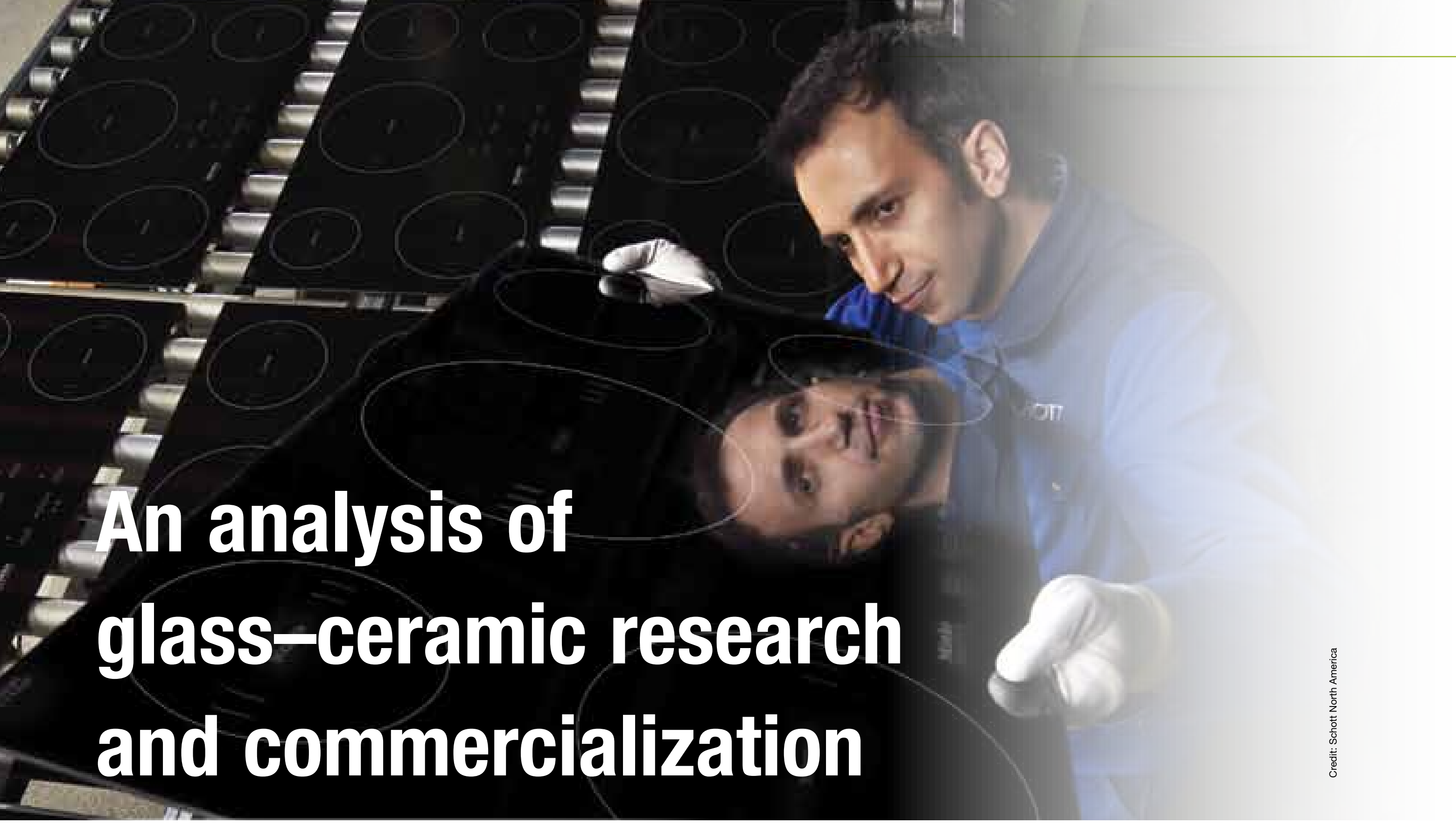
An analysis of glass–ceramic research and commercialization



Credit: Schott North America

Ceran glass-ceramic cooktop by Schott North America.

