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Centenary of a Serendipitous Inventor: Stookey and a Short Statistical Overview of Photosensitive Glass & Glass-Ceramics Science and Technology

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Abstract: In this short statistical report, we compile and analyze statistics on past and current scientific and technological research on photosensitive glass (PG) as well as glass-ceramics (GC). Their developments have traced remarkable histories since their first commercial discoveries in the 1940s and 1950s, both the work of Don Stookey. These products and processes have transformed modern life and are two of the most widely reported methods for special glass manufacturing. They provide security, are of high quality mass production. The U.S., Japan and China have been leaders in PG glass development, the second place going to China in terms of GC research communities. We have observed very significant progress in recent decades with an exponential growth in the number of scientific publications and patents for PGs and GCs due to new publications, author keywords, affiliations and primary characterization techniques. More than 6,497 patents were filed globally prior to 2015 with the terms "photosensitive and glass" and 9,738 with the terms "glass and ceramics" within the title or abstract according to the European Patent Office. These numbers have continued to grow along with worldwide PG and GC-related sales. Based on the Scopus database, for the same period 1,405 PG documents and 30,819 GC-related (primarily manuscripts) were published with the same terms in the title, abstract or keywords list. From this statistical analysis, both PG and GC will continue to be fascinating materials for further research, development and uses in the near future.

Keywords: Glass, glass-ceramics, history, patent, photosensitive, Stookey, technology.

1. INTRODUCTION

The first patents and manuscripts for two new types of commercial innovative materials were published in the 1940s one decade after they were developed: photosensitive glass (PG) [1-3] and glass-ceramics (GC) [4], the latter a *serendipitous* invention [5]. In other words, it means that nobody planned to invent it. Both were discovered by the same prolific inventor, the American chemist Stanley Donald Stookey (1915-2014) at Corning. These new products belong to the field of materials sciences and engineering and are based on the kinetics and crystallization mechanisms of glassy materials, which are essential processes for the development of special glasses. They have a number of interesting and unique properties, as described below.

PGs were initially classified as a new type of photographic medium that made the permanent printing of 3D colored images within crystal-clear vitreous materials possible [2]. According to Stookey, the term "photosensitive glass" [6], refers to a special glass containing specific elements that are able to form stable photographic figures or images onto transparent glass when exposed to light. In fact, to replicate a figure, a negative is positioned on a clear glass and temporarily subjected to UV radiation. After the negative is removed, the image (or photograph) is fixed by increasing the glass temperature to approximately 600°C for some minutes [1, 2]. The innovation of the method was in incorporating metallic nanocrystals (e.g., copper, gold or silver) in minor quantities to the glass batch; cerium oxide is occasionally added as a reducer. Such photochemical reactions occur in liquids, but they had never been seen in glass before. On further heat treatments these nanocrystals, formed during cooling or at the beginning of the further heating treatment, acted as crystallization centers or nuclei for the development of nonmetallic crystals. Thus crystallization phenomena occur, forming a figure or image [1, 2] - this characterizes PG as a particular derivative of GC, and both innovations are related, as we shall see below.

The first patent taking into account the use of copper as a nucleating agent was filed by Dalton in 1943 (studies started in 1937 [7]), a colleague of Stookey's at Corning [8]. However, the expression "photosensitive" was not mentioned in this patent and it was not possible to produce figures or dis-

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play crystallization kinetics in this material, as was later proposed by Stookey himself [6, 7]. Furthermore, Dalton's studies were based in copper ruby glass, a well known *art glass* used since the XVI century in Italy and Germany [9, 10]. Photochemical reactions were known for liquids at the time, but never in vitreous (i.e. solid) materials. In fact, this particular patent was published only seven years later, on July 8th, 1950 [3]. More precisely, two patents (out of 12 filed by Stookey up to 1950 alone) were awarded to Stookey at the time: U.S. Patetns. No. 2,515,937 and 2,515,943, the former shown in Fig. (**1a**). Stookey found that other colors, such as purple, green or even ruby, vary with the size of metallic nanocrystals, controlled by the photographic process of exposure and heat treatment [9, 10]. As an image application of the photosensitive process, there is a bluish portrait of the author as the first figure described in the patent Fig. (**1b**). He applied gold particles (in ppm) with a basic glass to seed nanocrystals and form images, applying heat treatments between 500 to 600°C over a few minutes and Fotalite® was born.

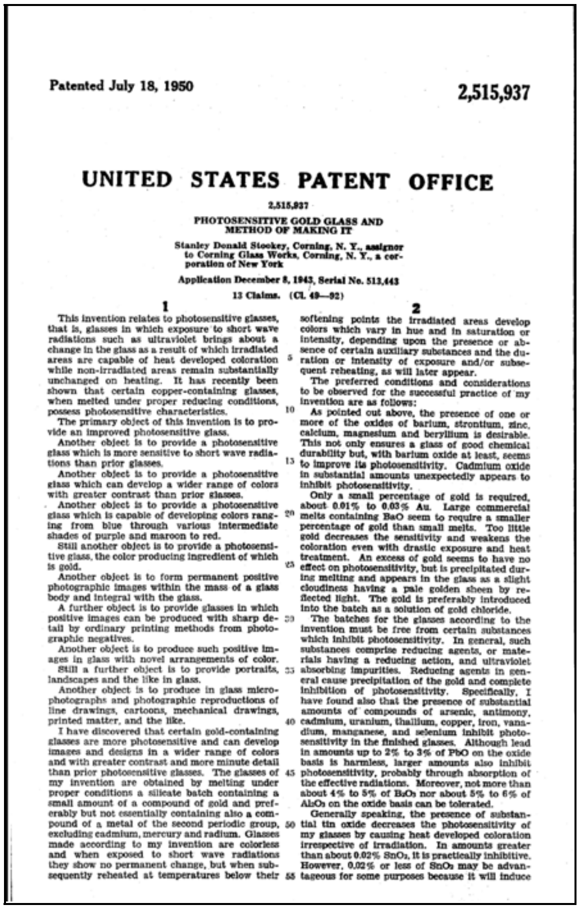
At the very beginning, the understanding of glass-ceramics was strictly empirical, and based on trial-and-error experimentation. The first book to provide technical instructions for the production of glass was written during the Renaissance by the Italian priest and glassmaker Antonio Neri (1576-1614), who compiled many of the procedures, methods and glass manufacturing secrets in his work "*L'Arte Vetraria*" ("*The Art of Glass*") in 1612. This book became a glassmaking manual for nearly two hundred years. In the book's preface ("Al Curioso Lettore", or "To the Curious Reader"), the author expressed his passion: "Glass is one of the true fruits of the Art of Fire" ("*vetro è uno dei veri frutti dell'Arte del fuoco*") [11]. In this work it is possible to read the first notes on gold ruby glass [9, 10].

The history of GC production dates back to the experiments of the French polymath René-Antoine Ferchault de Réaumur (1683-1757). Many glassmakers over the centuries practicing the "Art of Fire" probably started to note that glass could be controllably crystallized by some heat treatments, but Réaumur was the first to produce and published results of a partially crystallized glass after heat-treated soda-lime-silica glass bottles in a bed of gypsum and sand after several days ("*premier mémoire*"). However, there was no control over the final product which was deformed [12]. His intention was to produce new materials transforming "Verre en Porcelaine". The theoretical basis of crystallization antecedes the fundamental work of Josiah Willard Gibbs (1839 - 1903), more precisely on the thermodynamic description of heterogeneous systems first published in 1874 [13].

