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ScienceDirect

Ceramics International 41 (2015) 6693–6701

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Review paper

Silver doping of glasses

Francesco Gonella

Department of Molecular Sciences and Nanosystems, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy

Received 10 February 2015; accepted 10 February 2015
Available online 17 February 2015

Abstract

Silicate glasses containing silver in both ionic and aggregate forms have been used since decades for application in several fields, e.g., optical waveguides, sensoristics, electrochemistry, optoelectronics, photonic materials, and more recently for sensitizing effects. The doping of selected regions of glass systems has been faced following a variety of techniques, among which the ion-exchange has played a major role, as witnessed by the continuing publication of new results and novel refinements of the preparation procedures. In this work, a short overview is presented on the application and preparation aspects of silver glass doping, with particular emphasis given to the ion-exchange technique. Basic and experimental questions still open in the understanding of both silver-doped glasses formation and properties are finally addressed.

Keywords: D. Glass; Silver; Functional properties; Nanomaterials

Contents

1. Introduction

Since several decades, silver has gained a peculiar place among the dopants for obtaining glassy materials with specific prescribed properties. Among these, Ag coloring of the glass is perhaps the oldest one to be exploited, especially for silver embedded in the form of nanosized aggregates. As a matter of fact, empirical recipes to obtain silver nanostructured glasses have been used since literally millennia in the production of glass artworks exhibiting peculiar optical properties [1–3]. The most famous examples are probably the artistic manufacts of Roman empire glassmakers, as well as the stained glass windows of medieval cathedrals that may be found throughout the whole western Europe. The functionalization of glasses by doping with silver has drawn the attention of the scientific community since the very early development of several materials science fields, such as for example optoelectronics and photonics. With the birth of nanostructured glasses, and in general of nanoscience issues related to almost all the materials science research, the application of silver-containing glasses has then extended to biomaterials, solar technologies, plasmonics, catalysis, sensoristics, and in general to a wide range of specific functional nanostructured glasses. In Fig. 1(a), data are presented taken from the main science search engines (Scopus, Web of Science) showing the number of quoted

E-mail address: gonella@unive.it

http://dx.doi.org/10.1016/j.ceramint.2015.02.058
0272-8842/

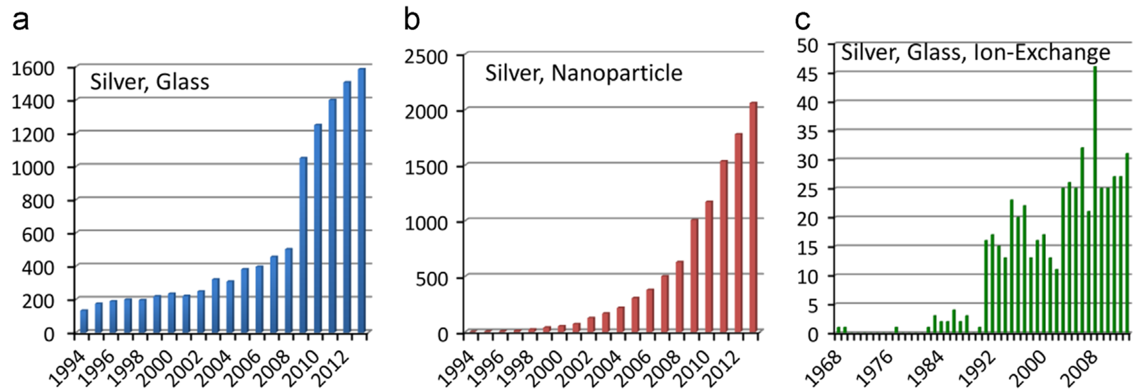

Fig. 1. Data taken from the main science search engines (Scopus, Web of Science) showing the number of quoted articles containing (a) "silver" and "glass", (b) "silver" and "nanoparticle" and (c) "silver", "glass" and "ion-exchange" as keyword identifiers.