By Maziar Montazerian, Shiv Prakash Singh, and Edgar Dutra Zanotto

Glass has been an important material since the early stages of civilization. Glass–ceramics are polycrystalline materials obtained by controlled crystallization of certain glasses that contain one or more crystalline phases dispersed in a residual glass matrix. The distinct chemical nature of these phases and their nanostructures or microstructures have led to various unusual combinations of properties and applications in the domestic, space, defense, health, electronics, architecture, chemical, energy, and waste management fields.[1–3]

In 1739, French chemist René-Antoine Ferchault de Réaumur was the first person known to produce partially crystallized glass.[4] Réaumur heat-treated soda–lime–silica glass bottles in a bed of gypsum and sand for several days, and the process turned the glass into a porcelain-like opaque material. Although Réaumur had succeeded in converting glass into a polycrystalline material, unfortunately the new product sagged, deformed, and had low strength because of uncontrolled surface crystallization.[4,5]

The late Stanley Donald Stookey of Corning Glass Works (now Corning Incorporated, Corning, N.Y.) discovered glass–ceramics in 1953.[6–8] Stookey accidentally crystallized Fotoform—a photosensitive lithium silicate glass containing silver nanoparticles dispersed in the glass matrix. From the parent glass Fotoform, Stookey and colleagues at Corning Incorporated, which holds the first patent on glass–ceramics, derived the glass–ceramic Fotoceram. The main crystal phases of this glass-ceramic are lithium disilicate ($Li_2Si_2O_5$) and quartz (SiO_2).

Since then, the glass–ceramics field has matured with fundamental research and development detailing chemical compositions, nucleating agents, heat treatments, microstructures, properties, and potential applications of several materials.[3,5,9–15] A recent article revealed that the term "crystallization" is the top keyword in the history of glass science.[16] However, researchers still are keen to understand further the kinetics of transformation from glass to a polycrystalline material and to study the associated changes in thermal, optical, electrical, magnetic, and mechanical properties. Nonetheless, several commercial glass–ceramic innovations already have been marketed for domestic and high-tech uses, such as transparent and heat-resistant cookware, fireproof doors and windows, artificial teeth, bioactive materials for bone replacement, chemically and mechanically machinable materials, and electronic and optical devices.

Review articles surveyed the properties and existing uses of glass–ceramics and suggested several possible new applications for these materials.[9–17] Here we report on the results of a statistical

Capsule summary

BACKGROUND

Glass–ceramics are polycrystalline materials derived from glass with distinct properties that give them unique applications in domestic, space, defense, health, electronics, architecture, chemical, energy, and waste management.

ANALYSIS

Through a database search of published papers and filed patents, the authors statistically evaluate the evolution of scientific and technological research and development of glass–ceramics during the past 60 years.

KEY POINT

The field of glass–ceramics has grown during the past 60 years and continues to show signs of exponential growth. Analysis of patent applications has identified a few areas of promising growth that may serve as a guide for future commercial endeavors in this field of unique materials.

search evaluating the evolution of scientific and technological research and development of glass–ceramics during the past 60 years. We made an electronic search of published research articles, granted patents, and patent applications since the discovery of glass–ceramics in 1953.

For a more in-depth assessment of recent trends and developments in this field, we manually searched and reviewed 1,000 granted patents and applications filed during the past decade. Here we break down these numbers into main property classes (thermal, mechanical, optical, electrical, etc.) and proposed applications. The overall objective of this short article is to give students, academics, and industrial researchers some insight about the evolution of and perspectives for applications of this class of materials. We hope it also may be a useful source of ideas for new research projects.

Database search

We surveyed the Scopus Elsevier, Free Patents Online (FPO), and Derwent World Patents Index (DWPI) databases for patents and papers published in glass–ceramic science and technology. We searched the Scopus database for scientific publications 1955—2014 using the keywords "sittal", "vitroceramic*", "glass–ceramic*", or "glass ceramic*" in the article title or, in a separate search, in the title, abstract, and keywords. Keywords "glass–ceramic" and "glass ceramic" predominate by a large margin. We then sorted articles by publication year, affiliation, and country.

Additionally, we extracted DWPI records of granted patents by searching for keywords "glass–ceramic*"or "glass ceramic*" in patent titles from 1968—July 2014. We ranked the number of published patents per year as well as the most prolific companies from the records.

Further, we searched the same keywords in patent titles from FPO records from January 2001—December 2013. In this case, we searched granted patents and patent applications and found 1,964 records. After sorting and eliminating sister patents submitted to different offices, we identified 1,000 single granted patents and applications, which we categorized manually according to main property or proposed use of the glass–ceramic.

