

Industrial Developments in the Field of Optically Transparent Inorganic Materials: A Survey of Recent Patents

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Abstract: Continuous development of advanced technologies brings about the constant need for new materials with suitable properties to even stricter demands. A special interest has been given to the development of inorganic transparent materials, not only for optical and lighting applications, but also in the electronic, aerospace, civil construction and armour industries. The major motivations are generally weight reduction and enhancement of mechanical properties, also at high temperatures, while simultaneously keeping or, in some cases, increasing the optical transparency. A review of the latest industrial developments in the field of transparent inorganic materials is presented in this paper. Relevant patents disclosed for polycrystalline ceramics, glass-ceramics and composites, in which transparency is claimed as one of the main properties achieved, are described and discussed. Only fully inorganic materials have been considered, therefore, in the case of composite materials, laminate systems including polymeric layers (commonly used in armour applications or security glass) were not included in the review. Moreover, focus is on structural applications, while optical and telecommunication-related materials are not covered in detail.

Keywords: Transparent ceramics, glass-ceramics, composites, inorganic materials, armour, electro-optical devices, polycrystalline alumina, aluminum oxynitride, perovskites, yttrium aluminum garnet, lead-lanthanum-zirconate-titanate, spinels, yttrium oxide, rare earth oxides, beta-quartz glass-ceramic.

INTRODUCTION

In applications where optical transparency is the main requirement, conventional transparent non-crystalline materials (e.g. inorganic glasses and polymers) are usually employed. However, applications that demand superior mechanical and/or thermal properties in addition to optical transparency have driven the development of transparent polycrystalline and single crystalline ceramics as well as glass-ceramics and composites. These materials have been developed with the aim of overcoming the limitations implied from the use of glasses and polymers such as low mechanical strength and fracture toughness, limited thermal resistance and stability, besides poor electrical properties and chemical resistance, in the case of some polymers. Enhancement of the mechanical properties and impact resistance has been a significant aim in the development of numerous types of strong transparent materials, as reviewed recently by Krell *et al.* [1].

Silicate glasses, in particular, have been used in traditional applications requiring transparency, mainly in the packaging, pharmaceutical, lab ware and building industries. Where higher levels of mechanical resistance are required, toughening or coating processes have been commercially developed including thermal and chemical strengthening and toughening of glass, which confer glass higher mechanical resistance, but more importantly, fail-safe mechanisms are activated, and glass sheets dice instead of shattering into sharp pieces. Reinforced glasses have been developed (e.g. wired glass) or the well established laminated glass, for

impact resistance (armour applications in some cases), in which the reinforcing element (wires or polymeric layers in the case of laminated glass) holds the shatters together, even after high impact loads. The level of mechanical resistance of commercially available reinforced glasses is, however, not significantly high, compared to the levels required for structural applications. Laminated glasses, on the other hand, have high weight/area ratio and reasonable resistance to ballistic impact but poor high temperature resistance. These facts explain the interest in improving the mechanical properties of transparent inorganic materials (transparent polycrystalline and monocrystalline ceramics and glass-ceramics) and composites (glass, glass-ceramic or ceramic matrices).

Extensive scientific research has been carried out in developing and characterising new transparent inorganic composite materials, and authors have described the advances in research in this field, mainly in university based laboratories [2-17]. However, no previous review has been published that focussed exclusively on commercially available materials, thus summarizing the advances in the industry, where materials and methods reproducible in large scale have been patented. This fact has been the motivation for the present review, in which a comprehensive analysis of existing patents which claim new compositions or methods of production of transparent inorganic materials and composites with improved mechanical properties has been carried out.

The United States Patent & Trademark Office retains most of the developments in the area, and usually also contains work registered with other organizations (e.g. The UK Patent Office, World Intellectual Property Office (WIPO), European Patent Office (EPO), Japan Patent Office (JPO)). The enormous development in the area limited the

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patents research, however, to the most recent inventions (since the late 1970s), which are discussed in this review.

The review is organized on the basis of the different types of materials considered. An important group is that of transparent polycrystalline ceramics, or “optoceramics”. The main applications that motivated the development of these materials are in the fields of electro-optical devices (display devices, high intensity discharge (HID) lamps, among others), as well as military and aeronautic industries (monitoring windows, radomes and armour). Single crystalline transparent ceramics are also discussed which are more expensive and complex to manufacture in comparison with their polycrystalline counterparts. Another important group of materials that has been industrially extensively developed is that of silicate glass-ceramics. Obtained upon crystallization of glasses, opacification is usually observed, however several patents demonstrate compositions and methods for crystallization of glasses where the optical transparency is retained. As a fourth more recent group of transparent inorganic materials, glass and glass-ceramic matrix composites, developed mainly for structural applications, architecture and instrument windows, will also be discussed in this review.

TRANSPARENT POLYCRYSTALLINE CERAMICS

A number of polycrystalline ceramics are commercially available. Most of the research has been carried out in the fields of electro-optical devices and high intensity discharge (HID) lamps (Fig. 1). Among the materials developed, perovskites, lead-lanthanum-zirconatetitanate (PLZT) ceramics, aluminum oxynitride, polycrystalline alumina and yttria are the most common transparent polycrystalline materials available [18,19]. Not only different compositions, dopants or sintering aids, but also several different fabrication methods, have been disclosed and will be described in the following sections.

Aluminum Oxide

Transparent aluminum oxide ceramics are particularly useful in the construction of sodium vapour high-pressure electric lamp tubes, because of their high chemical resistance to aggressive vapour, in relation to that of traditionally used silica glass or quartz [20, 21]. US Pat. No. 4952539 (Greber and Melas, 1990) [20] describes a method for production of

transparent aluminum oxide, from acid containing aluminum oxide, where, contrary to previous methods reported calcination or contact grinding is not required, and a high purity fine powder is obtained. The method consists in hydrolyzing and peptisizing an aluminum alkoxide with a mixture of water and acid vapours. Another method for production of transparent aluminum oxide is presented in U S Pat. No. 6734128 (Asano *et al.*, 2004) [21]. The method involves the production of polycrystalline alumina, with the addition of MgO and La₂O₃, for controlling the size of alumina crystal grains and wintering temperature, thus extending the life service of the lamp. Previous technologies employed MgO in higher levels, which caused a blacking phenomenon, and acceleration of electrodes oxidation. As proposed by Asano *et al.* [21], sintering is carried out in a reducing atmosphere and excellent grain size uniformity and transparency are obtained.

Aluminum Oxynitride

Aluminum oxynitride ceramics have also been produced for use not only in HID lamps, but also in general applications where transparency is required on top of the ceramic materials properties. This material was first reported by McCauley *et al.* in US Pat. 4241000 (1980) [22]. This first method consisted of obtaining cubic aluminum oxynitride spinel from the reaction sintering of a mixture of fine grained Al₂O₃ and AlN, suitable for applications such as vehicle armour, radar and infrared domes, HID lamp envelopes and sodium vapour envelopes. Raytheon Company (Lexington, US) later disclosed a series of patents for different methods for fabricating transparent aluminum oxynitride. US Pat. No. 4686070 (Maguire *et al.*, 1987) [23] describes the production of aluminum oxynitride by carbonitriding of gamma alumina to form a mixture of alpha alumina and aluminum nitride, which is heated for conversion into gamma-aluminum oxynitride powder. A long grinding period (16 h) is necessary for obtaining fine grain sizes. In US Pat. No. 4720362 (Gentilman *et al.* 1988) [24], aluminum nitride and α -alumina, both of high purity, are mixed and heated, resulting in an agglomerate of γ -aluminum oxynitride powder. A longer grinding time (72 h) is required, but finer particles are obtained. More recently, US Pat. No. 5688730 (FR 93 03718, Bachelard *et al.*, 1997) [25] claimed a process, where alumina of high specific

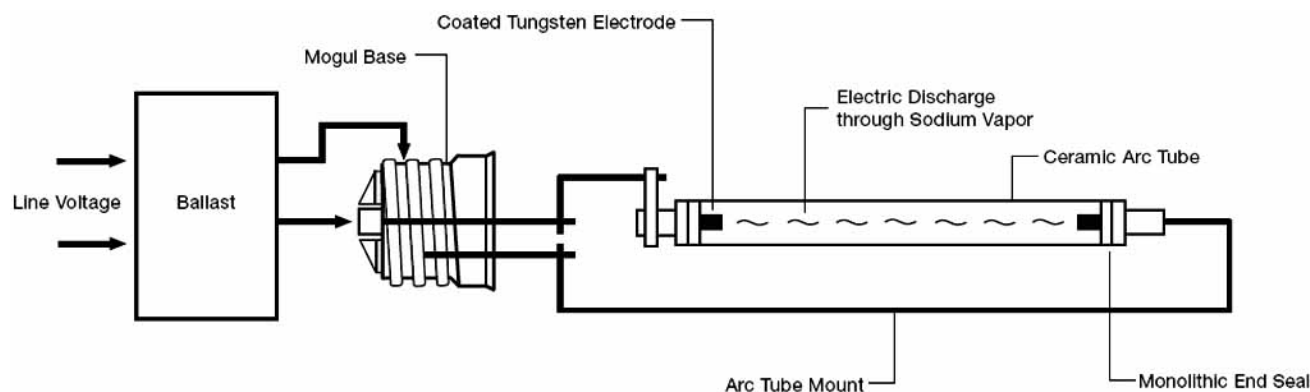


Fig. (1). Schematic diagram of a HID lamp (Osram Sylvania, with permission) [19].

surface is included in the mixture. The material can also be employed in the field of military aeronautics (sighting windows for missiles) besides specialised lighting (transparent housing for vapour lights).