In 1898 the Russian chemist Gustav Heinrich Johann Apollon Tammann (1861-1938) [14], proposed and published the first modern scientific paper which describes the behavior of GC production by controlling the nucleation I and growth U rate processes. In Fig. (**1a**, *right*) the U.S. Patent No. 2,920,971 is shown, filed in June 4th, 1956 and published January 12th, 1960, related to the discovery of GC, with a hundred compositions and some measured properties, such as expansion coefficient, density and strength. Tammann studied the crystallization of organic liquids and suggested the following procedure, which is now known as the Tammann or "development" method [15]. Crystals nucleated into a glass at a lower temperature T_n, are developed at a higher temperature, $T_d > T_n$ to produce crystals of sufficient sizes for microscopic observations. The development temperature T_d is chosen based on the behavior of the experimental nucleation (I) and growth (U) rates. In brief, the nucleation rate at T_d ($I(T_d)$) should be inferior to the nucleation rate at T_n ($I(T_n)$) and the growth rate at T_d ($U(T_d)$) should be superior to the growth rate at T_n ($U(T_n)$). In practical terms, T_n is a temperature around the glass transition temperature T_g. Experimental I and U curves of the disilicate glass ($Li_2Si_2O_5$) are shown in Fig. (**2**) to illustrate this method. This particular glass system inspired Stookey to prepare compositions for his first crystallization experiments. Please note that nucleation reaches a maximum near T_g and crystal growth a maximum at a higher temperature, near the melting point (T_m) in Fig. (**2**). Thus, he empirically determined the characteristic temperatures T_n and T_d of photosensitive glasses, and T_d was chosen as a temperature between the maximum nucleation and crystal growth rates, as shown in Fig. (**2**) for the lithium disilicate case, considering a plethora of experimental data in nucleation [16-21] and crystal growth rate kinetics [21-32].

In the last half century, this process has gained extensive popularity in academia as a method for the production of homogeneous glassy materials. GC (also known as vitrocerams, pyrocerams or sittals) are polycrystalline materials obtained by controlled crystallization of some vitreous materials that present one or more crystalline phases dispersed in a remaining glass matrix. Such a phenomenon also takes place when glass, incorporated with a nucleation agent - an additive such as titanium oxide, phosphorus, silver or copper oxide - is present. They are interesting substances of scientific exploration and numerous researchers are keen to comprehend the transformation kinetics from glass to polycrystals and to study the changes in properties, as for example thermal, electrical, optical, mechanical and magnetic properties. In fact, Mauro & Zanotto [33] observed that "glass-ceramics" (i.e. crystallization) has been one of the top *keywords* in the history of glass science. Undoubtedly, the first commercial GC can be compared with the most important technological advance in the late 19th century: the discovery of borosilicate glass.

In recent years, Glebov [34] proposed a kinetics model of a photoinduced procedure based on a new photosensitive composition for the production of a tridimensional hologram named photo-thermo-refractive glass (PTRG). PTRG is a multicomponent sodium silicate glass composition doped with silver, fluorine and cerium as the primary dopants (cerium works as a reducer), which presents a gradient of the refractive index after UV exposure followed by a thermal heat treatment. In this vitreous material, a sequence of photochemical and photo-physical reactions occur as follows: *i*) a UV light exposure photoionizes Ce^{3+}; *ii*) a released electron is captured by a silver ion which is changed to the metallic state (Ag°); *iii*) a thermal heat treatment of a UV-exposed glass originates the diffusion of silver atoms and creates silver nanocrystals which promote the formation of nucleation centers that control the precipitation of the NaF crystalline phase; *iv*) additional interactions between sodium fluoride nanocrystals and the glass matrix at higher temperatures causes a modification of the refractive index; *v*) a difference between the crystallization rates in exposed and



Patented July 18, 1950 **2,515,937**

UNITED STATES PATENT OFFICE

2,515,937

PHOTOSENSITIVE GOLD GLASS AND METHOD OF MAKING IT

Stanley Donald Stookey, Corning, N. Y., assignor to Corning Glass Works, Corning, N. Y., a corporation of New York

Application December 8, 1943, Serial No. 513,443

13 Claims. (Cl. 49—92)

1

This invention relates to photosensitive glasses, that is, glasses in which exposure to short wave radiations such as ultraviolet brings about a change in the glass as a result of which irradiated areas are capable of heat developed coloration while non-irradiated areas remain substantially unchanged on heating. It has recently been shown that certain copper-containing glasses, when melted under proper reducing conditions, possess photosensitive characteristics.

The primary object of this invention is to provide an improved photosensitive glass.

Another object is to provide a photosensitive glass which is more sensitive to short wave radiations than prior glasses.

Another object is to provide a photosensitive glass which can develop a wider range of colors with greater contrast than prior glasses.

Another object is to provide a photosensitive glass which is capable of developing colors ranging from blue through various intermediate shades of purple and maroon to red.

Still another object is to provide a photosensitive glass, the color producing ingredient of which is gold.

Another object is to form permanent positive photographic images within the mass of a glass body and integral with the glass.

A further object is to provide glasses in which positive images can be produced with sharp detail by ordinary printing methods from photographic negatives.

Another object is to produce such positive images in glass with novel arrangements of color.

Still a further object is to provide portraits, landscapes and the like in glass.

Another object is to produce in glass microphotographs and photographic reproductions of line drawings, cartoons, mechanical drawings, printed matter, and the like.

I have discovered that certain gold-containing glasses are more photosensitive and can develop images and designs in a wider range of colors and with greater contrast and more minute detail than prior photosensitive glasses. The glasses of my invention are obtained by melting under proper conditions a silicate batch containing a small amount of a compound of gold and preferably but not essentially containing also a compound of a metal of the second periodic group, excluding cadmium, mercury and radium. Glasses made according to my invention are colorless and when exposed to short wave radiations they show no permanent change, but when subsequently reheated at temperatures below their

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softening points the irradiated areas develop colors which vary in hue and in saturation or intensity, depending upon the presence or absence of certain auxiliary substances and the duration or intensity of exposure and/or subsequent reheating, as will later appear.

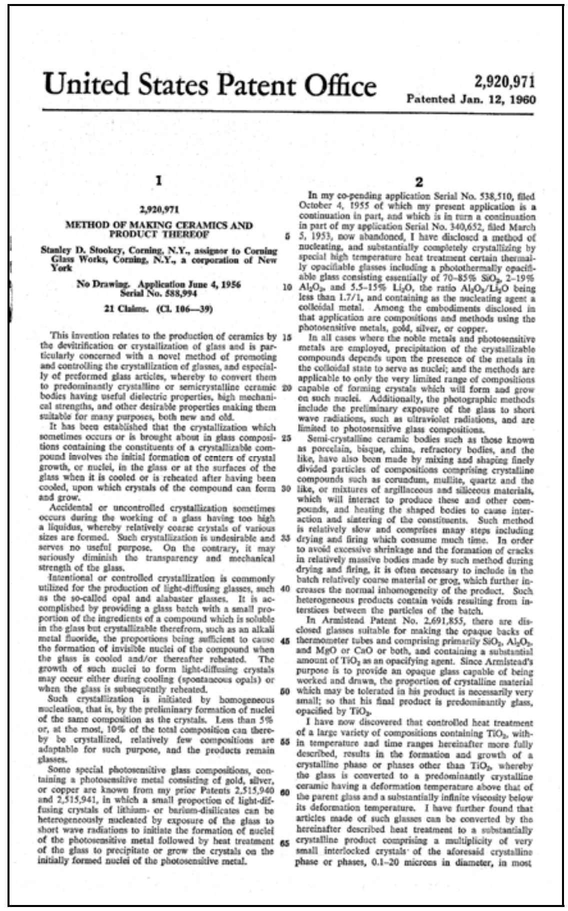
The preferred conditions and considerations to be observed for the successful practice of my invention are as follows:

As pointed out above, the presence of one or more of the oxides of barium, strontium, zinc, calcium, magnesium and beryllium is desirable. This not only ensures a glass of good chemical durability but, with barium oxide at least, seems to improve its photosensitivity. Cadmium oxide in substantial amounts unexpectedly appears to inhibit photosensitivity.

Only a small percentage of gold is required, about 0.01% to 0.03% Au. Large commercial melts containing BaO seem to require a smaller percentage of gold than small melts. Too little gold decreases the sensitivity and weakens the coloration even with drastic exposure and heat treatment. An excess of gold seems to have no effect on photosensitivity, but is precipitated during melting and appears in the glass as a slight cloudiness having a pale golden sheen by reflected light. The gold is preferably introduced into the batch as a solution of gold chloride.