Published glass–ceramic papers

Searching Scopus for keywords only in article titles provided cleaner results than searching within abstracts, but this limited search failed to capture all glass–ceramic publications. The search yielded 7,040 papers, which, thus, represents only a lower bound. Conversely, expanding the selected keyword search to article titles, abstracts, and keywords yielded 12,806 papers, including several that are only minimally related to glass–ceramics. Therefore, the actual number of glass–ceramic publications lies between these two extremes. Figure 1 shows that, using either search strategy, the number of articles shows some annual fluctuation, although both strategies reveal an exponential increase. Currently, about 500–800 papers on glass–ceramics are published annually.

The 40 most prolific authors (not shown here) include researchers with 40–130 published articles on several aspects of glass–ceramic materials. The first paper on glass–ceramics listed in the Scopus database is authored by W.W. Shaver and S.D. Stookey in 1959, which proposes the name of Pyroceram for the new class of materials.[18] A second paper, authored by G.W. McLellan in the same year, discusses possible applications of glass–ceramics in the automotive industry.[19]

Figure 2 reveals the number of publications authored by researchers with particular affiliations, most of which are universities. Kyoto University in Japan holds

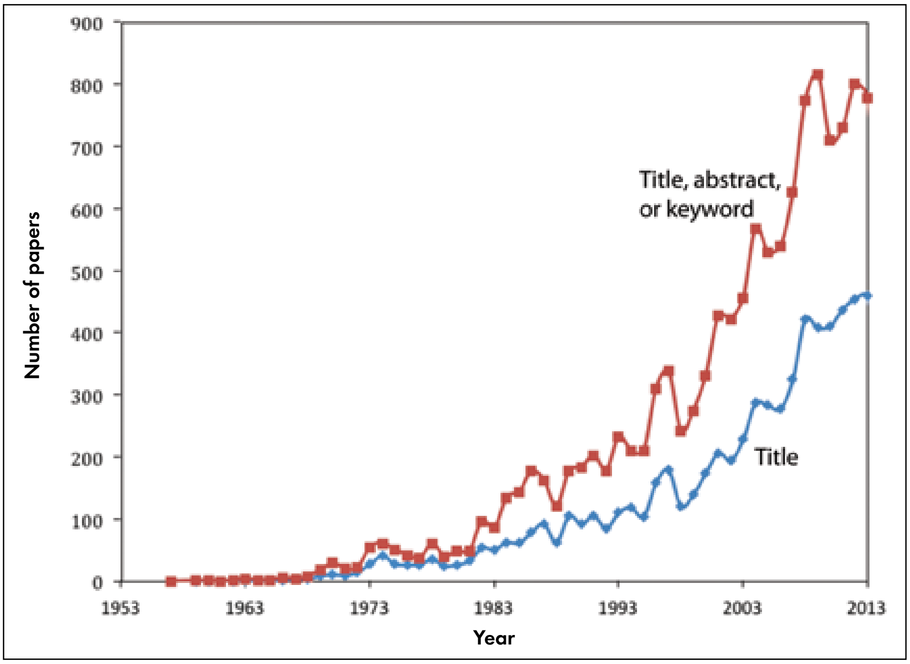


Figure 1. Number of published articles per year extracted from the Scopus database by searching the keywords "sittal", "vitroceramic*", "glass–ceramic*", or "glass ceramic*" in article titles (blue) or in article titles, abstracts, or keywords (red).