Perovskites

Ceramic materials with perovskite structure have been more widely exploited for manufacture of HID lamps ceramic envelopes, and in some cases for optical applications. US Pat. No. 4019915 (JP48116839; JP49107821; JP49109552; JP49109553) (Myiauchi *et al.*, 1977) [26] describes a method for producing transparent ceramics of the perovskite-type structure and general formula ABO_3 , which does not contain La. Component A includes Pb and Ba or Sr, or both, and component B is Zr or both Zr and Ti. Calcination of a green compact of a mixture of complex oxides consisted of A and B, to form a transparent perovskite ceramic of structure ABO_3 . The material is a ferroelectric ceramic, which exhibits superior electro-optic properties, and is therefore useful for applications in light modulators and for image storage and display devices. Materials previously known in the art are in general scarcely pervious to light.

Another perovskite structure material with general formula ABO_3 is disclosed in US Pat. No. 4197957 (Buhrer, 1980) [27], concurrently with US Pat. 4211758 (Buhrer, 1980) [28], which describes the manufacture of vacuum tight assembly consisted of Al/La/Ce transparent ceramic, and the composition of the ceramic type, respectively. The compounds $LaAlO_3$, $CeAlO_3$, $PrAlO_3$, $NdAlO_3$ can be obtained, which have a cubic perovskite structure or a lower symmetry perovskite structure. Each of them has a melting point approximating that of alumina but a lower dissociation pressure of aluminum and oxygen. Reaction of their component simple oxides in a non-reactive atmosphere can be carried out for production of such materials, however a powder of finer crystalline structure is obtained by the coprecipitation of the A and B ions from a salt mixture and possibly further milling. Direct reaction of an oxide of A ion and an oxide of B ion is also possible.

Some rather complex oxide systems of perovskite structure have also been developed. US Pat. No. 4131479 (Ichinose *et al.*, 1978) [29] provides good optical transmission poreless ceramics with general formula $(Sr_{1-x}Me'_x)(Li_{1/4}Me''_{3/4})O_3$, where Me' is at least one of the elements from the group Ca, Ba and Pb, and Me'' is Nb and/or Ta. Excellent thermal, chemical and optical properties are other characteristics of the material disclosed, which is thus suitable for use in fabrication of, for example, cryston tubes, power tubes, antenna windows, integral circuit substrates, high pressure gas-discharge tubes and rocket nozzles as substitute for conventional ceramics such as Al_2O_3 , MgO , Y_2O_3 , BeO , Gd_2O_3 , $LiAl_5O_8$, CaO , ThO_2 , $MgAl_2O_5$, $(Pb,La)(Ti,Zr)O_3$. These complex perovskite ceramics overcome some of the disadvantages of conventional ceramics concerning dielectric and thermal constants, besides high processing cost.

A translucent composite perovskite ceramic is disclosed in US Pat. 6908872 (GB2376230 A/B; JP2000387730) (Tanaka *et al.*, 2005) [30], for use as optical parts of optical devices, such as lens, prisms or optical path control plates (Fig. 2). The material is represented by the formulas:

$Ba\{(Sn_uZr_{1-u})_xMg_yTa_z\}_vO_w$; $Ba\{(Sn_uZr_{1-u})_xZn_tMg_{1-t}_yNb_z\}_vO_w$. Materials conventionally used are glass, plastics and single crystals of, for instance lithium niobate. These materials have limitations such as low moisture resistance, refractive index and birefringence, in the case of plastics, or limitations in miniaturization and slimming in the case of glasses, while the single crystals also exhibit birefringence, in spite of its high refractive index. The ceramics disclosed, on the other hand, possess a high refractive index, good light transmittance (greater than 20 %) and are paraelectric, i.e. do not show double refraction.



Fig. (2). Transparent ceramic lenses from Murata Manufacturing Co., Ltd. (LUMICERA™) (courtesy of Murata Manufacturing Co., Ltd.) [31].

Very recently, a perovskite compound has been disclosed, in patent WO07049434 A1 (Kintaka, Murata Manufacturing Co., Ltd., 2007). The transparent material has a high refractive index and Abbe's number, thus it is useful for application in gauss-type lens optical systems (e.g. for single-lens reflex camera), for aberration correction [32].

Yttrium Aluminum Garnet (YAG)

Another material that has been exploited for use in HID lamps is transparent polycrystalline yttrium aluminum garnet (YAG). Unlike conventional polycrystalline alumina, YAG ceramics have no birefringence effect at the grain boundaries and, therefore, exhibit higher in-line light transmittance than alumina, which makes YAG suitable for applications such as automotive headlamps and photo-optical lamps. Moreover, YAG has a cubic symmetry and exhibits isotropic thermal expansion, whereas alumina has expansion-anisotropy induced residual stresses at the grain boundaries. The elastic constants are about the same for both materials, and YAG has a high resistance to creep deformation at elevated temperatures. US Pat. No. 6844285 (Wei, 2005) [33] describes a co-doping strategy, with MgO and ZrO_2 , for sintering transparent YAG from commercially available YAG powders. The advantage of the method is the suppression of sintering aids that could induce the formation of secondary grain boundary phases derived from the dopants, or promote the formation of atomic defects, mainly oxygen vacancies and interstitials, which would affect the discoloration behaviour, and therefore the quality and durability of

the lamp. Similar co-dopants had been previously used for processing of polycrystalline alumina.

A system comprising one or a mixture of aluminium, yttrium or silicon oxides, yttrium-silicon or aluminium-silicon composite oxide, or compounds having a garnet structure is disclosed in patent WO06106745A1 (Suzuki and Ikada, 2006) [34]. The ceramic is obtained by liquid phase synthesis and shows high space filling ratio and excellent light transmittance.

PLZT Ceramics

Transparent PLZT ceramics have also been developed mainly for use in electro-optical devices such as optical modulation devices that use the Pockels effect, optical shutters and switchers that use the Kerr effect or electro-optical scattering effect and image memory devices which utilize the memory, surface electrostriction and photochromic or optical ferroelectric effect.

High transparency is the key property for such application, hence complete removal of porosity is essential. In US Pat. No. 5032304 (Toyota, 1991) [35], a method for producing transparent, high density green PLZT ceramic bodies is disclosed. Conventional processes used previously offered difficulty for removal of pores. The method disclosed in ref. 33 allows for obtaining high density and at least 65 % light transmittance, in only 2 h processing time, thus representing an economically favourable route. The technique consists in sintering a green compact of lead, lanthanum, zirconium and titanium in vacuum and then fabricating the sintered product into a sheet of less than 1.5 mm thickness, which is embedded in a heat resistant vessel, and then subjected to HIP processing. Moreover, the present method results in finer grained structures than the ones previously obtained by conventional methods such as uniaxial pressing and HIP. US Pat. 5139689 (JP242630, Kitoh *et al.*, 1992) [36] discloses a method for the production of a transparent PLZT ceramic with composition $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-0.25x}\text{O}_3$. Sintering of the PLZT ceramic is carried out from cheap raw materials (Pb, La, Zr and Ti oxides or compounds that can be converted into them), different to coprecipitation and alkoxide methods that require expensive raw materials. The method is thus a dry method (calcination), with Sm_2O_3 and Bi_2O_3 as auxiliary agents. The technique offers good reproducibility by forming it into a moulded product that is subjected to normal-pressure calcination in an oxygen gas and Pb vapour atmosphere. The resultant material exhibits high light transmittance.

US Pat. 4057324, JA49105695 (Kawashima *et al.*, 1977) [37] relates to an electro-optical system that includes a hot-pressed transparent ferroelectric ceramic element consisting of a solid solution in the ternary system lead magnesium niobate-lead titanate-lead zirconate. The invention can be utilized in electro-optical systems, in which single crystalline materials were previously used from the belief that satisfactory polycrystalline materials could not be produced free from deleterious surface effects, and with sufficient transparency to provide electro-optical effects. Prior methods included the addition of an excess PbO for obtaining high transparency, which caused solidification of ZrO_2 and Al_2O_3 powder spacer surrounding the hot-pressed ceramic, spoiling

the Al_2O_3 die. The use of a smaller amount of PbO vapour is thus proposed for calcining a mixture of the oxides, in appropriate proportion, followed by grinding and hot-pressing.

Spinel

Spinel structure ceramics have also been exploited for manufacturing transparent ceramic bodies, and a few innovative methods are available. These materials offer high hardness and strength, besides being transparent, thus finding potential application in high temperature resistant (monitoring) windows, encapsulation for ionized alkali vapour lamps and other applications where transparency, in combination with high heat resistance, mechanical strength and good thermal shock resistance is required. Traditional processing of spinel involves high cost and difficulty for the production of complex shapes and large sizes. The transparency is also often affected during processing, leading to light scattering caused by the presence of defects and inclusions [38].