The batches for the glasses according to the invention must be free from certain substances which inhibit photosensitivity. In general, such substances comprise reducing agents, or materials having a reducing action, and ultraviolet absorbing impurities. Reducing agents in general cause precipitation of the gold and complete inhibition of photosensitivity. Specifically, I have found also that the presence of substantial amounts of compounds of arsenic, antimony, cadmium, uranium, thallium, copper, iron, vanadium, manganese, and selenium inhibit photosensitivity in the finished glasses. Although lead in amounts up to 2% to 3% of PbO on the oxide basis is harmless, larger amounts also inhibit photosensitivity, probably through absorption of the effective radiations. Moreover, not more than about 4% to 5% of B_2O_3 nor about 5% to 6% of Al_2O_3 on the oxide basis can be tolerated.

Generally speaking, the presence of substantial tin oxide decreases the photosensitivity of my glasses by causing heat developed coloration irrespective of irradiation. In amounts greater than about 0.02% SnO_2, it is practically inhibitive. However, 0.02% or less of SnO_2 may be advantageous for some purposes because it will induce



United States Patent Office

2,920,971
Patented Jan. 12, 1960

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2,920,971

METHOD OF MAKING CERAMICS AND PRODUCT THEREOF

Stanley D. Stookey, Corning, N.Y., assignor to Corning Glass Works, Corning, N.Y., a corporation of New York

No Drawing. Application June 4, 1956
Serial No. 588,994

21 Claims. (Cl. 106—39)

This invention relates to the production of ceramics by the devitrification or crystallization of glass and is particularly concerned with a novel method of promoting and controlling the crystallization of glasses, and especially of preformed glass articles, whereby to convert them to predominantly crystalline or semicrystalline ceramic bodies having useful dielectric properties, high mechanical strengths, and other desirable properties making them suitable for many purposes, both new and old.

It has been established that the crystallization which sometimes occurs or is brought about in glass compositions containing the constituents of a crystallizable compound involves the initial formation of centers of crystal growth, or nuclei, in the glass or at the surfaces of the glass when it is cooled or is reheated after having been cooled, upon which crystals of the compound can form and grow.

Accidental or uncontrolled crystallization sometimes occurs during the working of a glass having too high a liquidus, whereby relatively coarse crystals of various sizes are formed. Such crystallization is undesirable and serves no useful purpose. On the contrary, it may seriously diminish the transparency and mechanical strength of the glass.

Intentional or controlled crystallization is commonly utilized for the production of light-diffusing glasses, such as the so-called opal and alabaster glasses. It is accomplished by providing a glass batch with a small proportion of the ingredients of a compound which is soluble in the glass but crystallizable therefrom, such as an alkali metal fluoride, the proportions being sufficient to cause the formation of invisible nuclei of the compound when the glass is cooled and/or thereafter reheated. The growth of such nuclei to form light-diffusing crystals may occur either during cooling (spontaneous opals) or when the glass is subsequently reheated.

Such crystallization is initiated by homogeneous nucleation, that is, by the preliminary formation of nuclei of the same composition as the crystals. Less than 5% or, at the most, 10% of the total composition can thereby be crystallized, relatively few compositions are adaptable for such purpose, and the products remain glasses.

Some special photosensitive glass compositions, containing a photosensitive metal consisting of gold, silver, or copper are known from my prior Patents 2,515,940 and 2,515,941, in which a small proportion of light-diffusing crystals of lithium- or barium-disilicates can be heterogeneously nucleated by exposure of the glass to short wave radiations to initiate the formation of nuclei of the photosensitive metal followed by heat treatment of the glass to precipitate or grow the crystals on the initially formed nuclei of the photosensitive metal.

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In my co-pending application Serial No. 538,510, filed October 4, 1955 of which my present application is a continuation in part, and which is in turn a continuation in part of my application Serial No. 340,652, filed March 5, 1953, now abandoned, I have disclosed a method of nucleating, and substantially completely crystallizing by special high temperature heat treatment certain thermally opacifiable glasses including a photothermally opacifiable glass consisting essentially of 70–85% SiO_2, 2–19% Al_2O_3, and 5.5–15% Li_2O, the ratio Al_2O_3/Li_2O being less than 1.7/1, and containing as the nucleating agent a colloidal metal. Among the embodiments disclosed in that application are compositions and methods using the photosensitive metals, gold, silver, or copper.

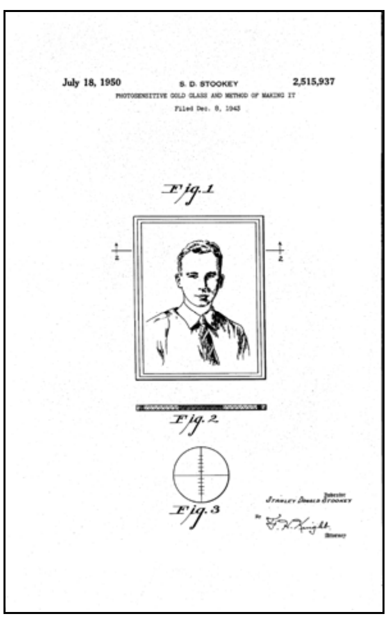
In all cases where the noble metals and photosensitive metals are employed, precipitation of the crystallizable compounds depends upon the presence of the metals in the colloidal state to serve as nuclei; and the methods are applicable to only the very limited range of compositions capable of forming crystals which will form and grow on such nuclei. Additionally, the photographic methods include the preliminary exposure of the glass to short wave radiations, such as ultraviolet radiations, and are limited to photosensitive glass compositions.

Semi-crystalline ceramic bodies such as those known as porcelain, bisque, china, refractory bodies, and the like, have also been made by mixing and shaping finely divided particles of compositions comprising crystalline compounds such as corundum, mullite, quartz and the like, or mixtures of argillaceous and siliceous materials, which will interact to produce these and other compounds, and heating the shaped bodies to cause interaction and sintering of the constituents. Such method is relatively slow and comprises many steps including drying and firing which consume much time. In order to avoid excessive shrinkage and the formation of cracks in relatively massive bodies made by such method during drying and firing, it is often necessary to include in the batch relatively coarse material or grog, which further increases the normal inhomogeneity of the product. Such heterogeneous products contain voids resulting from interstices between the particles of the batch.

In Armistead Patent No. 2,691,855, there are disclosed glasses suitable for making the opaque backs of thermometer tubes and comprising primarily SiO_2, Al_2O_3, and MgO or CaO or both, and containing a substantial amount of TiO_2 as an opacifying agent. Since Armistead's purpose is to provide an opaque glass capable of being worked and drawn, the proportion of crystalline material which may be tolerated in his product is necessarily very small; so that his final product is predominantly glass, opacified by TiO_2.

I have now discovered that controlled heat treatment of a large variety of compositions containing TiO_2, within temperature and time ranges hereinafter more fully described, results in the formation and growth of a crystalline phase or phases other than TiO_2, whereby the glass is converted to a predominantly crystalline ceramic having a deformation temperature above that of the parent glass and a substantially infinite viscosity below its deformation temperature. I have further found that articles made of such glasses can be converted by the hereinafter described heat treatment to a substantially crystalline product comprising a multiplicity of very small interlocked crystals of the aforesaid crystalline phase or phases, 0.1–20 microns in diameter, in most

a)



b)

Fig. (1). a) *Left*: the first page of United States photosensitive glass patent US 2,515,937 applied on December 8th, 1943 [3] and published in July 8th, 1950. *Right*: the first page of United States glass-ceramics patent 2,920,971 applied on June 4th, 1956 and published in January 12th, 1960 [4]. Both were patented by Stookey, www.uspto.gov. **b**) *Left*: An image application of the photosensitive process, patent US 2,920,971. There is a bluish portrait of the author as the first figure in the patent. At that time he used gold particles with a basic glass, with heat treatments between 500 to 600°C over a few minutes. See www.uspto.gov. *Right*: A photograph of Stookey in 1950 preparing a piece of photosensitive glass to expose an image to ultraviolet light. *Courtesy* of the Corning Incorporated Department of Archives & Records Management, Corning, NY.