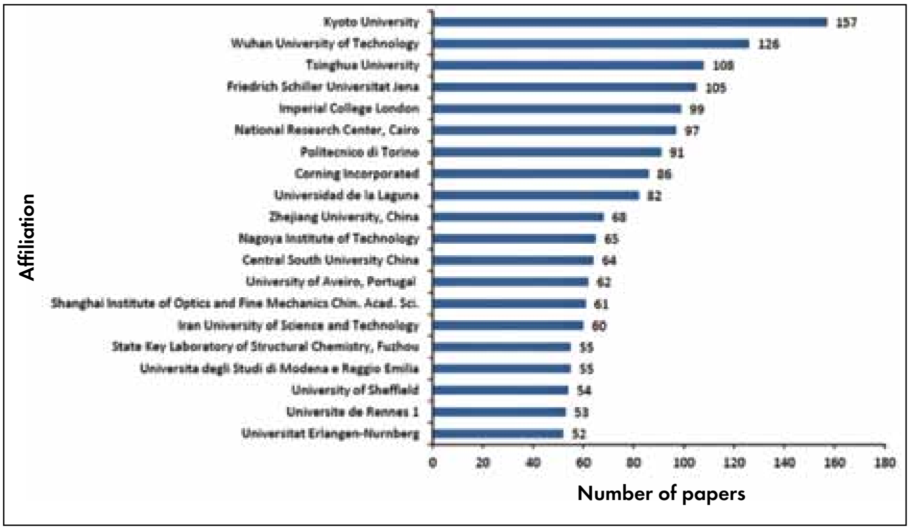


Figure 2. Total glass–ceramic publications in the Scopus database from 1955–July 2014, sorted by affiliation. Counted articles contained keywords "sittal", "vitroceramic*", "glass–ceramic*", or "glass ceramic*" in the article title.

the top position with 157 articles, followed by several Chinese and European universities and two institutions in emerging countries—Iran University of Science and Technology in Tehran, Iran, and the National Research Center in Cairo, Egypt. The only company in this ranking is Corning Incorporated, and it is no surprise that most scientific research in this field is conducted in academia. However, patent rankings tell a different story.

In terms of statistics by country, Chinese investigators lead glass–ceramic research with 1,557 papers, followed by researchers from the U.S. (718 papers), Japan (663 papers), Germany (462 papers), and the United Kingdom (404 papers). Most countries in this ranking are industrially developed. However, it is somewhat surprising that several emerging countries, such as India, Brazil, Egypt, Iran, Turkey, and Romania, also are well ranked.

Patents for glass–ceramics

In addition to publications related to glass–ceramics, analysis of the status of glass–ceramic patents compiles an overall view of technological developments in the field. Similar to searching the publications database, searching the DWPI patent database for keywords "glass–ceramic*"or "glass ceramic*" only in patent titles provided cleaner results, but this limited search failed to capture all glass–ceramic patents. However, this particular search engine provided no other possible search strategies.

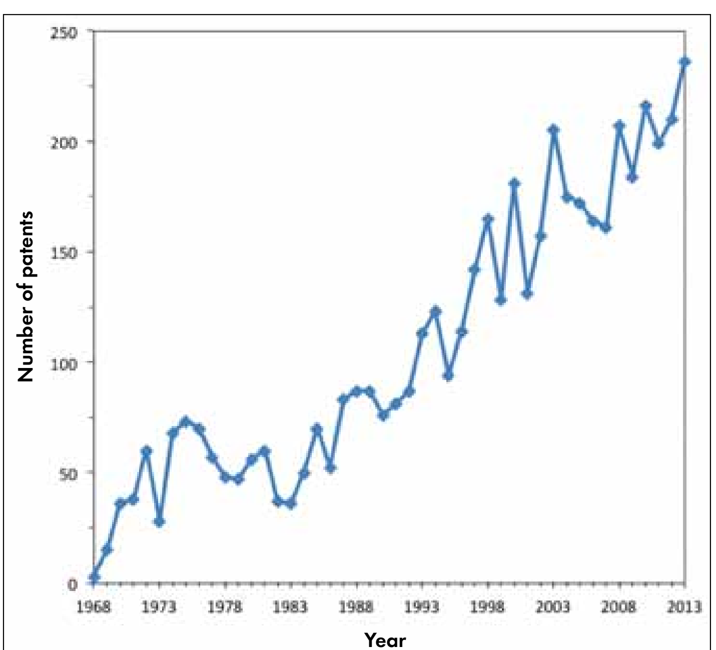


Figure 3. Number of patents granted per year, extracted from the DWPI database by searching for keywords "glass–ceramic*" or "glass ceramic*" in the patent title.

With this restrictive search strategy, the total number of glass–ceramics patents granted—which thus represents a minimum—up to December 2013 is 4,882. Although granted patents have fluctuated somewhat over the years, the number has steadily grown in the past two decades (Figure 3). During 1975–1979 and 2003–2008, total patents declined monotonically, whereas the number increased 1994–1998. Overall, about 220 new patents are granted each year. Our analysis reveals that glass–ceramic technology is growing rapidly and several potential new products are emerging every year.

