, the high temperatures needed for this energetically expensive process may be problematic for the integrity of materials themselves and their substrates.

A promising solution to easily obtain crystalline metal oxides and semiconductors at lower temperature conditions is constituted by the so-called Metal-Induced Crystallization (MIC). [1] MIC is a solid-state process in which the starting amorphous material crystallizes via contact with a metal, significantly reducing the crystallization temperature. The most interesting studies in the literature report the effective employment of this method to obtain crystalline phases of Si, Ge, SiO₂, TiO₂. [1-3]

It is believed that the metal cation that catalysed the structural transition does not become part of the lattice, whereas it migrates through the structure of the compound and weakens its bonds, allowing the rearrangement of the atoms into a lower energy crystalline phase. [4]

Nevertheless, a detailed description of MIC mechanisms should be further clarified because of its complexity arising from the different factors involved (i.e. the various synthesis techniques for the starting amorphous material, the kind of catalyst employed, the related thermal treatments).

In this work we investigate the mechanisms related to metal-induced crystallization of amorphous silica synthesised via sol-gel method. We have observed that it is possible to obtain different crystalline SiO₂ phases (i.e. tridymite or cristobalite) using different kind of metal cations as catalysis (Na⁺, K⁺, Ca²⁺, Mg²⁺, Zn²⁺, Al³⁺ etc.). We have also studied the role of several parameters and conditions that could significantly affect the crystallization process, as for example the relative concentration of the metal cation or the thermal treatments employed to activate the structural transformation. We consider the possibility that under certain conditions this process consists of a heterogeneous type of catalysis, as it does not foresee diffusion phenomena within the lattice.

References

- [1] Wang, Z.; Jeurgens, L. P. H.; Mittemeijer, E. J. Metal-Induced Crystallization Fundamentals and Applications; Pan Stanford Publishing, 2015.
- [2] Venezia, A. M.; La Parola, V.; Longo, A.; Martorana, A. Effect of Alkali Ions on the Amorphous to Crystalline Phase Transition of Silica. *J. Solid State Chem.* **2001**, *161* (2), 373–378.
- [3] Vargas, S.; Arroyo, R.; Haro, E.; Rodríguez, R. Effects of Cationic Dopants on the Phase Transition Temperature of Titania Prepared by the Sol-Gel Method. J. Mater. Res. 1999, 14 (10), 3932–3937
- [4] Lermusiaux L., Mazel A., Carretero-Genevrier A., Sanchez C., Drisko G. L. Metal-Induced Crystallization in Metal Oxides. Accounts of Chemical Research 2022 55 (2), 171-185.