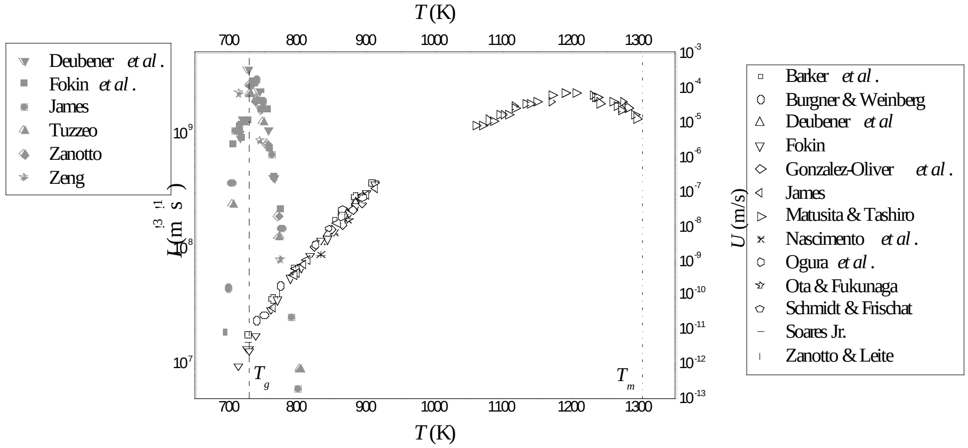


Fig. (2). Experimental data on nucleation $I(T)$ [16,21] and crystal growth $U(T)$ [21,32] rates in lithium disilicate ($Li_2Si_2O_5$) glass, showing the Tammann or "development" method. The glass transition temperature (T_g) and the melting point (T_m) are indicated. The development temperature $T_{d,}$ due to Tammann, is a select temperature where a crystallization process is applied, first increasing nuclei at a determined temperature T_n (around T_g) at an appropriate heat treatment time, and thus, at a higher temperature (T_d), growing such nucleated crystals in another time.

unexposed areas develops a photo-controlled refractive index modulation.

PG and GC have some characteristics in common: they can be transparent, uniform, strong, tough, chemically durable, and have low or zero porosity. Under certain heat treatments GC can be even opal. This is why these particular materials have been used in a wide array of engineering applications, ranging from domestic to high-tech uses, such as portraits and figures, photographic murals, 3D images, displays, decorative windows, ornamental tiles, kitchen utensils, especially stovetops on electric stoves, computer hard disk substrates, huge mirrors for telescopes, artificial teeth, and many military uses.

Glass has been a key material for mankind from the very early stages of civilization. Its history dates back approximately five millennia, making it one of the most key and impressive materials made by man. The glassmaking process basically consists of melting raw materials, such as sand, alkali carbonates and lime to approximately 1400^{o}C. This technique has been used throughout recorded history due to its simplicity, adaptability and potential applications in a number of fields. Glassmaking can also be modified for mass production. As observed by Zanotto [35, 36], the thermodynamics and kinetics of nucleation and crystal growth are key scientific problems that control the glass-forming ability of molten liquids and the ultimate stability of glass against devitrification. The basics behind the nature and rules of glass crystallization involve the thermodynamics, mechanisms and kinetics of crystal nucleation, growth and overall crystallization, as described in the early works of Gibbs [13] and Tammann [14].

Our goal is to present an overview of the historical tendencies and current status of PG and GC studies. We hope this paper can be used as an exploratory study for discussion about future guidelines for photosensitive as well as glass-ceramics research, based on the same origin: its inventor and innovator - Don Stookey.

2. STANLEY DONALD STOOKEY AND A BRIEF HISTORY OF COMMERCIAL PHOTOSENSITIVE GLASS AND GLASS-CERAMICS

According to Dr. Stanley D. Stookey's autobiography [9,10] (published twice with different names, changing from "*Journey to the Center of the Crystal Ball*" to "*Explorations in Glass*" 15 years later), he held 58 patents and wrote 29 scientific papers. According to the European Patent Office (EPO), there are 116 patents under his name, covering glass and ceramics, some solely his while others were filed jointly with colleagues, and not only in the USA or Canada. In fact, this number difference is simply explained by the sister patents submitted to different offices around the world, a common industrial practice as pointed out by Mauro & Zanotto [33]. Indeed, his inventions and discoveries have influenced the development of new glass and ceramic compositions considerably, such as sunglasses, eyeglasses, cookware, military systems, and electronics. At Corning he was a research director for 47 years and promoted research & development in glass and ceramics.

Stookey attended Coe College from 1934 to 1936 and obtained his first *Magna Cum Laude* degree in chemistry and mathematics. After graduation, Stookey then went to Lafayette College in Easton, Pennsylvania in 1937. The following year he received his MSc degree in chemistry from Lafayette College. Stookey then did PhD in chemistry at the Massachusetts Institute of Technology (MIT) in Cambridge finishing in 1940. He was hired by Corning Glass Works the same year [10] - despite knowing almost nothing about the vitreous state. This was how he started his career in glass-ceramics which led him to several innovations. Within his new multimillion dollar products, new glass factories were built around the world and over 10,000 jobs created (according to his obituary published in the *Washington Post*). The names Fotalite®, Fotoform® glass Fotoceram®, Cercor®, Pyroceram®, opal glass, a heat resistant glass used in supersonic missile nose cones, and the well-known photochromic glass, that darkens and clears reversibly according to environmental circumstances are just some products he was responsible for developing. These particular types of glass were first made accessible to consumers by Corning as sunglasses in the 1960s [37].

Serendipity is related to the occurrence and development of events by chance in a happy or beneficial way. A serendipitous invention made by Stookey in 1953 was when he took a piece of a transparent composition based on lithium disilicate glass, the same composition which nucleation and crystal growth rate data shown in Fig. (**2**). His Fotoform® composition had lithium disilicate and precipitated silver particles, that produced a permanent photographic image after heat treated in a furnace. While doing such experiments, this special glass was mistakenly heated to a developing temperature T_d of 900°C (1,652 degrees Fahrenheit), 300°C higher than he intended when an oven thermometer got stuck on the highest temperature. Stookey had accidentally created the first glass-ceramic, Fotoceram®. "Damn it, I ruined a furnace" was his first thought [10]. According to Zanotto [38], instead of a melted pool of glass, the astonished Stookey noted a dense and white crystalline material that had not modified its shape [5]. He also accidentally dropped a piece on the ground to find that it did not break into small pieces, contrary to what would normally have been expected. He also heard a metallic sound [5]. Surprised by its unusual toughness, he discovered a new fine-grained crystalline material using a simple thermal treatment that produced a stronger, harder material with high electrical resistivity. He noted that silver particles were effective as seeds for what turned out to be lithium disilicate nanocrystals. In fact the new material was lighter than aluminum and about nine times stronger than plate glass. He rapidly realized that, in theory at least, all glass materials could be modified to polycrystalline ceramics by a crystallization process [37].

As Stookey had accidentally created the first GC, this eventually led to the development of CorningWare in 1956 (a lithium-aluminosilicate glass-ceramic: www.corningware.com) [5]. This was an outstanding glass innovation, a new thermal-shock-resistant GC that would change cooking forever (*US* 2,920,971). It allows one to bake a casserole and freeze the leftovers in the same dish. CorningWare is also used to produce all sorts of dishes and stove tops. This invention entered the consumer marketplace in 1958 and became another of his several million dollar products creating thousands of jobs. It also influenced the development of Visions®, transparent cookware later. VisionWare was patented by Corning in 1966 (*US* 3,282,770). A particular application of his Pyroceram® glass-ceramic has properties that can be applied by the military in missile nose cones to be guided by an internal antenna. These special properties include extreme hardness, low thermal expansion coefficient, super strength, good dielectric properties, resistance to high heat and transparency to microwave signals, based on magnesium aluminosilicate glass-ceramics [5]. Another important discovery made by Stookey and his team was *Gorilla* Glass (originally called Chemcor®, a very strong and flexible glass) now used in iPhones and other electronic displays that include an ion-diffusion procedure to improve strengthening (as shown in US 2,779,136). The fourth generation of Gorilla glass has recently been produced by means of an *isopipe* process. Briefly, *isopipe* is a method of making a glass sheet using an overflow fusion in a downdraw way [39]. The Willow® thin and flexible glass, similar to the composition of Gorilla glass, can be used as a substrate for the next generation of ultra-slim displays [40].