Further, we searched DWPI for keywords "glass–ceramic*" or "glass ceramic*" in patent titles and found that several companies around the world manufacture glass–ceramic products (Table 1). Several companies hold glass–ceramics patents, but only some are commercializing such products. Likewise, some companies manufacture and sell commercial glass–ceramics, although they are not among the top patenting companies.

Figure 4 shows the 20 most prolific companies from DWPI that were granted glass–ceramic patents in 1968–2014. Schott AG, Corning Incorporated, Kyocera, and Nippon Electric Glass hold the top four positions. All others are Japanese, German, or American companies, with the exception of dental glass–ceramic company Ivoclar Vivadent from Liechtenstein. Some companies, such as Owens–Illinois, were very active during the 1970s—when they filed several patents on glass–ceramics—but then halted their activity in this field. However, most of these companies still engage in R&D and manufacture various types of commercial glass–ceramics.[5,9]

Commercial applications of glass–ceramics

DWPI allows automatic breakdown of granted patents per field, which reveals a wide spectrum of knowledge, spanning from traditional fields, such as chemistry, engineering, and materials science, to unexpected areas, such as polymer science, food science, and environmental fields (Figure 5).

For a more comprehensive view, we manually searched the FPO database, which allows separate searching of granted patents and patent applications, by reading abstracts (and some text) of about 2,000 of the most recently filed and granted patents.

Glass–ceramics with specific properties, such as thermal (e.g., low thermal expansion, insulating, high thermal stability, etc.), electrical, (e.g., high ionic conductivity), or optical (e.g., high transparency, high luminescence efficiency) properties, have attracted considerable attention from industries and technologists in the past decade. This special interest has resulted in more than 550 patents on various glass–ceramics intended for electronic components, wiring board substrates, cooktop panels, insulators, sealants, heat reflector substrates, and more (Table 2). Some patents also have been granted for glass–ceramics with architectural, biological, magnetic, armor, energy, nuclear, and waste immobilization applications and for applications in combined fields, such as electrooptics.

Overall trends in current patent applications—which are more recent than granted patents—are decreased electrical, electronic, and magnetic applications and increased dental, biomedical, optical, energy, chemical, waste management, refractory, and "other" applications for glass–ceramics. These results suggest that those areas are potential thrust fields for advanced technology. The above-listed trend applications are in line with current demands of new products, suggesting prospects for industrial growth in these areas.

Future growth

A great deal already is known about glass–ceramics, but several challenges and opportunities in glass–ceramics research and development remain to be explored for desired properties and new applications of these materials. A few important areas for further exploration follow.

Fundamental and technological studies

• Search for new or more potent nucleating agents for the synthesis of glass–ceramics using data mining techniques, theoretical equations, and mod-

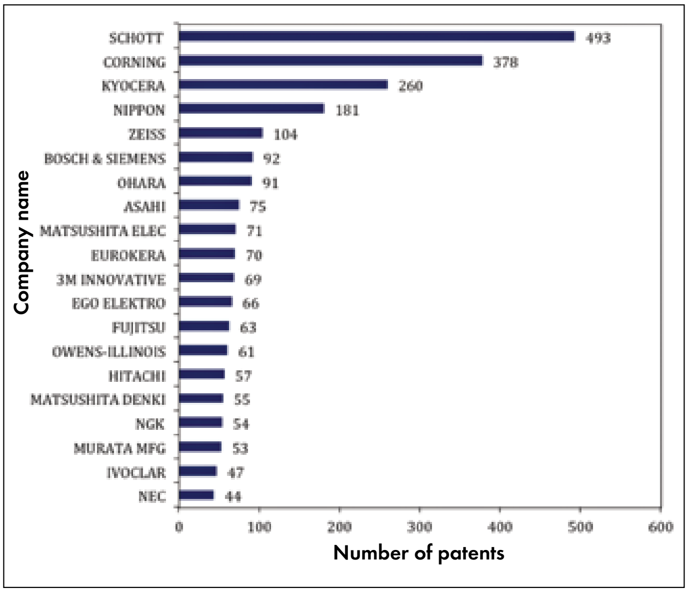


Figure 4. Twenty companies with the most glass–ceramic patents granted 1968–2014, extracted from records in the DWPI database by searching for the keywords "glass–ceramic*" or "glass ceramic*" in the title.