US Pat. No. 3974249 (Roy and Stermole, 1976) [39] provides a method for producing transparent ceramic bodies containing at least 98 % in weight of magnesia-alumina spinel. The process offers a relatively low cost as a hot-pressing operation is not necessary. Cold-pressing of a pre-calcined mixture of MgO and Al_2O_3 with an addition of lithium fluoride is carried out. Complete spinel formation is achieved only during sintering of the pre-calcined powder. The precise role of lithium fluoride in the mixture is not described but the high transparency obtained is associated to the substantial spinel forming reaction that occurs during the sintering operation.

Villalobos *et al.* (WO06104540A2) [38] disclosed a method for sintering magnesium aluminate spinel (90 wt. %). In order to avoid the presence of defects and inclusions resultant from the inhomogeneous distribution of the sintering aid, the method proposes that such sintering aid is added as a coating to the starting spinel particles. The ceramic shows low scattering and absorption losses (less than 0.2/cm), and can be used in the area of transparent ceramic windows and domes, consumer electronics, lighting, transparent ceramics, electronics, refractory, structural ceramics and intermetallics.

Yttrium Oxide and Related Rare Earth Oxides

Transparent yttrium oxide has been used for applications where high durability and optical transparency are required, both in the visible and infrared optical bands, and under elevated temperatures. Examples are metal vapour lamps, optical windows and military systems. Two methods are available for producing transparent yttrium oxide. The first one, in U S Pat. No. 4761390 (Hartnett *et al.*, 1988) [40], consists of pressing the powder with a binder in a teflon-coated aluminium die. A three steps firing is used, the first one for burning out the binder and the consecutive ones for further densification. Further annealing is required to induce transparency by restoring the oxygen in the bodies. The Y_2O_3 material obtained exhibits high thermal conductivity and thermal shock resistance than those of Y_2O_3 bodies that contain dopant additives. The other method described in US Pat. No. 5004712 (Borglum, 1991) [41] requires no use of

dopants besides suppressing the need for an annealing step for restoring the oxygen stoichiometry. A suitable O_2 partial pressure is provided around the sample maintaining stoichiometry, thus resulting in higher transparency.

Transparent yttria gadolinia ceramics have been developed for specific application as computerized tomography (CT) detectors, as well as detectors of other radiations, such as x-ray, gamma and nuclear radiation. The materials must be efficient converters of x-ray or gamma radiation into optical radiation. US Pats. Nos. 4473513 and 4518545 (Cusano *et al.* 1984 and 1985, respectively) [42, 43] describe a method for producing high density transparent rare-earth doped yttria-gadolinia ceramic scintillators by cold-pressing a multicomponent powder. Substitution of transparent promoters/densifying agents such as ThO_2 , ZrO_2 , HfO_2 , and Ta_2O_5 by CaO and SrO and the addition of rare earth elements such as Eu, Nd, Yb, Dy, Tb and Pr were found to restore the light output when a maximum scintillating effect is desired.

An alternative ceramic scintillator material is disclosed in US Pats. Nos. 6246744 and 6358441 (Duclos and Srivastava, 2001 and 2002, respectively) [44, 45]. The material is sintered from a polycrystalline ceramic (phosphor), that has a cubic garnet host and praseodymium as an activator. The cubic structure of the host provides a reduced light scattering, in comparison to that of polycrystalline materials with hexagonal structure. In addition to high transparency, the cubic garnet has low afterglow and short primary decay, thus can be integrated into fast response x-ray detector systems.

Transparent Ceramic Microspheres or Particles

The previous sections covered the development of several types of transparent ceramics and methods for obtaining the material and to process it into a solid transparent body. However there is an interest in obtaining transparent materials in the form of microspheres or in some cases particulates. The materials of this type that have been patented are mostly directed to use in retroreflective pavements, but are also suitable in other applications, e.g. as abrasive particles, blasting media, to be used as reinforcements in composites or to be formed or sintered into solid transparent bodies.

Glass microspheres in the system soda-lime-silicate have been traditionally used for such applications. Although they have acceptable durability, these amorphous microspheres exhibit refractive index of only about 1.5, which limits their retroreflective brightness. Higher index glass microspheres of improved durability have been developed, but a higher degree of durability is still desirable. Silica-zirconia microspheres obtained by the sol-gel process have been developed, which have, however, smaller diameter than that required for pavement markings. A diameter between 150 and 1000 μm is generally required, to ensure that the light-gathering portion of the material will not be obscured by road dirt. In addition to the size, the resistances to scratching, chipping, cracking and fracture are also important [46].

The fabrication of ZrO_2 and SiO_2/ZrO_2 microspheres has been disclosed in US Pat. 4772511 (Wood *et al.*, 1988) [46]. The material offers a combination of retroreflectiveness, brightness and durability as a result of its high density (close

to the theoretical), and consequently fewer internal imperfections and inclusions, besides its relatively high hardness (>400 Knoop), toughness (due to its grainy structure), crush resistance (between 1200 and 1600 MPa), compared to that of glass microspheres (between 350 and 525 MPa). It also shows sphericity and retroreflectiveness as great or greater than that of glass beads or microspheres traditionally used. The microspheres are produced via a sol-gel process with a thermal extractive gelling process instead of a dehydrative gelation process. Microspheres with an average diameter greater than 125 μm are obtained, with a refractive index between 1.4 and 2.6, adjustable depending on the application [46]. Methods for producing a pavement containing these microspheres have also been developed [47]. The microspheres produced can also be used in other applications such as peening materials, high temperature ball bearings, fillers and reinforcing agents in glasses, refractory materials, ceramics, metal matrix composites and polymers [46].

Recently, a method for obtaining transparent $Al_2O_3-ZrO_2$ abrasive particles has been patented (Rosenflanz, US20050137076A1, WO05066096A1, 2005) [48]. The method involves flame forming a melt from the compounds containing the desired oxides (preferably Al_2O_3 and ZrO_2), cooling the melt into the transparent fused crystalline ceramic, which is then crushed into the desired particle size and shape. Cooling can be carried out in a cooling medium (e.g. water), or between rollers (roll-chilling). The faster the cooling, the smaller the crystallite size, although excessively fast cooling may lead to an amorphous material. The melt can also be shaped before cooling, for the production of spheres. Other oxides can be included in the composition, depending on the starting materials. The spheres or particles produced can be used as abrasive particles, reflective and optical components, and as grinding and sand blasting media [48].

US Pat. No. 4349456 (Sowman, Minnesota Mining and Manufacturing Company, 1982) [49] relates to a process for making shaped and fired, spherical, non-vitreous ceramic microcapsules of polycrystalline ceramic metal oxide, preferably titania. A sol-gel technique is used involving the steps of liquid-liquid extraction, drying and firing. Moreover, the invention relates to composites containing said microspheres. More specifically, the material disclosed consists in unicellular, hollow particles, whose interior can be evacuated or filled with a gas, liquid or solid, made of homogeneous, non-vitreous ceramic polycrystalline or amorphous metal oxide convertible to polycrystalline ceramic upon direct firing at elevated temperature. The size and thickness of the microcapsules can be controlled by the concentration of the precursor sol. The pressure within the capsules can also be varied and depends on the gas contained and its pressure at processing temperature. TiO_2 , Fe_2O_3 , SnO_2 , ZnO , or further WO_3 , ThO_2 , Y_2O_3 , HfO_2 , Nb_2O_5 , UO_2 , BeO , In_2O_3 , Sb_2O_3 , SnO_2 , as single metal oxides or mixtures of them can be produced by slight modifications of the technique. The microcapsules can also be filled in with liquids and solids, by evacuation and pressurization of a liquid or molten solid, equilibrating a gaseous sublimation product, or deposition from a salt or compound. Additionally, metathesis or precipitation reactions can also be used for filling the porous

microcapsules. The ceramic micro-capsules are suitable for refractory applications, or where their chemical stability and inertness as well as properties such as mechanical strength, imperviousness and micro-scopic dimensions and shape lend themselves to advantage. Some area of utility of the disclosed material is as fillers or reinforcements for structural plastic, elastomeric, metallic, or ceramic composites. The evacuated microspheres can be also used in composites for thermal insulation applications. The filled ones, on the other hand, can be used to store and transport the filler gas, e.g. inert, radioactive, reactive or other gas, releasing it if and when desirable by mechanical fracture of the microcapsules [49].

Other Non-Oxide Ceramics

US Pat. 4772304 (JP60220389, Nakae *et al.*, 1988) [50] describes the development of a transparent BN-type ceramic material comprising B, N and Si, which finds applications as window or lenses material for high temperature use, or as mask support material for X-ray lithography. The invention consists in the continuation of a previous Japanese patent application (Laid-Open No. 58145665) on a transparent brown coloured Si_3N_4 -BN-type material. The ceramic presented exhibits amorphous (non-crystalline) structure, shows no crystallization even after heat treatment and is produced by chemical vapour deposition.

Table 1 summarizes the patents on transparent polycrystalline ceramics described in this section.

TRANSPARENT SINGLE-CRYSTALLINE CERAMICS

Single crystalline transparent ceramics have been widely used in applications such as lasers and mechanical watches. In comparison to glasses and polycrystalline ceramics, their manufacture is more expensive and limited to simpler shapes and their mechanical strength and hardness can be usually inferior to those of their quasi-isotropic polycrystalline counterparts. On the other hand, the single crystalline materials show very high transparency as well as very good chemical and thermal stability [1]. Single crystalline oxides have been industrially produced by growth processes from the melt. A number of patents have been disclosed in the last decades, as described below.