According to its inventor, it was a lucky accident that launched glass-ceramics [9, 10]. Stookey said once: "I am most proud of opening up a whole new field of science - the nucleation of crystallization of glass - that produced all kinds of new crystalline products with so many different useful properties" [37]. Stookey retired from Corning Glass Works in 1987 and died November 4th 2014 in Pittsford, N.Y., due to complications from hip surgery, according to his *Washington Post* obituary.

3. METHOD

In this work, we considered more than 23,400 publications of an estimated 30,000 around the world [41]. This research was based on "Life Sciences" libraries (which comprise 4,300 journal titles), "Health Sciences" (6,800 titles), "Physical Sciences" (7,200 titles) and "Social Sciences & Humanities" (5,300 titles) libraries of the Scopus bibliographic database from Elsevier. The number of libraries consulted was due to the broad application range of PGs and CGs. A search for papers using the keywords "photosensitive and glass," "glass and ceramics" in the *title*, *abstract* or *keywords* of the article was carried out. Following this specific search procedure, many other glass-ceramics and photosensitive-related articles were excluded. Nevertheless, this approach provided a broader dataset to work with and consequently sufficient data for statistical analysis. We found that the terms "glass-ceramic" or "glass ceramic" predominate over 'vitroceramics', 'sittals' or 'pyroceramics' keywords by a large margin, as also observed recently by Montazerian *et al*. [42].

The total amount of PG-related publications registered on Scopus was about 1,405 based on the keywords ("photosensitive and glass") appearing in the article *title*, *abstract*, or *keyword* list, for all document types, including letters, technical notes, conference proceedings and *errata* between 1940 up to 2015. The same procedure for GC listed 30,819 documents. To further simplify our results the search for journal article abstracts was restricted. Our search returned 1,010 photosensitive glass-related manuscripts from the Scopus database, 23,062 documents related to glass and ceramics studies. An analogous search carried out using the *Web of Science* (Thomson Reuters Scientific) resulted in 1,334 (and 6,914) papers when searching for the terms *photosensitive* and *glass* in the title (and topic), and 24,781 (and 86,740) for *glass* and *ceramics* keywords, respectively. The articles retrieved using this approach were organized according to the research fields, including journal title, publication date, affiliation, country of origin, and type of glass studied. Here we can consider such different values as representative of the actual number of genuine PG and GC papers that lie between these extremes.

A complementary search of the patent literature was carried out using the *European Patent Office* database. This search took into account patents awarded between 1940 and 2015 with the keywords in the *title* and *title* or *abstract* as was previously done in the Scopus search. They resulted in 6,497 PG as well as 9,738 GC patents, both issued worldwide. These patents were sorted according to issue date and grantee.

4. RESULTS & DISCUSSION

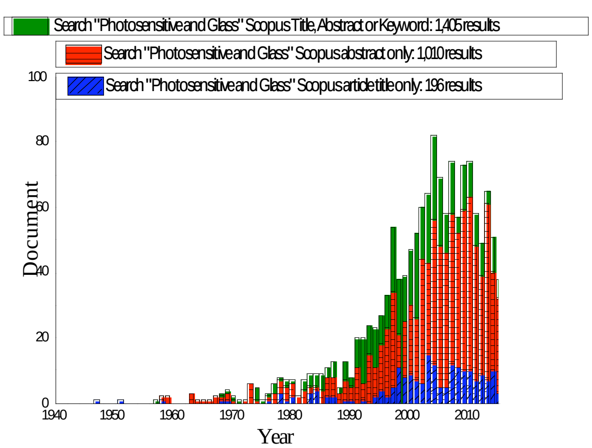
Figures **3a & 3b** show a comparison of the number of photosensitive glass and glass-ceramics-related documents and patents granted and published by decade found using the Scopus database. The following search strategies were considered: including any of the specified keywords in the *article titles*, *abstracts* or *keywords* (1,405 PG and 30,819 GC document results); only *abstracts* (1,010 PG and 23,062 GC document results) and just titles (196 PG and 9,208 GC document results). From Fig. (**3b**) it is possible to see that granted patents with GC as a topic have been progressively reported at a higher rate since 1950s when viewed in comparison with Fig. (**3a**). The first paper on glass-ceramics listed in the Scopus database was authored by Shaver and Stookey [43] in 1959. A second paper, authored by McLellan [44] in the same year, discussed different potential GC applications in the automotive industry. Sakamoto and Yamamoto [45] reviewed the typical compositions of commercial CG products due to bulk or surface crystallization. Sintered GC applied to biomedicine, architecture and electronics were introduced as successful examples of GC surface crystallization in the following years.

It is important to note that Montazerian *et al.* [42] found a similar number of GC results, around 7,040 papers just considering GC keywords in the title, but between 2001 and 2014. According to these authors, this number represents only a lower bound of which they named *genuine* GC. On the other hand, the other type of search done by Montazerian *et al.* [42] (with the selected keywords in the article title or abstract or article keywords) yielded 12,806 papers within same period, but included several that are only minimally related to glass-ceramics. This number is less than a half of our results, but obtained in a different period. In our research we considered GC of any type of glass composition (i.e., organic or inorganic). In fact, in recent years an impressive number of publications were found. For example, about 1,258 GC papers were published in 2014 alone and another 1,123 just in 2015 (according to keyword search using title only in the Web of Science).

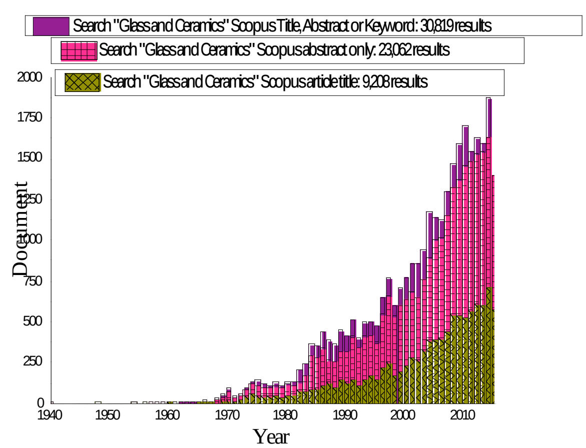
Figures **3a & 3b** show that the number of publications on PG as well as GC based research works increased rapidly during the period 1995-2005, reflecting the observations made by Mauro and Zanotto [33]. Regarding PG, the first manuscript was published anonymously in 1947 [2], in the *Chemical Engineering News* magazine, more precisely in the column “The Chemical News Parade”. Of these PG documents, 63.6% were Articles, 30.3% were Conference Papers and only 1.2% were Reviews. Other reported categories included Book Chapters, Reports, Conference Reviews and Letters. Similar results, of 69.3% Articles, 19.93% Conference Papers and only 2.5% Reviews, were obtained considering glass-ceramics research documents.

According to Fig. (**4a)**, the University of Central Florida (UCF) in USA was the most productive institution in terms of PG publications. Asian universities and organizations, including the Institute of Physical and Chemical Research (RIKEN, Japan), the University of Southampton (UK), the Tokyo Institute of Technology (Japan) and the Nanyang Technological University (Singapore) were also included in the top five institutions in a list of 160 organizations. The most prolific authors in this period were Profs. Leonid Glebov from UCF, plus Koji Sugioka and Katsumi Midorikawa, both from RIKEN. The list of top 10 authors included scientists with between 13 and 47 published manuscripts on many aspects of PG in this period.