Table 1. Prominent companies and some of their glass–ceramic inventions[5,9–11]

Company	Product	Crystal type	Applications
Schott, Germany	Foturan	Lithium silicate	Photosensitive and etched patterned materials
	Zerodur	β-quartz(*ss*)	Telescope mirrors
	Ceran/Robax	β-quartz(*ss*)	Cookware, cooktops, and oven doors
	Nextrema	Lithium aluminosilicate	Fireproof window and doors
Corning Inc., U.S.	Pyroceram	β-spodumene(*ss*)	Cookware
	Fotoform/Fotoceram	Lithium silicate	Photosensitive and etched patterned materials
	Cercor	β-spodumene(*ss*)	Gas turbines and heat exchangers
	Centura	Barium silicate	Tableware
	Vision	β-quartz(*ss*)	Cookware and cooktops
	9606	Cordierite	Radomes
	MACOR	Mica	Machinable glass–ceramics
	9664	Spinel–enstatite	Magnetic memory disk substrates
	DICOR	Mica	Dental restorations
Nippon Electric Glass, Japan	ML-05	Lithium disilicate	Magnetic memory disk substrates
	Neoparies	β-wollastonite	Architectural glass–ceramics
	Firelite	β-quartz(*ss*)	Architectural fire-resistant windows
	Neoceram N-11	β-spodumene(*ss*)	Cooktops and kitchenware
	Narumi	β-quartz(*ss*)	Low-thermal-expansion glass–ceramics
	Neoceram N-0	β-quartz(*ss*)	Color filter substrates for LCD panels
	Cerabone A-W	Apatite–wollastonite	Bioactive implants
Ivoclar Vivadent AG, Liechtenstein	IPS Series	Leucite/lithium silicate/leucite–apatite	Dental restorations
Eurokera, U.S./France	Keralite	β-quartz(*ss*)	Fire-resistant windows and doors
	Eclair	β-quartz(*ss*)	Transparent architectural glass–ceramics
	Keraglas	β-quartz(*ss*)	Cookware and cooktops
Asahi Glass Co., Japan	Cryston	β-wollastonite	Architectural glass–ceramics
Kyushu Co., Japan	Crys-Cera	Calcium metaphosphate	Dental restorations
Leitz, Wetzlar Co., Germany	Ceravital	Apatite	Bioactive glass–ceramics
Ohara Inc., Japan	LiC-GC	Nasicon(*ss*)	Lithium-conducting glass–ceramics
	TS-10	Lithium disilicate	Magnetic memory disk substrates
Owens-Illinois, U.S.	Cer-Vit	β-spodumene(*ss*)	Cookware and kitchenware
Pentron Ceramic Inc., U.S.	3G OPC	Lithium disilicate	Dental crowns
PPG, U.S.	Hercuvit	β-spodumene(*ss*)	Cookware and domestic-ware
Vitron, Germany	Bioverit series and Vitronit	Mica/mica–apatite/ phosphate type	Biomaterials and machinable glass–ceramics
Sumikin Photon, Japan	Fotovel/ Photoveel	Mica type	Dental and insulator materials
Yata Dental MFG Co., Japan	Casmic	Apatite–magnesium titanate	Bioactive and dental glass–ceramics