An apparatus comprising an endless seed crystal gripping and pulling means was disclosed by Mermelstein (US Pat. No. 3607112 1971) [51]. The device offers alternative modes of operation, i.e. with a moving carriage that pulls the growing and stationary belts, or by keeping the carriage stationary and moving the belts instead. This allows the apparatus to be used to grow crystal shapes of relatively short or indefinite lengths of sapphire or other single-crystalline materials. Another growing method has been described in US Pat. No. 3898051 (Schmid, 1975) [52]. According to the method, single crystals are grown by extracting heat from a central portion of the bottom of the crucible containing the melt. The seed crystal is positioned over the gas heat exchanger, engaged at the bottom of the crucible and the crucible walls are kept at a temperature above the melting point of the material until it has all been solidified. The process is suitable for growing sapphire

single crystals, with or without a seed crystal, besides other materials, including metal single crystals.

The edge-defined film-fed growth technique (EFG) is commercially well established, i.e. several manufacturers use the process for fabricating monocrystalline materials from different compounds. It has been initially disclosed in US Pat. No. 3591348 (La Belle, Tyco Laboratories, 1971) [53]. Elongated bodies of predetermined constant cross-section can be grown by using this technique. A shaping member is provided, whose edge configuration defines the desired cross-sectional shape of the body to be grown (edge-defined). A liquid film of the material is established on the surface, and the body is then continuously grown from the liquid film, while material is simultaneously fed to replenish the film by capillary action. Crystalline bodies of α -alumina, barium titanate, lithium niobate and yttrium aluminum garnet can be grown with the method described in the form of both round tubes or flat ribbons [54].

An improvement of the process was later disclosed by Mlavsky and Pandiscio (US Pat. No. 3868228 1975) [55]. Tubes produced by the EFG process are suitable for use as envelopes for HID lamps. The improvement method described allows for the production of tubes terminating in integral end walls or flanges. Moreover, tubes of varying cross section or series of connected tubular sections, i.e. connected by transition sections of smaller inner diameter, can also be obtained.

More recently, pyrolytic graphite tubes have been developed to substitute the previously employed transition metals (e.g. tungsten) tubes for the crucible support system (Berkman *et al.*, US Pat. No. 42512061981) [56]. The invented support system is more stable than the ones previously employed at the high temperatures to which the crucible is exposed of approximately 2000°C. This allows for higher quality single crystals to be grown due to lower coefficient of thermal expansion and higher thermal stability of pyrolytic graphite in comparison to the metals, which soften upon exposure to high temperatures.

Sapphire filaments, tubes and sheets have been produced by the EFG process by Saint Gobain Crystals (Fig. 3) [57]. The sheets are used as strike face material in laminated composite armour [58] and aerospace windows, while filaments and tubes are produced for use in laser and plasma systems [57].

Chen and Abraham have developed an improved growth process for transparent single crystals of alkaline earth oxides by the submerged arc method (US Pat. No. 3829391, 1974) [59]. In the process, an appropriate powder is placed in a water-cooled container within which three electrodes are submerged. The powder is then fused by the heat generated from the arc, forming a cavity within the volume immediately surrounding the arc, while a layer of fused material rests below the cavity on a stratum of sintered material. This causes crystallization of the border of the fused material in contact with the sintered stratum. The amount of crystals formed is determined by the radius of the cavity, which is in turn determined by the power generated at the arc. The process is attractive for growing high purity crystals due to the absence of any contaminating material

Table 1. Summary of Patents on Transparent Polycrystalline Ceramics

Material	Assignee	Inventor	Year	Patent No.
Alumina: HID lamps	Vereinigte Aluminium-Werke Aktiengesellschaft (Germany)	Greber <i>et al.</i>	1990	US4952539 (20)
	NGK Insulators, Ltd. (Japan)	Asano	2004	US20046734128 PCT/JP0202114 (21)
Aluminum oxynitride	The United States of America as represented by the Secretary of the Army (United States)	McCauley & Corbin	1980	US4241000 (22)
	Raytheon Company (United States)	Maguire <i>et al.</i>	1987	US4686070 (23)
	Raytheon Company (United States)	Gentilman <i>et al.</i>	1988	US4720362 (24)
	Elf Atochem S.A. (France)	Bachelard <i>et al.</i>	1997	US5688730 FR9303718 (25)
Perovskites: HID lamps and electro-optical devices	Hitachi Ltd. (Japan)	Myiauchi <i>et al.</i>	1977	US4019915 JP48116839; JP49107821; JP49109552; JP49109553 (26)
	GTE Laboratories Incorporated (United States)	Buhrer	1980	US4197957 (27) and 4211758 (28)
	Tokyo Shibaura Electric Co., Ltd. (Japan)	Ichinose <i>et al.</i>	1978	US4131479 (29)
	Murata Manufacturing Co., Ltd. (Japan)	Tanaka <i>et al.</i>	2005	US20056908872 GB2376230 A/B JP387730 (30)
		Kintaka	2007	WO07049434A1 JP310217 (32)
YAG: HID lamps	Osram Sylvania Inc. (United States)	Wei	2005	US20056844285 (33)
	Fuji Photo Film Co., Ltd. (Japan)	Suzuki & Ikada	2006	WO06106745 A1 (33)
PLZT: electro-optical devices	Sumitomo Special Metal Co. Ltd. (Japan)	Toyota	1991	US5032304 (35)
	Ube Industries, Ltd. (Japan)	Kitoh <i>et al.</i>	1992	US5139689 JP42630 (36)
	Matsushita Electric Industrial Co., Ltd. (Japan)	Kawashima <i>et al.</i>	1977	US4057324 JA 49-105695 (37)
Spinel: HID lamps high T monitoring windows	Coors Porcelain Company (United States)	Roy & Stermole	1976	US3974249 (39)
	The government of the United States of America as represented by the secretary of the Navy	Villalobos <i>et al.</i>	2006	WO06104540A2 (38)

(Table 1) Contd....

Material	Assignee	Inventor	Year	Patent No.
Yttrium oxide: HID lamps, optical windows and military systems.	Raytheon Company (United States)	Hartnett & Gentilman	1988	US4761390 (40)
	Raytheon Company (United States)	Borglum	1991	US5004712 (41)
Ytria-gadolinia: ceramic scintillators	General Electric Company (United States)	Cusano <i>et al.</i>	1984	US4473513 (42)
			1985	US4518545 (43)
Cubic garnets: ceramic scintillators		Duclos & Srivastava	2001	US20016246744 (44)
			2002	US20026358441 (45)
Microsphere and particles: retroreflective pavements, abrasive or reinforcing particles	Minnesota Mining and Manufacturing Company (United States)	Wood and Lange	1988	US4772511 (46)
		Sowman	1982	US4349456 (49)
	3M Innovative Properties Company (United States)	Rosenflanz <i>et al.</i>	2005	WO05066096 A1 (48)
Non-oxide ceramics: BN for X-ray lithography	Reasearch Development Corporation of Japan Japan Metals & Chemicals Co., Ltd. The Furukawa Electric Co., Ltd. Hirai Toshio	Nakae <i>et al.</i>	1988	US4772304 JP60220389 (50)

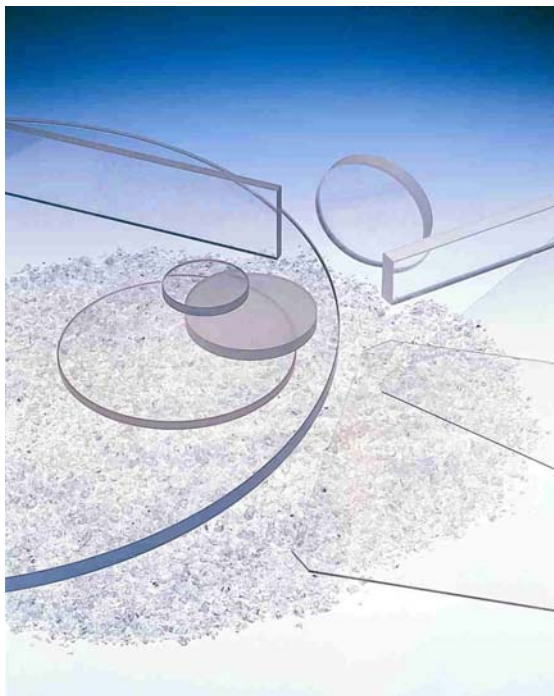


Fig. (3). Sapphire products grown by the EFG™ process (courtesy of Saint Gobain Crystals) [57].

(e.g. from a crucible). Reduction of the power supplied to the arc after the initial formation of a boule from a starting powder (in the usual manner), prevents the formation of microscopic bubbles within the individual crystal, resulting in higher light transmittance material for applications such as lasers and photovoltaic devices.

A thin transparent sapphire film has been produced by a distinctive plasma process, according to Japanese patent JP 1100270, granted to Wasaburo *et al.* (1989) [60]. The patent claims the production of sapphire films with improved light transmittance by formation in plasma state with controlled pressure of a gaseous mixture of oxygen and argon, impressed grid voltage and film forming velocity.