Figure **4b** shows similar data for glass-ceramics. The top five institutions, however, are not the same as the previous and were related to labs at Japan’s Kyoto University, at Imperial College London, at Tsinghua University in China, at Wuhan University of Technology in China, and the Friedrich Schiller Universitat Jena, related to the Otto Schott Institute of Materials Research in Germany. The most prolific authors in the period analyzed were Prof. Aldo Boccaccini, for many

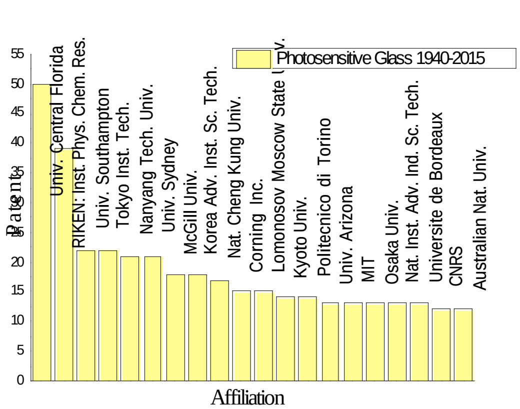


a)

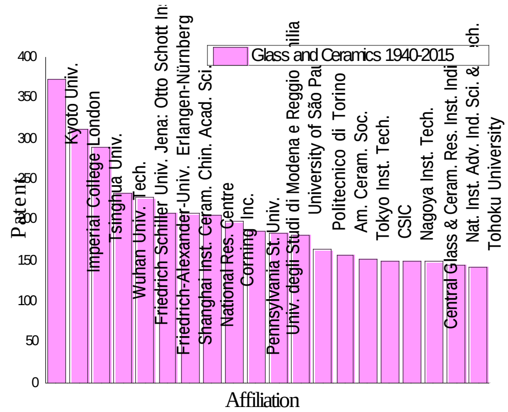


b)

Fig. (3). Publication results for “Photosensitive glass” (**a**): considering keyword in the article title, abstract or keyword (1,405 results); only abstract (1,010 results) and only title (196 results). Publication results for “Glass and Ceramics” (**b**): considering keyword in the article title, abstract or keyword (30,819 results); only abstract (23,062 results) and only title (9,208 results). Data from www.scopus.com.



a)



b)

Fig. (4). (**a**) Total number of publications about photosensitive glass (1940-2015), sorted by affiliation (top 20). University of Central Florida of United States leads this ranking, followed by RIKEN: The Institute of Physical and Chemical Research of Japan. (**b**) The same procedure of total number of publications about glass-ceramics (1940-2015), sorted by affiliation (top 20), was Kyoto University, followed by Imperial College of London (UK). Overall, there is a mix of Asian, European, and American institutions. It is relevant to stress the presence of Corning Inc. among the 20 most prolific institutions in these rankings as well as the Otto-Schott Institute (via the Friedrich-Schiller-Universität in Jena). Data from www.scopus.com.

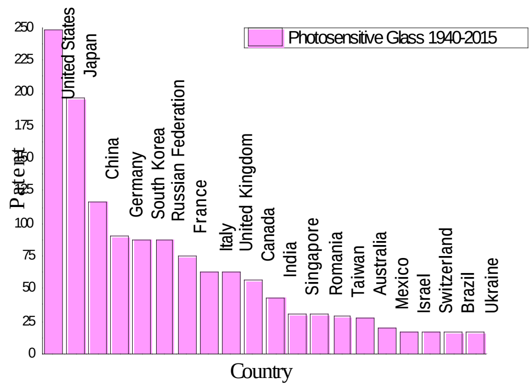
years at Imperial College (UK) and now at Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany, with 231 documents published in this period, followed by Prof. Takashi Nakamura from University of Tokyo with 136 documents published. The top 10 authors include researchers between 86 and 231 published manuscripts on many GC aspects. Several Asian, European and American universities also appear among the most overall prolific institutions. It is interesting to note that there is a Brazilian university in this rank (University of São Paulo, at 12th position) and at least two industrial research labs: Corning Inc. and Otto Schott Institute of Materials Research (at Friedrich Schiller Universität Jena), both in high positions on this list.

If one considers the amount of photosensitive and glass-ceramics-related publications by country (see Figs. (**5a & 5b**)), the United States had the highest number of overall publications, followed by Japan and China, changing second place in the lists. Except for South Korea, Germany, the Russian Federation, France, Italy and the United Kingdom were ranked as top ten in both lists (Figs. (**5a & 5b**)), changing positions between one or another ranking. This is not surprising as (according to Mauro and Zanotto [33]) two of these three first nations were leaders in glass research, followed by Russia and three European countries (Germany, France, and the United Kingdom). Outside Europe, Canada and India were also ranked in the top ten, as can be seen in Figs. (**5a & 5b**).

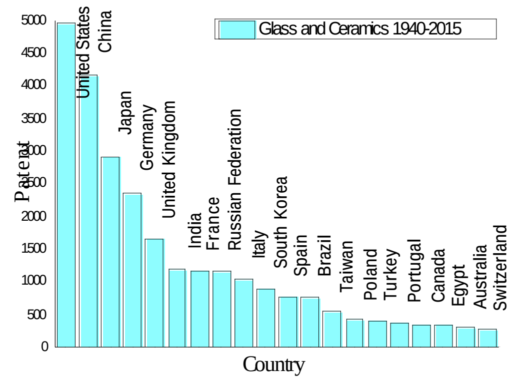
Considering the most productive nations, Fig. (**5a**) also shows the geographical analysis of active researchers in the PG field. The United States had the highest percentage of 17.7% of 68 countries in PG research, followed by Japan (14.0%), China (8.3%), Germany (6.4%) and South Korea/the Russian Federation (both with 6.3%). The high percentage of Asian researchers (taking into account only the top five institutions) was probably due to greater contributions of government allocated funds for the area of physics, astronomy and materials science. Note that Brazil was 19th on the list with 16 patents, the same number as the Ukraine.

A detailed breakdown of the active development of "glass-ceramics" topic *viz*. universities and academic institutes focusing on GC production based on geography is also shown in Fig. (**5b**). Again the USA occupies first position of 16.1% of 109 countries in GC research, followed by China (13.5%), Japan (9.4%), Germany (7.6%) and United Kingdom (5.4%). Mauro and Zanotto [33] observed an increasing rate of glass research in Chinese institutions in recent years, surpassing those of every other country. Other countries that have demonstrated prominent expansion in research activities in this area were India, France, the Russian Federation, Italy and South Korea. Since the mid-nineties both rates have grown rapidly, while the growth rates in research activity have diminished or even become negative in all the other traditional countries. The rapid growth of Chinese research is correlated with a perceptible reduction of the general glass research growth rate in the USA [34], at least in general glass research. Although this decline is disturbing, the fall in research rates was more remarkable in many of the other long-established countries, such as Japan, Germany, and Russia, all of which actually have produced fewer research publications in the last two decades. It is surprising that several emerging counties, such as Spain, Brazil, Taiwan, Poland, Turkey and Portugal were also well ranked. According to the data shown in Fig. (**5**), North America and Asia have become prominent centers for new technological developments to make better PG and GC products.

The five major journals that publish the results of the PG community include *Proceedings of SPIE*, from the International Society for Optical Engineering (12.5%), *Journal of Non Crystalline Solids* (3.7%), *Optics Letters* (2.1%), *Applied Physics Letters* (1.7%) and *Optics Express* (1.5%). The main journal published more than three times the number of photosensitive glass-related articles compared with the second most popular journal, as shown in Fig. (**6a**). From Fig. (**6b**), if considered GC as the topic, we observed few preferences for the same first prominent journals: *Journal of the American Ceramic Society* (5.2%), *Journal of Non-*

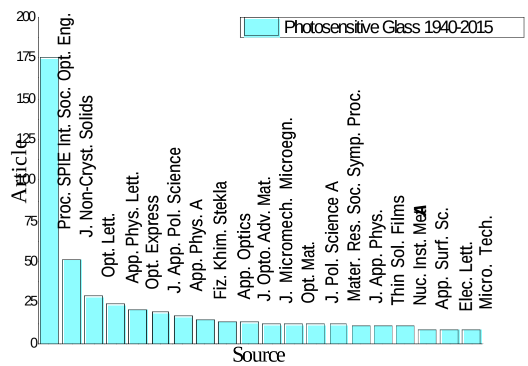


a)