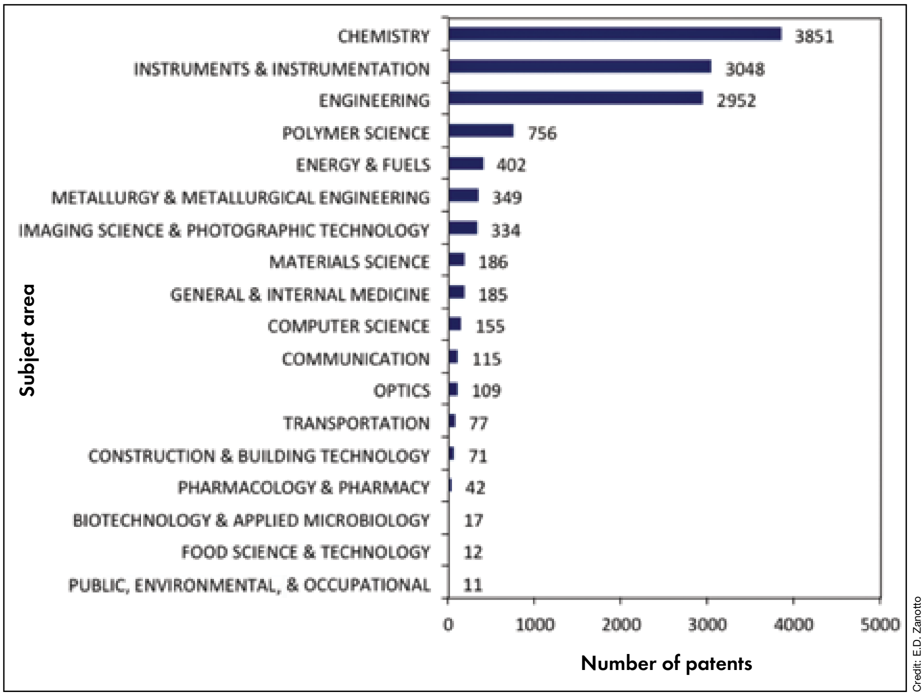


Figure 5. DWPI database breakdown of number of patents granted in various fields by searching keywords "glass–ceramic*" or "glass ceramic*" in patent titles from 1968–2014.

Table 2. Proposed uses for glass–ceramics in patent applications and granted patents in FPO database from January 2001–July 2014

Subject	Number of patents		Proposed uses
	Applications	Granted	
Thermal	141	145	Cookware, cooktops, hot plates, low-thermal-expansion glass–ceramics, sealants, and fireproof windows and doors
Electrical	52	95	Solid electrolytes, lithium-ion-conducting glass–ceramics, and semiconductor substrates
Electronics	24	96	Electronic components, substrates for electronic devices, and plasma display panels
Optical	63	55	Transparent glass–ceramics, luminescent glass–ceramics, colored glass–ceramics, lasers, lens, and mirrors
Dental	38	21	Dental restorations and dental prosthetic devices
Mechanical	29	30	Abrasives, machinable glass–ceramics, and high-strength glass–ceramics
Chemical	25	23	Catalytically active glass–ceramics, photocatalyst supports, corrosion-resistant glass–ceramics, ion-exchanged glass–ceramics, and glues
Architecture	15	13	Decorative substrates and building construction glass–ceramics
Biology	17	10	Bioactive scaffolds, antimicrobial glass–ceramics, antiinflammatory glass–ceramics, and glass–ceramic powders for cosmetics
Energy	10	7	SOFCs, LEDs, and solar cells
Magnetic	6	11	Magnetic head actuators, magnetic information storage media, and substrates for magnetic storage devices
Armor	8	7	Bulletproof and missileproof glass–ceramic components and bulletproof vests

eling rather than empirical trials;

- Development of stronger, chemically resistant chalcogenide glass–ceramics with novel electric and optical properties;
- Development of new or improved crystallization processes, such as microwave heating, biomimetic assemblage of crystals, textured crystallization, laser crystallization, and electron beam crystallization;
- Deeper understanding and control of photothermal-induced nucleation;
- Engineering adequate matrices for development of hierarchical nanostructured glass–ceramics based on variations in size, distribution, and composition of nanoscale crystals;
- Confinement of the glassy phase (nanoglass) within the glass–ceramic matrix by reverse engineering based on novel synthesis processes;
- Fabrication of 2-D and 3-D single crystals within glass matrices via direct laser heating or photothermal-induced crystallization; and
- Understanding the role of the residual glass phase in the properties of glass–ceramics.

Desired material properties

- Highly bioactive glass–ceramics for tissue engineering or drug delivery and for preventive treatments that slow down deterioration and maintain health of tissues;
- Development of harder, stiffer, stronger, and tougher glass-ceramics, for instance, *HV* > 11 GPa, *E* > 150 GPa, four-point-fracture strength > 400 MPa, and K_{IC} >3 MPa·m$^{1/2}$;
- Nanocrystalline glass–ceramics with greater transparency in the ultraviolet, visible, or infrared spectral regions;
- Highly transparent and efficient scintillator glass–ceramics; and
- Glass–ceramics with ionic conductivities >10^{-3} S/cm.