More recently, monocrystalline ceramic fibres have been produced according to the method disclosed in US Pat. 5200370 (Lennox *et al.*, 1993) [61]. The process comprises the conversion of polycrystalline ceramic fibres into substantially single-crystalline fibres. The polycrystalline fibers are initially coated with a refractory material by the CVD technique. The coated fibers are then heated up to a temperature above the melting point of the ceramic, but below the melting point of the refractory coating, and subsequently cooled at a sufficiently fast rate to crystallize the ceramic in a monocrystalline form. Tows containing as many as 200 filaments or more can be produced, with filaments of about 8-20 μm of diameter each, while previous

methods allow for growing fibers of a minimal diameter of 50 μm (e.g. EFG and LFZ methods), besides allowing for greater production speed and thus lower costs.

Another method was disclosed in the Japanese patent JP 7165485 (Sukotsuto *et al.*, 1995) [62], also published as US Pat. No. 5549746 (Scott *et al.*, 1996) [63], for conversion of polycrystalline bodies into single crystals. The method comprises heating the polycrystalline body to form a joint with the seed crystal, the joint then being heated to reduce grain growth inhibitors, and finally the joined structure is further heated above the minimum temperature required for crystallite growth, though not high enough to melt the material and distort the original shape of the body. The process has been used to convert polycrystalline alumina into a single crystal (sapphire). A similar process for bulk conversion of alumina to sapphire was disclosed by Scott *et al.*, in US Pat. 5451553 (1995) [64]. The process involves heating the material to a temperature above one half of the melting point of the ceramic, therefore melting is not involved. The method disclosed involves thermal treatment of polycrystalline bodies containing less than 100 wppm of magnesia, directed to use in high pressure sodium arc discharge lamps.

Table 2 summarizes the patents on transparent single-crystalline ceramics described in this section.

TRANSPARENT GLASS-CERAMICS

Glass-ceramic materials, in particular silicate based glass-ceramics, have been largely exploited for a diversity of applications. A wide range of compositions is commercially available [65]. Accordingly to the purpose of the present review, only patents that claim optical transparency as a main property of the material were considered. Those can, in principle, be separated into two groups: (a) transparent glass-ceramics for preferably structural applications, mainly silicates, that are usually produced in the form of sheets, and (b) transparent glass ceramics for optical and telecommunication applications (e.g. oxyfluorides, germanates *e.t.c.*) where mechanical properties are not of primary interest. The first group is the main subject of the present review, while the second group will be discussed only briefly. Materials from group (b), often in the form of fibers, have been proposed for applications ranging from infrared optics to optical amplifiers to 3D-displays.

The most commonly industrially exploited transparent glass-ceramic comprises beta-quartz solid solution as the

Table 2. Summary of Patents on Transparent Single-Crystalline Ceramics

Method	Materials	Assignee	Inventor	Year	Patent No.
Continuous crystal growth from seed	Gripping and pulling apparatus	Tyco Laboratories, Inc. (United States)	Mermelstein	1971	US3607112 (51)
	Heat extraction	Crystal Systems, Inc. (United States)	Schmid	1975	US3898051 (52)
	Edge-defined film-fed growth (EFG)	Tyco Laboratories (United States)	La Belle	1971	US3591348 (53)
	Improved shaping apparatus for EFG		Mlavsky & Pandiscio	1975	US3868228 (55)
	Pryolytic graphite tubes for crucible support for EFG apparatus	RCA Corporation (United States)	Berkman <i>et al.</i>	1981	US4251206 (56)
Crystal growth	Submerged arc method	United States Atomic Energy Commission (United States)	Chen & Abraham	1974	US382939 (59)
	Plasma film formation	Ricoh KK	Wasaburo <i>et al.</i>	1989	JP1100270 (60)
Solid conversion from poly to single-crystalline	Fibre tow conversion	Fiber Materials, Inc. (United States)	Lennox <i>et al.</i>	1993	US5200370 (61)
	Bulk conversion of solid bodies	General Electric Company (United States)	Sukotsuto <i>et al.</i>	1995	JP 7165485 (62)
			Scott <i>et al.</i>	1996	US5549746 (63)
			Scott <i>et al.</i>	1995	US5451553 (64)

main crystalline phase, however a few other compositions comprising different crystalline phases have also been disclosed. The materials described will thus be divided into “ β -quartz” and “other crystalline phases” glass-ceramics, in the following sections.

Glass-Ceramic Materials with β -Quartz Solid Solution as the Main Crystalline Phase

Nowadays, transparent glass ceramics with β -quartz solid solution as the main crystalline phase have found their main application in cooktops (often in colored versions). Although many other applications exist, they do not reach the former in terms of market size yet. Development of those materials is driven by three major companies: French Eurokera (a joint venture between Corning and Saint Gobain companies), German Schott and Japanese Nippon Electric Glass. Fig. 4 shows one of the glass ceramic products commercially available, produced by Schott AG, Schott Robax® [66]. The material has zero coefficient of thermal expansion, and is used in applications such as stove windows and fireplaces.

Most of the glass-ceramics based on beta-quartz solid solution are formed in the system $\text{LiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$. Significant interest in this system arose already in the 1950s, when the first glass ceramics (lithium disilicate) were invented by D. Stookey, of Corning, Inc. This was because near-zero or even negative thermal expansion was expected (and subsequently achieved) for such compositions, while the use of TiO_2 and ZrO_2 as nucleating agents enabled very high nucleating rates and, thus, nanometer-scale crystallites. In the following decades, high thermal shock resistance coupled with optical transparency determined the great potential for this material. Compositional ranges and resulting properties have seen some considerable evolution, most visible in ongoing publications of patent applications and grants.

Nowadays, there are approximately around 100 patent applications and granted patents published comprising transparent β -quartz glass ceramics as the principal claim. In most cases, those patents address at least one of five main issues: (a) nucleating agents, nucleation strategies; (b) coloration; (c) clarity and ultra-high transparency; (d) environmentally friendly compositions [67, 68]; and (e)

melting, fining [69, 70] and forming. The study of nucleation strategies is usually motivated by the wish to shorten crystallization cycles, to derive smaller or more homogeneously distributed crystallites and, in conjunction with (c), decrease optical haze. While early inventions were mainly based on nucleation by ZrO_2 [71], and later TiO_2 and combinations of the two, the use of Ta_2O_5 [72], SnO_2 [67] and metallic particles (e.g. silicon [73]) has been claimed.

Regarding coloration methods, mainly consumer applications have motivated the invention of a wide range of coloring strategies, from burgundy [74] to blue [75] to black, to give just a few examples to black. On the other hand, while conventional (transparent) glass-ceramics often exhibit yellowish tints which are related to the presence of iron and titania, products with neutral color and very high transparency in the visible range have been highly desired, and many strategies have been disclosed to achieve this. In recent years, mainly forthcoming national and international regulations have driven inventions of products that do not contain toxic components (e.g. oxides of arsenic as fining agent). Finally, as precursor glasses usually require very high melting temperatures and are generally difficult to form (e.g. into sheet), there has always been potential for new inventions in melting and forming. An example is floatable compositions, i.e. compositions that are compatible with the process that is commonly used for mass-production of architectural glasses [76].

In 1977, Rittler (Corning Glass Works) was granted a patent for the compositional range of 3-4 wt% Li_2O , 20-30 wt% Al_2O_3 , 50-65 wt% SiO_2 , 3-7 wt% TiO_2 , 1.5-3 wt% ZrO_2 and 2-5 wt% P_2O_5 (US Pat. No. 4009042) [77]. It is claimed that the material shows low coefficient of thermal expansion, good mechanical strength, excellent chemical durability and resistance to detergent attack and staining, at least 40 % transmittance of infrared radiation at a wavelength of 3.5 μm in 4 mm thick samples, and therefore is suitable for use in cooking devices. Glass-ceramics in a similar compositional range, but free of P_2O_5 , were disclosed in US Pat. 4018612 (Corning Glass Works, Chyung, 1977) [78], also for application in cooking devices. The glass-ceramic product was reported to be highly-crystalline and transparent, exhibiting infrared transmittance superior to 75 % at a

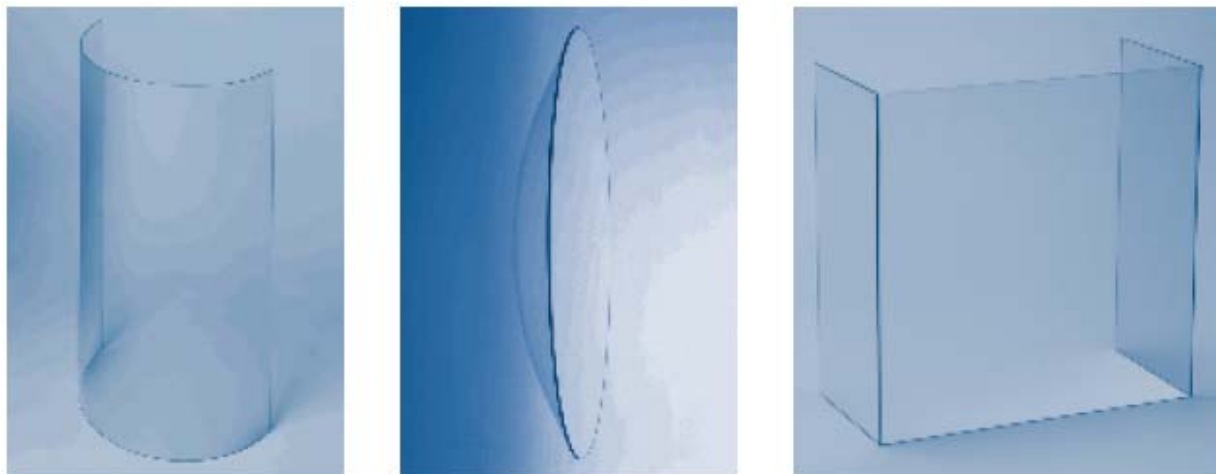


Fig. (4). Schott Robax® transparent glass-ceramic (courtesy Schott Glass, Germany) [66].

wavelength of 2.5 microns (3 mm thick samples). Improved uniformity of crystal size is provided by the use of a two step crystallization process.