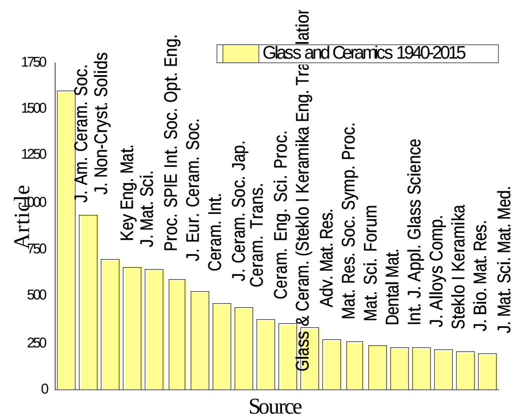


b)

Fig. (5). Most prolific 20 countries in the history of photosensitive glass (**a**) and glass-ceramics (**b**) research (1940-2015). The United States, Japan and China are the leaders overall in photosensitive glass, and second place is held by China when it comes to glass-ceramics. Data from www.scopus.com.



a)



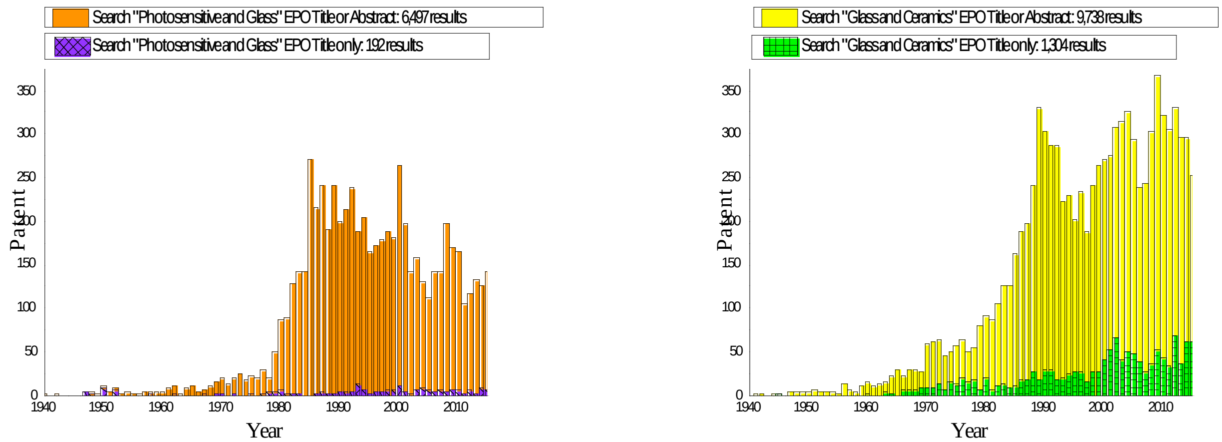
b)

Fig. (6). (**a**) Cumulative number of photosensitive glass-related publications by journal from 1940 to 2015. *Proceedings SPIE* leads this journal ranking by a relative margin. It is interesting to note that several physics/optical journals follow in the ranking, as well as traditional glass-related journals. (**b**) The same research considering glass-ceramics-related publications, where it is possible to note many ceramics as well as biomedical journals. The data are from around 160 sources worldwide in the period analyzed in both cases from www.scopus.com.

Crystalline Solids (3.0%), *Key Engineering Materials* (2.2%), followed by *Journal of Materials Science* (2.1%) and *Proceedings of SPIE*, from the International Society for Optical Engineering (2.1%) as the top five. It is important to note that a very recent publication, the *Int. J. Appl. Glass Science*, started in 2010, is highly cited within the top 20.

PG-related publications were also organized by wide scientific fields, such as *Physics and Astronomy* (48.8%), followed by *Materials Science* (44.2%), *Engineering* (41.9%), *Chemistry* (12.2%) and *Computer Science* (7.5%). The next subjects are *Mathematics* (4.8%) and *Chemical Engineering* (4.6%). It is important to remember that it is possible to cite more than one category. Similar results were obtained in glass-ceramics research: *Materials Science* (59.5%), followed by *Engineering* (33.5%), *Physics and Astronomy* (22.9%), *Chemistry* (8.7%) and *Chemical Engineering* (7.8%). The next subjects are *Dentistry* (4.9%) and *Medicine* (4.6%). All these results also show that some research carried out for photosensitive glass are related to GC given the overlap of these fields. Another noteworthy trend is the presence of relevant specialized journals in the period.

Analyzing data from *European Patent Office* (EPO), more than 6,497 PG patents were granted between 1940 and 2015 (Fig. (**7a**)), and 9,738 GC patents for the same period (Fig. (**7b**)). These results suggest a considerable number of inventive studies toward the development of new PG and GC applications in industry. There has been a marked decline in the amount of published PG patents since 1980, as shown in Fig. (**7a**). This was also noted by Mazurin and Priven [46] when they investigated the amount of glass publications and patents for different year ranges: *i*) a sluggish growth rate (up to 1960's for patents and 1950's for scientific publications), with a noteworthy reduction during the World War II; *ii*) an increasing growth rate between 1960 to 1973; and *iii*) unsystematic fluctuations with a general and regular positive growth rate after 1973 coinciding with the worldwide oil crisis. Montazerian *et al.* [42] also observed a similar fluctuation of GC patent publications over the years, especially during the periods 1975-1979 and 2003-2008, with a notable increase between 1994 and 1998. As observed above, it is worth noting that still there is a widespread industrial practice worldwide to register numerous related patent applications in different countries for the same invention [33].



a) b)

Fig. (7). Frequency distribution results for patent search using (**a**) "Photosensitive and Glass" in the *title* only and *title or abstract*; (**b**) search using "Glass and Ceramics" in the *title* only and *title or abstract*. Data considering year results between 1940 up to 2015 from www.epo.org.

Therefore, the number of patents is greater than the real number of isolated innovations documented. This is seen in other high tech glass products, including glassy X-ray tube patents [47] and even the industrial flat glass process [48].

Governments have a significant responsibility to improve, support and provide guidelines for innovation and produce potential commercial patents. Government agencies, such as the National Science Foundation (USA), the National Natural Science Foundation of China (NSFC), the Japan Science and Technology Agency (JST), the European Union, the Engineering and Physical Sciences Research Council (EPSRC) of the UK, the Deutsche Forschungsgemeinschaft of Germany (DFG), and CAPES, CNPq and FAPESP in Brazil are example of programs that have supported scientists, institutes, industries and companies in the development of energy efficient, green-technological solutions. PG and GC technologies have undoubtedly considerable promise and new performance-enhancing materials have been planned as a result of the progressively growing research communities and funding supports.

An investigation at the EPO database for the abovementioned keywords in the title and abstract fields indicated that the top five companies in PG research were: NEC Corp., Corning Inc., IBM, Nippon Sheet Glass Co. and Saint Gobain. For GC research the results were: Corning *Inc*., Schott, NEC Corp., Nippon Sheet/Electric Glass Co. and Ivoclar Vivadent AG. For the purposes of comparison, the five most productive GC companies obtained by Montazerian *et al.* [42] in the period 1968-2014 using the *Derwent World Patents Index* database were: Schott AG, Corning *Inc*., Kyocera, Nippon Electric Glass and Zeiss. The observable differences in both results came mainly from the period analyzed, different databases, sister patents as well as the difficulty in recognizing many different company names of the same group. It is also important to note that Montazerian *et al.* [42] found just a thousand single patents and applications (from 2 thousand available between 2001 and 2014 according to Derwent World Patents Index database), after eliminating sister patents submitted to different offices, such as USPTO, World patents, Japanese, German and European patent offices for the almost same period under study. Thus, more detailed research must be done manually (or using a precise *data mining* tool), similar to the method presented by Montazerian *et al.* [42] over a longer period.

5. RECENT PATENT COVERAGE

As Zanotto [38] asserts, much is already known about GC (as well as PG) technologies, but many challenges in both the PG and GC developments remain. These include new alternative compositions, more potent nucleating agents, and new or improved crystallization processes. Challenges include biomimetic microstructures, microwave heating, textured crystallization demonstrated by Christian Russel of OSIM in Jena (www.osim.uni-jena.de) and laser crystallization verified by Takayuki Komatsu of Nagaoka University of Technology in Japan (http://mst.nagaokaut.ac.jp). A profound understanding of the control process that governs photothermal-induced nucleation with or without chemical etching and the development of stiffer, stronger, harder and tougher GC, and GC with improved conductivity or transparency are also timely. These types of glass have a wide range of potential properties due to their variety of compositions, thermal heat treatments and resulting microstructures. Combined with the flexibility of high-speed hot-glass fabrication techniques, these will ensure the continued growth of GC technology [38].