Possible applications

- Glass–ceramics for solar cell applications with improved optical, thermal, electrical, and mechanical properties for use as substrates, matrices, and solar light concentrators;
- Glass–ceramics as self-healing sealant materials with high longevity for fuel cells and electronic devices;
- Glass–ceramics as smart architectural building materials with antifungal and self-cleaning properties; automatic energy generators for building energy consumption, multisensor security, and antifire systems; and materials with dynamic color-changing abilities;
- Glass–ceramic compositions for immobilization of nuclear waste products;
- Glass–ceramics to replace existing materials (polymers) currently used in a variety of electronic products, such as computers, mobile phones, IC chips, and mother boards, to address future environmental problems associated with electronics waste;
- Glass–ceramics for nanopatterning and nanolithography in high-tech materials;
- Glass–ceramics for treatment of cancer using thermal or photosensitive therapies;
- Glass–ceramics for components in space research and similar sophisti-

cated environments;

• Ultrafast crystallizable chalcogenide glass–ceramics for rewritable optical disks and PRAM devices; and

• Glass–ceramics with low thermal conductivity, high electrical conductivity, and adequate Seebeck coefficient developed into thermoelectric power generators, which could produce renewable and sustainable energy in vehicle exhaust manifolds, furnace exhausts, and building windows.

In addition, other unexpected applications will probably emerge that require new combinations of material properties.

Past growth in research expected to continue

Statistics on published scientific articles and patents indicate that glass–ceramic research has grown exponentially during the past 60 years, with no signs of slowing down. The above analysis provides an overall picture in terms of numbers as well as traditional and new areas of applications for the advancement of glass-ceramics. Commercially successful products include those intended for domestic and high-tech applications—such as cookware, chemically or mechanically machinable materials, telescope mirrors, hard-disk substrates, cooktop plates, artificial bones, and dental prostheses—but the breadth of uses proposed in patents is much wider. Analyses of patent applications of glass–ceramics versus number of granted patents in the past decade reveal significant growth in dental, biomedical, waste management, and optical applications.

We hope this report serves as a motivation and guide for students, professors, technologists, and researchers when thinking of future research directions and, most importantly, encourages researchers to dig deeper to find new glass–ceramic compositions, nucleating agents, and heat treatments that lead to novel structures and properties. Such considerations may result in materials with uniquely organized nanostructures or microstructures or with useful combinations of properties that are well suited for new applications.

Acknowledgments

The authors dedicate this article to S.D. Stookey—although he passed away on November 4, 2014, his important discoveries and legacy will remain forever.

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Realizing the potential of glass–ceramics in industry

by John C. Mauro, Corning Incorporated

The accidental discovery of glass–ceramics by S. Donald Stookey in 1953 revolutionized the glass industry by enabling new properties, such as exceptionally high fracture toughness and low thermal expansion coefficient compared with traditional glasses. Although glassy materials are noncrystalline by definition, glass–ceramics are based on controlled nucleation and growth of crystallites within a glassy matrix. Concentration, size, and chemistry of the crystallites can be controlled through careful design of the base glass chemistry and the heat-treatment cycle used for nucleation and crystal growth. These composition and process parameters give new dimensions for optimizing the properties of industrial glass–ceramics.

Table 1 provides an excellent summary of commercialized glass–ceramic products. The success of these products is based on achieving unique combinations of attributes, including appropriate optical, thermal, mechanical, and biological properties, often which cannot be achieved by an "ordinary" noncrystalline glass. For many of these products, such as MACOR and dental glass–ceramics, forming and machining behavior of the glass–ceramic materials are also of critical concern.

Successful design of next-generation industrial glass–ceramic products should be aided by a renewed focus on the fundamental physics and chemistry governing these high-tech materials. Although the thermodynamic and kinetic aspects of crystallization are of the utmost importance for designing industrial materials, there remains insufficient theoretical understanding of these basic processes in glass–ceramics. Future development of new theoretically rigorous modeling capabilities will hopefully enable quantitatively accurate predictions of glass–ceramic microstructures and properties.

A detailed understanding of glass–ceramic materials is an exceptionally challenging problem, especially for many-component oxide systems that are the basis for most industrial glass–ceramic products. However, this presents a unique opportunity to build a solid foundation for realizing the many exciting future applications of glass–ceramics described in the accompanying article and to train the next generation of industrial glass–ceramic scientists.