A decoloration method is disclosed in US Pat. No. 4093468 (Corning Glass Works, Boitel and Renault, 1978) [79], comprising incorporation of neodymium oxide into a β -quartz glass-ceramic composition containing TiO_2 and possibly Fe_2O_3 . The yellowish tint that results from interactions between TiO_2 and iron oxide can be compensated by blue-to-violet absorption of neodymium ions, resulting in grayish but sensibly transparent products.

Another glass ceramic material is available, disclosed in US Pat. 4455160 (Corning Glass Works Rittler, 1984) [80], especially for use as window in coal or wood-burning stoves. The precursor glass was subjected to an ion exchange process to increase its mechanical performance. This process causes the formation of β -quartz crystals on the surface, which prevents crazing to occur due to volume reduction. Other uses are proposed for the invention, mainly in cooking appliances and as cookware, in patent number US Pat. No. 4,461839 [81], where colourless transparency is not necessary, and therefore a broader range of composition for the precursor glass can be employed.

A transparent glass-ceramic material with similar composition, in the range of 3-6 wt% Li_2O -17-23 wt% Al_2O_3 -1-4 wt% B_2O_3 -60-70 wt% SiO_2 -3-6 wt% TiO_2 and/or ZrO_2 , was disclosed in US Pat. No. 4940674 (Corning Incorporated, Beall *et al.*, 1990) [82]. Cr_2O_3 and a glass modifying oxide (0-3 % K_2O and 0-2.5 % SrO and/or BaO) are added and a beta-quartz solid solution is obtained as the main crystalline phase. Moderate strength (close to 68.95 MPa) and no haze are observed, and the material is therefore directed to use in cooking ware. US Pat. No. 4341543 (Corning Glass Works, Andrus *et al.*, 1982) [83], comprises the production of another glass-ceramic material with composition in the range (weight %): 2.5-6 Li_2O , 0.5-5 RO (ZnO , BaO , CaO , MgO and SrO), 16-25 Al_2O_3 , 64-73 SiO_2 , and 3.0-6 Ro_2 (0-6 TiO_2 and 0-3.5 ZrO_2). Exposure of a glass of such composition to vapours of SO_2 , and subsequent in situ crystallization treatment is carried out, creating beta-quartz solid solution as essentially the sole crystalline phase. Glass-ceramics with low coefficient of thermal expansion can be produced, as well as a surface crystallized glass, with about the same coefficient of thermal expansion as the untreated glass, and a partially body-crystallized glass with coefficient of thermal expansion between those of the glass-ceramic and the surface crystallized glass. The final products are transparent and strengthening is observed in the crystallized glasses in comparison to the untreated glass, as a result of the mechanisms of differential density and expansion phenomena.

US Pat. 5070045 (Comte, 1991) [84] describes another glass composition for use as cooktop plates, cookware, microwave bottom tray, woodstove window and fire protection door or window. The material has the required viscosity for rolling of plates and sheets, the ability to be crystallised into a transparent glass-ceramic, with adjustable visible and infrared transmission, very low or zero coefficient of thermal expansion and minimal distortion during the thermal crystallization treatment.

Jenaer Glaswerk Schott & Gen. (Germany) developed a glass-ceramic composition with low coefficient of thermal expansion (US Pat. 3977886, Muller, 1976) [85]. The material is suitable for general applications where such property is required. Its composition comprises the oxides Li_2O , MgO , ZnO , P_2O_5 and Al_2O_3 , and the crystalline phase present is beta-quartz solid solution, e.g. the properties are expected to be very similar to those of the Corning materials described above.

Significant work has also been carried out by some Japanese companies. Nippon Sheet Glass Co. Ltd. disclosed the production of a transparent glass-ceramic article with an external and internal portion, in US Pat. 4755488 (Nagashima, 1988) [86]. The internal portion consists of 55 to 75 wt% SiO_2 , 15 to 30 wt% Al_2O_3 , 2 to 6 wt%, Li_2O , 1 to 5 wt% Na_2O , and 2 to 9 wt% $\text{TiO}_2+\text{ZrO}_2+\text{P}_2\text{O}_5$, while the exterior portion has the same composition but with part of the Na^+ ions exchanged with K^+ . This is achieved by immersion in a molten bath of KNO_3 , which provides enhanced mechanical properties. The crystalline phase is a beta-quartz solid solution and high hardness and mechanical strength are obtained. The material is therefore suitable for applications such as cover for watches and the like, as a substitute for the materials usually employed, such as plastics, glasses or sapphire. The two formers lack in hardness, while the later has high production costs as discussed above.

Central Glass Company, also from Japan, described a beta-quartz and beta-eucryptite glass-ceramic in US Pat. 5017519 [87], JP1111442 and GB2234504A [88] (Morimoto, 1991). The material consists essentially of (wt %) 63-69 SiO_2 , 18-22 Al_2O_3 , 3-5 Li_2O , 1-3 MgO , 4-6 ZrO_2 , 0-2 ZnO , 0-2 P_2O_5 , 0-2 Na_2O , 0-2 BaO , 0.3-1 As_2O_3 , is colourless and highly transparent, and exhibits a coefficient of thermal expansion close to zero. It is thus suitable for use in heat resistant monitoring windows, aircraft windshields and electronic device substrates where high transparency and no traces of colours are allowed.

Another Japanese invention comprising a low coefficient of thermal expansion transparent glass-ceramic is disclosed in US Pat. 5591682 (JP6244683; JP6285920; Goto 1997) [89], by the Company Kabushiki Kaisya Ohara. The material is obtained by restricting the ratio in weight of P_2O_5 to SiO_2 , and adding Li_2O , MgO , ZnO , CaO and BaO in a base glass in the system $\text{SiO}_2\text{-P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$, containing TiO_2 and ZrO_2 as nucleating agents. Beta-quartz solid solution is the main crystalline phase, and excellent optical homogeneity is obtained. Applications in optical parts, materials for large type telescope mirror blanks, ring laser gyroscopes, reference gauges for precision measurement and various electronic materials are considered for the disclosed glass-ceramic.

A novel glass-ceramic material and articles made there from were disclosed by Eurokera in patent WO 2005/058766 A1 (Comte and Peschiera, 2005) [90]. This novel glass-ceramic has a composition in the range (wt.%): 65 to 70 SiO_2 ; 18 to 23 Al_2O_3 ; > 4 to 5 Li_2O ; 0 to < 1 MgO ; 1 to 3 ZnO ; 0 to 2 BaO ; 1.8 to 4 TiO_2 ; 1 to 2.5 ZrO_2 ; 0.4 to 1 K_2O and/or Na_2O . With the disclosed composition and method of manufacture, a β -spodumene solid solution crystalline structure can be formed at high temperature, without undergoing cracking or mechanical strength reduction, even though no

special precaution is taken with regard to the water content of the precursor glass, as reported for prior similar materials. A β -quartz can also be obtained according to the invention. Another property of the material is its high transmission in the wavelength region between about 400 and 2500 nm. The glass-ceramic can be used in the production of transparent articles such as cooktops, cooking utensils, stove windows and the like.

Finally, a few β -quartz glass-ceramics have been developed for other applications than cookware. A glass-ceramic material was disclosed by Corning Glass Works (USA) (Chyung *et al.*, US Pat. No. 4707458, 1987) [91], where the bodies exhibit properties especially suitable for use in ring laser gyros, such as small coefficient of thermal expansion, particularly less than $0.66 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$, besides optical transparency. The composition comprises (wt%): 64-67 SiO_2 ; 21-24 Al_2O_3 ; 2.6-3.7 Li_2O ; 0.8-1.5 MgO ; 0.7-4.2 ZnO ; 2.0-3.25 TiO_2 ; 1.25-2.5 ZrO_2 ; 4-5.25 $\text{TiO}_2+\text{ZrO}_2$.

Another invention by Kabushiki Kaishya Ohara (Itoh and Goto, US Pat. No. 6001445 1999) [92] discloses a β -quartz glass-ceramic with composition (wt%): 48-65 SiO_2 ; 0-15 P_2O_5 ; 15-30 Al_2O_3 ; 2-10 Li_2O ; 0-8 MgO ; 0-8 ZnO ; 0-8 CaO ; 0-7 BaO ; 0-7 TiO_2 ; 0-7 ZrO_2 -0.2 $\text{As}_2\text{O}_3+\text{Sb}_2\text{O}_3$. The material shows low electric resistivity ($10^8 \text{ } \Omega\cdot\text{cm}$) and therefore is suitable for use as a transparent simulation disk used in place of a magnetic disk for measuring the flying height of a magnetic head.