A search in the *Derwent Innovations Index* showed that three of the most cited patents using the keywords "*photosensitive* and *glass*" just considering the title were: US5881197 [49], US2005089794 [50] and US 7,326,500 [51]. From 1,134 results in this database for the period 1963-2015, the first patent is related to a new fiber optics technology, the second to new improvements to plasma display panels and the third is a new method for hologram production in glass, respectively. The most cited patent is still that of Stookey and his colleague Pierson, deposited by Corning in 1977 [52].

Related to CG, similar research resulted in some of the following patents: WO9902107 [53], WO200034196 [54] and DE4428839 [55]. In fact, 2,537 patents were found just considering "glass and ceramics" keywords in the title. The first is related to a moldable bioactive glass and glass-ceramics compositions for bone repair; the second to a special lithium disilicate glass-ceramics composition for use in dental restoration; and the third to special glass and glass ceramics materials with low thermal expansion coefficient, respectively. It is important to note that some of Stookey's products, such as CorningWare® and Visions® are still in production [5]. According to Beall [5], Corning no longer produce PG, but other companies, such as Schott, produce a similar material, Foturan®.

Montazerian *et al*. [42] presented not only the main companies but also a list of some of their GC inventions, as well as proposed uses from the last thirteen years in thermal, electrical, optical applications among others. Hench in particular [56] showed recently that innovative transforming technologies for the healthcare and the energy sectors demonstrate that basic glass and GC development and research present great future potential. Sakamoto and Yamamoto [45] highlight prospective applications for next-generation devices such as luminous GC for high-power lighting and LED display systems, electrode materials for rechargeable batteries and position selective laser-crystallized glass using new high-tech GC applications.

Thus, the overall photosensitive and glass-ceramics portfolios are considered promising research targets, due to the number of applications in industry and relevance among researchers and academicians. Therefore, a large amount of potential publications / patents / products / and processes are expected in the coming years. In particular, new advances in the relevancy of special types of glass and many new inventions are in the pipeline [2, 10].

6. CURRENT & FUTURE DEVELOPMENTS

To the layman, glass is a transparent solid with excellent chemical durability that breaks easily. It is considered one of the most primordial materials made by humanity and it seems paradoxical that our knowledge of its structure is far from being complete. Upon closer examination, photosensitive glass and glass-ceramics constitute an intriguing class of materials both from the viewpoints of basic science and industrial applications, certainly due to their longevity as commercial glass products. In his autobiography, Stookey stated that PG could be considered in fact a "smart material" [10] due to its interesting and unique properties.

For photosensitive glass, current patents show a *luminous* future related to better new fiber optics, new dispositive holograms and large TV panels. A deeper understanding and control of photothermal-induced nucleation is also expected. For example, it is possible to cite new fluorescent photosensitive glass and glass-ceramics for data storage recording media and systems. Some new high-density data storage, using commercially available low power lasers and optics, can achieved capacities of more than a million gigabyte (or 1 petabyte) just using a hyper-CD size disk of 120mm in diameter and 1.2mm thick (see: www.storextechnologies.com). It is also possible, using these new fluorescent photosensitive glass and GC to development novel materials dedicated to optical nanolithography (1 - 5nm) [57-59]. For glass-ceramics a *tenacious* future with new compositions and processes for biomedical applications, laser crystallization, new dielectric/conductive GCs (mainly applied to rechargeable batteries) [45], porous materials, new and specific solders, as well as low thermal coefficient and transparent materials for tableware is expected. Another field of both scientific and technological innovations to transform the world is related to health, as pointed by Hench [56]. A search for new or even more potent nucleating agents for GC synthesis is imminent, as well as new ways to avoid residual porosity. Furthermore, something related to tiny, thin and large (or "jumbo") PG as well as new CG materials with new composition-processing-properties investigations are expected over the next two decades.

Certainly, more experiments, modeling and simulation studies on the fundamental properties of these new materials show great promise in a number of applications. GC is well-studied by academia and in terms of published patents it outstrips PG; however, the full comprehension of the structure and properties of these materials is still distant. The increasing interest in published manuscripts as well patents show this trend which reaches four orders of magnitude at present.

7. CONCLUSIONS

For many years researchers in glass and ceramics have been attempting to develop new materials that possess both natures. Innovative ceramics technologies are still transforming the world. In this work, the advances in PG and GC research since 1940's and 1950's has been presented. We also examined two of the most extensively used methods for special glass manufacturing and saw how these practices provided both elevated distinction and productivity for numerous industrial sectors. According to the European Patent Office, more than 6,497 patents have been filed around the world using the terms "*photosensitive* and *glass*" in the title or abstract and 9,738 with the term "*glass* and *ceramics*". More specifically about glass-ceramics, the numbers just continue to grow as do total sales worldwide. Considering the same period, there were 4,219 GC patents on the EPO database. Therefore we can conclude that the real number of GC patents is between half and one fourth of these, considering the general results. According to the Scopus database, since 1940's there have been 1,405 photosensitive glass documents and from 1950's there were 30,819 glass-ceramics-related published, and the majority were manuscripts. These GCs are in fact ceramics that mimic costly stones, such as marble and granite; bioglass, used to replace artificial bones and for dental treatment, as well as vitroceramics derived from blast furnace slags, a major industrial waste.

Patents can be used as indicators of flourishing innovations. Both first GCs and PGs are still in production worldwide. The amount of GC produced patents have been increasing exponentially, but not PG (at least in the last decade), as shown in this work. The key reasons for increasing trends in one but not the other include: *i*) the possible impact of such unusual glass; *ii*) their fast production, the quantity of products; *iii*) their renowned importance in industry. The behavior of PG produced patents in the last ten years could be viewed as just a statistical fluctuation. The next ten years will show if there is a real decrease in PG patents or not.

Comparison of results from papers and patents are useful because it is more plausible that the same filed patents can be reproduced in other languages, a more frequent procedure when comparing with the publication of manuscripts.

Publication rates have improved exponentially since the end of World War II. In general, the most noteworthy countries in terms of photosensitive and glass-ceramics research are the USA, China, and Japan (the second and third places inverting when dealing with PGs), which indicates high levels of advanced and research activities. As expected, most countries in both rankings are industrially developed, but it is surprising that some emerging countries also appeared in the analysis.

The popularity of the photosensitive and glass-ceramics processes is clear from the fact that around 160 universities and research institutes worldwide are studying various aspects of special glass processes. Recent years have been characterized by a rise in (scientific) university research, with University of Central Florida (USA) and RIKEN: The Institute of Physical and Chemical Research of Japan as the main university labs for PG research. It is important to note also that Kyoto University (Japan) and Imperial College of London (UK) have been the most prolific GC institutions in the past six decades. There is no longer any industrial research laboratory near the top 20 of both lists, except for Corning Incorporated, and the Otto-Schott Institute of Materials Research, linked to Friedrich-Schiller-Universität Jena, that published many works on glass-ceramics in the same period.

The history shows us the many challenges faced and still existing in both PG and GC process development and a considerable amount of fundamental questions remain open. At present, we require a better comprehension of the processes that rule nucleation and crystal growth in a myriad of vitreous materials. In the broad area of glass science, work is still in progress to explain the kinetic and thermodynamic processes from theories. In the field of glass technology, the literature presents new and enhanced photosensitive and glass-ceramics many of which have reached the commercial stage.

The USA boasts the most filed photosensitive and glass-ceramics patents. In particular, the first application of PG and GC by Stanley Donald Stookey and glass companies around the world continue to benefit from his work. From their glorious pasts, in one case starting with an accidental discovery of a serendipitous inventor, to successful commercial products, the impressive range of properties and exciting potential applications of photosensitive glasses and glass-ceramics (this in particular somewhat accidently discovered) indeed ensure a *bright* and *tough future* for optimistic glass researchers and explorers.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

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