articles containing "silver" and "glass" as keyword identifiers in the time span from 1994 to 2013. It is clear that we are still witnessing a continuous increase of interest in this topic, even taking into account the overall increase of materials science published papers. Presently, silver-containing systems can be found in many glass-based objects and devices [4], ranging from integrated photonic switches to stellar interferometers, food containers and antimicrobial orthopedic coatings. In this work, a short review is presented of the state-of-the-art of silver doping glasses, highlighting both the recent advances in the field and the open questions still to be addressed for an effective control of the synthesis of these materials. Even if the literature on this topic is particularly long-lasting and weighty, several recent developments of the research in this case deserves more attention than a comprehensive history, so the reader will find in the 135 selected references provided here all the further cross-references concerning any single aspect of the topic.

2. Properties of silver-doped glasses

Several properties concur to define the functional aspects that make silver suitable for the preparation of glass-based materials. Actually, silver exhibits a variety of interesting features in the state of isolated ion as well as in the form of aggregates, that in turn give rise to properties that depend on the detail of the aggregate structure: starting from dimer or trimer structures up to nanosized clusters formed by hundreds of silver atoms, the functional response of the material turns out to depend on many physical, chemical and structural parameters, so making the silver-doped glasses an extremely versatile class of materials. Besides the wide range of application, the research on silver-doped glasses allows also an insight on several phenomena, namely, the silver–glass interaction, the aggregate nucleation and growth, the silver diffusion into the glass, the origin of the photoluminescence and optical responses, the charge transfer mechanisms, and in general all those features that are at the basis of the prescribed material property.

In the literature, silver-doped glasses are the subject of several experimental research fields. Since the 1970s, optoelectronics and waveguide technology exploited the refractive index increase given by the presence of Ag^+ ions in glass for fabricating planar and channel light waveguides, and it is worth noting that, starting from the pioneering works by Izawa [5] and Giallorenzi [6], the number of published papers dealing with the use of silver for this purpose rapidly increased, and has since then remained almost constant through the last 4 decades, indicating that there has always been room for further improvements in both the basic science and the application aspects of Ag-based waveguides [7–10]. Nowadays, glass optical devices containing Ag waveguiding regions are commonly fabricated by the ion-exchange technique, and novel reviews on the topic have been also uninterruptedly published [11–14]. Among the most recent glass-system devices including silver waveguides are for example Bragg optical multiplexers [15], waveguide-based lasers [16–18], Y-junctions for integrated optical amplifiers [19], Mach–Zehnder interferometers [20] and chemical amplitude sensors [21]. The use of silver as an antimicrobial agent is also well-established since decades: silver ions doping of glasses is used for example for the synthesis of fungicidal antimicrobial glasses [22], glass-coated sutures for tissue engineering [23] and antibacterial bioactive glasses [24], prepared by a variety of different techniques.

Basic questions related to classical glass-making technologies are in general investigated in relation to silver adding properties. The role of silver in the structuring and stability of specific glasses has been recently studied for lead lithium borate glasses [25] as well as for specific soda-lime silicate [26,27] and more exotic glasses, such as $CaO–Al_2O_3–TiO_2–P_2O_5$ glasses [28] and $SiO_2–CaO–P_2O_5$ ternary systems [29]. As a matter of fact, the process of silver incorporation is often governed by non-equilibrium mechanisms that involve internal local feedbacks between the variables that drive the silver behavior, often preventing classical descriptions based on thermodynamic, chemistry and diffusion equations. In this sense, several spectroscopic investigations have been performed on the structural rearrangements in silicate glasses doped with silver by different non-equilibrium techniques [30–33] looking on one hand at a deeper understanding of the silver behavior in the matrix, and on the other hand at a comprehensive phenomenological descripition able to provide suitable recipes for the fabrication of glasses with prescribed features. The diffusion behavior of silver in glasses