Glass-ceramics with β -quartz solid solution as the predominant crystalline phase are further disclosed in US Pat. Nos. 5336643 [93] and 5591682 [89] (Goto, Kabu-shiki Kaisha Ohara, 1994 and 1997, respectively), which also show low coefficient of thermal expansion (-10 to $+10 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$).

Table 3 summarizes the patents on glass-ceramic of beta-quartz solid solution crystalline phase described above.

Table 3. Summary of Patents on Beta-Quartz Solid Solution Glass-Ceramics

Assignee	Inventor	Year	Patent No.
Corning Glass Works (United States)	Rittler	1977	US4009042 (77)
	Chyung	1977	US4018612 (78)
	Boitel & Renault	1978	US4093468 (79)
	Rittler	1984	US4455160 (80) US4461839 (81)
	Beall <i>et al.</i>	1990	US4940674 (82)
	Andrus <i>et al.</i>	1982	US4341543 (83)
	Comte	1991	US5070045 (84)
	Chyung <i>et al.</i>	1987	US4707458 (91)
Jenae Glaswerk Schott & Gen. (Germany)	Muller	1976	US3977886 (85)
Nippon Sheet glass Co. Ltd. (Japan)	Nagashima	1988	US4755488 (86)
Central Glass Company (Japan)	Morimoto & Sugiura	1991	US5017519 (87)
			JP1111442
			GB2234 504 A (88)
Kabushiki Kaishya Ohara	Goto	1997	US5591682 JP6244683 JP6285920 (89)
	Itoh & Goto	1999	US6001445 (92)
Eurokera	Comte & Peschiera	2005	WO05058766A1 (90)

Glass-Ceramic Materials with Different Types of Crystalline Phases

Although there is a large number of transparent glass ceramics available that are not based on β -quartz, their commercial role is still rather limited. Furthermore, the number of different products decreases substantially when only silicate-based, non-fluoridic (or, more generally, halide-free) compositions are considered. On the other hand, such silicate-based materials may be the only ones that are suitable for mass-production and in large sizes, e.g. sheets. Here, today's intellectual property is essentially built on transparent spinel, mullite and lithium disilicate glass-ceramics. Besides that, a few patents are available for willemite, gahnite and gehlenite -based materials. Since those materials usually do not exhibit low coefficients of thermal expansion, the proposed applications are very different from those of β -quartz glass-ceramics, e.g. optical, photovoltaic and display technology.

Transparent mullite glass-ceramics were disclosed by Beall *et al.* in US Pat. Nos. 4396720; 4519828 and 4526873 [94, 95, 96]. Besides optical transparency, this type of material exhibits broad absorption in the visible region of the radiation spectrum and strong fluorescence in the infrared region when doped with Cr^{3+} and therefore this glass-ceramic was proposed for use in tunable and infrared lasers and in solar collectors for silicon-based photovoltaic cells. Cr_2O_3 -doped gahnite glass-ceramics, on the other hand, have been proposed for similar applications, or also as matrix-material for LCD [96].

Transparent spinel glass-ceramics have been reported in US Pats. Nos. 3681102 (Beall, 1972) [97] and 5968857 (Pinckney, 1999) [98]. The former discloses a zinc-spinel glass-ceramic, capable of retaining transparency at 1200°C for short times, and at 1000 °C for extended service, thus suitable to use in high temperature lamp applications [97]. The later reports the production of spinel glass-ceramics for use as substrates for high temperature polysilicon thin films, solar cells and flat panel displays, but which are also useful as substrates in silicon-based electric, electronic and optoelectronic devices. Besides its optical properties, the advantage of this type of glass ceramics is their high strain point and coefficient of thermal expansion, which is compatible to that of polycrystalline silicon, and therefore allows for its fabrication without undergoing distortion, warping, or loosing transparency [98].

Applications where thermal stability, i.e. resistance to thermal deformation, and low coefficient of thermal expansion are a main requisite in addition to transparency, such as in telescope mirror blanks, optical lenses, high temperature reinforcing fibres or electronic substrates, have motivated the development of a few glass-ceramic compositions. The advantage of using glass-ceramics for such application is that, besides having the required properties, the part can be moulded from the glass melt, which is further submitted to crystallization. A method of making glass-ceramic telescope mirror blanks is disclosed in US Pat. No. 4285728 (Babcock *et al.*, Owen-Illinois, Inc., 1981) [99]. The method consists of a thermal in-situ crystallization heat-treatment from the glass melt, and lithium-containing crystals are the

predominant crystalline phase. The material shows a coefficient of thermal expansion of -10 to $+10 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$.

A transparent glass-ceramic armour base on lithium disilicate has also been developed, commercially known as TransarmTM, by GEC Alstom, disclosed in UK Patent, GB 2 284 655 B (Budd and Darrant, 1995) [100]. The preferred composition for the glass-ceramic armour is: 71.8 wt.% SiO_2 , 11 wt.% Li_2O , 8 wt.% ZrO_2 , 2 wt.% P_2O_5 , 4.5 wt.% Al_2O_3 , 0.5 wt.% ZnO , 2.2 wt.% K_2O . The manufacturing of the armour is carried out by heat-treating a base lithium disilicate glass to a transparent glass-ceramic, which is then submitted to a molten-salt to promote ion exchange at the surface of the material, resulting in an even higher level of resistance. The glass-ceramic armour can be attached to a transparent back-up plate (e.g. polycarbonate), so as to avoid the shards of the ballistically impacted sheet to spread, but also to absorb part of the impacting energy through ductility. This innovative armour material can be used in visors, vehicle observation and helicopter windscreens [100]. The process, however, involves relatively high nucleation temperatures (580 to 650 °C) and long crystallization times (between 12 and 102 h). Hence an optimized process was disclosed, in patent GB 2 379 659 A (Darrant and Thompson, 2003) [101]. In this process, a lower nucleation temperature is used (550 °C), for similar time (100 h), though rendering enhanced level of transparency, at a reasonable process cost. A process for producing the material in the form of sheet is also disclosed in that patent.

BPO_4 crystals are described as a tetragonal polymorph of β -cristobalite, with the advantageous absence of its inherent alpha to beta transformation. US Pat. No. 4576920 (MacDowell, Corning Glass Works, 1986) [102] describes the production of glass-ceramic articles containing BPO_4 crystals as the main crystalline phase, however its coefficient of thermal expansion is higher (45 to $65 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$) than that of previously described materials.

Oxyfluoride glass-ceramics doped with rare earth ions have been developed by many groups, e.g. Sumita Optical Glass Inc., to be used as wavelength up-conversion materials. Materials are disclosed in US Pat. Nos. 5420080 [103] and 5545595 [104] (Wang *et al.*, 1995, 1996). These materials show high conversion efficiency and allow for low-cost production, in comparison to the production of fluoride single crystals. Additionally, those oxyfluoride glass-ceramics also show higher mechanical and chemical stability than oxyfluoride glass fibres that were previously known in the art.

Corning Incorporated has also disclosed several inventions of glass-ceramics that contain fluoride crystals. US Pat. No. 5537505 (Borrelli *et al.*, 1996) [105] describes the preparation of glass-ceramics containing cubic fluoride crystals. The materials have high optical clarity and are doped with praseodymium, which imparts a high fluorescence lifetime. An oxyfluoride glass-ceramic material containing rare earth ions is disclosed in US Pat. No. 5955388 (Dejneka, 1999) [106]. The composition allows for a high content of the rare earth dopants, which partition into the crystallites, imparting high optical transparency and long fluorescence lifetime to the material. Two other patents have been disclosed for rare earth containing fluoride glass-cera-

mics. US Pat. No. 6281151 (Tick, 2001) [107] discloses a glass matrix containing lanthanum fluoride crystals and contains no silica, while US Pat. 6385384 (Wei, 2002) [108] discloses a silica-based perform containing rare earth fluorides embedded by solution chemistry, both directed to use in optical fibres or amplifiers.

There is a number of other, more exotic transparent glass ceramics disclosed that have not yet found major applications, but are often designed as host materials for rare earth ions (RE-ions) and, consequently, dedicated to optical and electrooptical applications. For example, forsterite-based materials were reported in US Pat. Nos. 6300262 [109] and 6632757 [110] (Beall, 2001 and 2003). Other related materials include: α and β -willemite (Pinckney, U S Pat. No. 6303527 2001) [111], orthosilicate (Beall and Pinckney, US Pat. 6531420 2003) [112] and aluminogallate (Beall *et al.* US Pat. No. 6632758 and Pinckney, US Pat. 6936555 2005) [113 114] as well as a tantalum-containing glass-ceramic comprising a mixture of pyrochlore and perovskite as crystalline phase (Aitken *et al.*, US Pat. 6268303 2001) [115]. Crystals of the apatite group may also show optical activity. Synthetic crystals of this group are potentially useful as low dielectric loss ceramic dielectrics and as luminescent materials. US Pat. 5952253 (Dejneka and Pinckney, 1999) [116] discloses the development of glass matrix materials containing apatite crystals, thus offering ease of forming in addition to the crystal's optical properties.

A few transparent ceramic materials have been described in the present review for application as scintillators for computer tomography imaging (see section 2.7). US Pat. No. 6498828 (Jiang, General Electric Company 2002) [117] discloses the invention of a scintillator for computer tomography that consists of a glass-ceramic with a high content of a cerium-doped lutetium orthosilicate crystalline phase. Sufficient light output and reduced decay time are the advantageous properties of the material.

Table 4 summarizes the patents on glass-ceramics which are not based on beta-quartz solid solution crystalline phase.

TRANSPARENT INORGANIC COMPOSITES

This section focuses on transparent composite materials with inorganic matrix, where particles or fibres are introduced to enhance the mechanical properties and structural integrity of the materials without compromising optical transparency. Conventional systems based on glass plates and polymer (PVC) layers, e.g. in security or laminate glass, are however not covered in this section.

A system was disclosed by Mathers and Frey (1992 - US Pat. No. 5096862) [118], comprising a combination of Al_2O_3 and AlMgON powders. The composition ranges from 45 to 65 vol% alumina and 55 to 35 vol% of aluminum magnesium oxynitride, and is directed to applications such as in the dental area, ferrules, gas tight envelopes, radomes and windows for infrared sensors, armour, chemical processing equipment and high temperature ovens, or other applications where structural properties of ceramics coupled with transparency are required.

Another system is described by Hirai and Komatsu (1995 - US Pat. No. 5424008) [119], which comprises a compo-

site system to be used as a coating for glass and polymers that are susceptible to generation of static electricity on their surface, causing rubbish and dust to be attached. The invention is especially useful for coating of glasses used in photocopying devices, screen and other displaying devices. It is formed by a transparent oxide, such as zirconia or silica, with homogeneously distributed conductive substances, which promote neutralization of electric charging. The coating material also exhibits excellent resistance to scuffing, adhesion to the substrate and durability.

A novel laminate glass system was patented in 2006 by Onishi *et al.* (2006 - EP 1 674 433 A1) [120]. The system comprises an interlayer film, with functional ultra-fine particles of diameter smaller than 0.2 μm dispersed, which is laminated between two transparent glass plates. The functional particles are made of high infrared radiation reflective substances, so as to produce a composite that is highly efficient in solar radiant energy shielding and shows high radio wave transmission.

Patent WO 2005/080280 A1 (Chung *et al.*, 2005) [121] discloses the invention of a multi-functional glass composite that has emitting functions of negative ions and far-infrared rays. The article is produced by adding a small amount of monazite to the conventional soda-calcium basic glass, which has the function of emitting the negative ions. The invention is directed to the building construction industry as an alternative solution to the excess of positive ions in the atmosphere caused by pollution, e.g. by exhaust gases, factory fumes, contaminated discharge water, chemical fertilizers and the volatile organic compounds contained in building materials. The unbalanced positive ion containing atmosphere is known to be one of the causes of "sick house syndrome", "chemical allergy", or "new apartment sickness" (headaches, dizziness and vomiting). The emission of negative ions by the new glass should therefore neutralize the excessive amount of positive ions in the ambient, decreasing the occurrence of such diseases.

Besides the described systems for use as windows and screens, a composite material is disclosed in patent WO 2005/119861 A2 (Riman and Ballato, 2005) [122] for use in long-haul communications. In this system, solid solution metal halide nanoparticles are dispersed in a transparent host matrix for the manufacture of optical fibres. The nanoparticles have a dispersed particle size between 1 and 100 nm, and are doped with rare earth active ions. The smaller size distribution in comparison to that of previous art materials (greater than 100 nm) ensures that minimal light scattering is obtained. The method also allows for a higher dopant content (up to 60 mol%), which provides a broader absorption and luminescence, hence a higher level of transmission and reception of infrared signals.

Considerable research is being carried out at universities in Japan [8-10, 12, 13], Germany [5, 11, 15, 17] and United Kingdom [4, 6] on 'optomechanical composites', where ceramic fibres are incorporated in glass or glass-ceramic matrices of high transparency. The authors are aware, however, of only two related patented systems, by Yano *et*

Table 4. Summary of Patents on Glass-Ceramics with Different Crystalline Phases

Assignee	Crystalline phase	Inventor	Year	Patent No.
Corning Glass Works (United States)	Mullite	Beall <i>et al.</i>	1983	US4396720 (94)
			1985	US4519828 (95)
			1985	US4526873 (96)
	Spinel	Pinckney	1999	US5968857 (98)
	BPO ₄ (tetragonal polymorph of β -crystalalite)	MacDowell	1986	US4576920 (102)
		Andrus <i>et al.</i>	1982	US4341543 (83)
		Comte	1991	US5070045 (84)
		Chyung <i>et al.</i>	1987	US4707458 (91)
Corning Incorporated (United States)	Rare earth containing oxyfluoride	Borrelli <i>et al.</i>	1996	US5537505 (105)
		Dejneka	1999	US5955388 (106)
		Tick	2001	US20016281151 (107)
		Wei	2002	US20026385384 (108)
	Forsterite	Beall	2001	US20016300262 (109)
			2003	US20036632757 (110)
	α and β -willemite	Pinckney	2001	US20016303527 (111)
	Orthosilicate	Beall & Pinckney	2003	US20036531420 (112)
	Aluminogallate	Beall <i>et al.</i>	2005	US20056632758 (113)
		Pinckney	2005	US20056936555 (114)
	Tantalum-containing pyrochlore and perovskite	Aitken <i>et al.</i>	2001	US20016268303 (115)
Apatite	Dejneka & Pinckney	1999	US5952253 (116)	
Owen-Illinois, Inc.	Lithium containing	Babcock <i>et al.</i>	1981	US4285728 (99)
GEC Alsthom	Lithium disilicate glass-ceramic armor	Budd & Darrant	1995	GB2284655 B (100)
		Darrant & Thompson	2003	GB2379659 A (101)
Sumita Optical Glass Inc.	Oxyfluoride doped with rare-earth ions	Wang <i>et al.</i>	1995	US5420080 (103)
			1996	US5545595 (104)
General Electric Company	Cerium-doped lutetium orthosilicate	Jiang	2002	US20026798828 (117)

al. (WO05012404A1 and WO06082803A1, 2006) [123, 124]. The former describes the development of a composite material by impregnation of a fibre assembly, the fibres having an average diameter of 4 to 200 nm. Light transmittance was of 60 % or over in the wavelength range 400 - 700 nm. The patent [124] discloses the invention of a highly transparent composite system comprising nanometric cellulose fibres also impregnated with the matrix material so that not only the moisture absorption attributed to the cellulose fibre is enhanced, but also the transparency.

Table 5 summarizes the transparent inorganic composite systems described above. It is worthwhile pointing out that conventional laminated (security) glass systems and wired glass have not been covered in this review, as they do not fit within the category of composites that are of interest for advanced technology other than the building industry, as explained previously.

CURRENT & FUTURE DEVELOPMENTS

Relevant patents on transparent inorganic materials, dating from the last 3 decades, have been reviewed. The development of transparent polycrystalline ceramics, single-crystal ceramics, glass-ceramics and composites has been driven by the necessity to overcome the limitations offered by the conventional materials (e.g. glasses, polymers), which are usually employed in applications where superior mechanical and thermal properties, in addition to the optical transparency, are necessary.

For glass-ceramic materials, a wide range of compositions and processes are commercially available. They found major applications in consumer products. Polycrystalline ceramics have also been developed, mostly in order to provide a wider range of suitable materials for electro-optical devices and HID materials. Only a few patents are available for transparent composites, considering the cases where particles or fibres are used as reinforcements, opposed to laminated and wired glass (i.e. security glass). Transparent composites are alternative materials that can offer functional properties, such as heat-resistance, or resistance to the attaching of dust, or simply enhanced mechanical strength, fracture toughness and thermal resistance.

Future developments should partly be focusing on transparent composite materials, considering the diversity of ceramic and glass-ceramic materials that are already commercially available. This could lead to the development of transparent, tough (failsafe) materials, or 'optomechanical composites'. Higher levels of strength could be obtained, which could yield a breakthrough for structural applications, mainly for the aerospace and armour industries, where there is an increasing need for lighter and stronger transparent materials.

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Table 5. Summary of Patents on Transparent Inorganic Composite Systems

Material	Assignee	Inventor	Year	Patent No.
Al ₂ O ₃ and AlMgON: dental area, ferrules, gas tight envelopes, radomes and windows for infrared sensors, armour, chemical processing equipment and high temperature ovens	Minnesota Mining and Manufacturing Company	Mathers & Frey	1992	US5096862 (118)
ZrO ₂ or SiO ₂ with conductive particles composite coating for neutralization of electric charging on photocopying devices, screen and other displaying devices	Catalysts & Chemical Industries Co., Ltd. (Japan)	Hirai <i>et al.</i>	1995	US5424008 (119)
Solar radiant energy shielding and high radio wave transmission laminated glass system	Central Glass Company, Ltd.	Onishi <i>et al.</i>	2006	EP1674433A1 (120)
Rare earth doped metal halide particles dispersed in transparent matrix optical fibres	Rutgers, the State University. (Unites States)	Riman & Ballato	2005	WO05119861A2 (122)
Nanofibre reinforced transparent composite	Kyoto University (Japan)	Yano	2005	WO05012404A1 (123)
Transparent cellulose nanofibre composite	Kyoto University (Japan)	Yano <i>et al.</i>	2006	WO06082803A1 (124)
Negative ions emitting glass composite	-	Chung <i>et al.</i>	2005	WO05080280A1 (121)

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