Review: The Use of Microwave Irradiation in the Processing of Glasses and Their Composites

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The use of microwave (MW) radiation in glass processing is reviewed and compared to the usual processing techniques, such as glass melting, sintering, sealing, devitrification, coating, reinforcement with various substances, deposition by layers, etc. MW heating is known as a much-faster process (requiring minutes rather than hours), yielding good product quality, in comparison with the prolonged conventional thermal treatment of glass precursors.

Introduction

Microwave (or dielectric) heating is known as a fast, clean, and economical synthesis route for a wide range of inorganic solids. The microwave frequency of usual kitchen ovens is 2.45 GHz. Materials, in relation to microwaves, generally fall into three categories: microwave reflectors, transmitters, and absorbers. A key requirement for direct microwave irradiation is that one or more of the major constituents of the batch must be a microwave absorber and couple strongly to the microwave field at room temperature. Presently, microwave energy is used on a large scale in food preparation, vulcanization of rubber, and manufacturing of polymer/wood composites. These processes, which have been reviewed by Clark et al.,[1,2] among other contributors, take advantage of the selective heating, large penetration depth (see Table 1), and fast heating that microwave energy provides, in comparison to conventional heating methods. Recently, it has been demonstrated that microwave energy can be used to process many types of materials,[3−13] including organics, ceramics, polymers, glasses, sol−gels, metals, and composites; moreover, almost 30 years after the first reports on the interaction of microwaves with matter in 1962,[14] the process of how materials absorb microwaves was successfully explained,[15] in terms of a recent theory, which involves absorbing entities such as vacancies, bivacancies, or interstitials, which must overcome an energy barrier to absorb microwaves to a significant extent. This microwave preparation procedure, which is relatively novel in synthetic chemistry, is applicable when at least one of the components of the mixtures absorbs microwaves. In some cases, the processing times are significantly shorter than with conventional methods, whereas in other cases, the properties of the microwave-processed materials are superior. Among other advantages over conventional heating, unlike conventional heating, the batch is heated from the inside outward. This minimizes undesirable decomposition, oxidation/reduction, loss of volatile materials, and other kinetically slow processes that can occur during conventional melting.[16]

For laboratory and teaching purposes, especially in the area of organic/organometallic synthesis, the slightly modified[18] domestic microwave ovens (see Figure 1)[19] are generally used. Thus, such a microwave oven and a melting pot for the fabrication of glass, the recycling of bottle glass, and enameling were described by Luhken et al.[20] Industrial microwave ovens[21] have a variety of forms, from cylindrical (see Figure 2a; it contains a ceramic tube in the center of the applicator, to carry the product through the microwave hot zone) to planar (see Figure 2b). The industrial microwave ovens are widely used for drying purposes (for powders, medicines, wood, mine, etc.) (see Figure 3).[22] The differences between domestic and industrial microwave ovens are as follows. The home/restaurant batch-type ovens that are available to date employ a relatively low power source, compared to the industrial power source. The power is usually in the range 700−1300 W, compared to that of industrial equipment, which varies over a range of 3−6 kW. The power is usually controlled by the time of exposure and not by the power level, unless the microwave oven is based on the invert technology. The typical home oven is considerably less efficient, up to 25% less, in converting electrical energy into microwave energy. By comparison, the industrial oven can be designed as either a batch or as a continuous system with much higher power and greatly increased throughputs, reducing the amount of handling required. In addition, a forced-air system also can be employed, which greatly improves moisture removal in drying applications. The advantages of industrial equipment (for example, that reported in ref 23, are the following: a high-energy power source with long life; the ability to use a unique internal protection feature that traps stray microwaves, thus making the system completely safe to operate; uniform exposure to the microwaves; and much-lower unit costs than with the batch process.

According to the revision of available literature, major glass plants produce a variety of glasses via the conventional heating of precursors.[24] At the same time, there is a certain number of reports on the microwave (MW) sintering glasses—in particular, those reinforced with metals or coated with films—as well as glass ceramics. In addition, the MW irradiation of glasses or their precursors is used for such important purposes as vitrification of radioactive wastes. This review is dedicated to the

Table 1. Penetration Depths of Microwaves (2.45 GHz) in Various Media[a]

material	temperature, T (C)	penetration depth (cm)
water	25	1.5
water	95	5.7
wood	25	3−350
hollow glass	25	35
quartz	25	1600
porcelain	25	56
epoxy resin	25	4100
Teflon	25	9200

[a] Data taken from ref 17.

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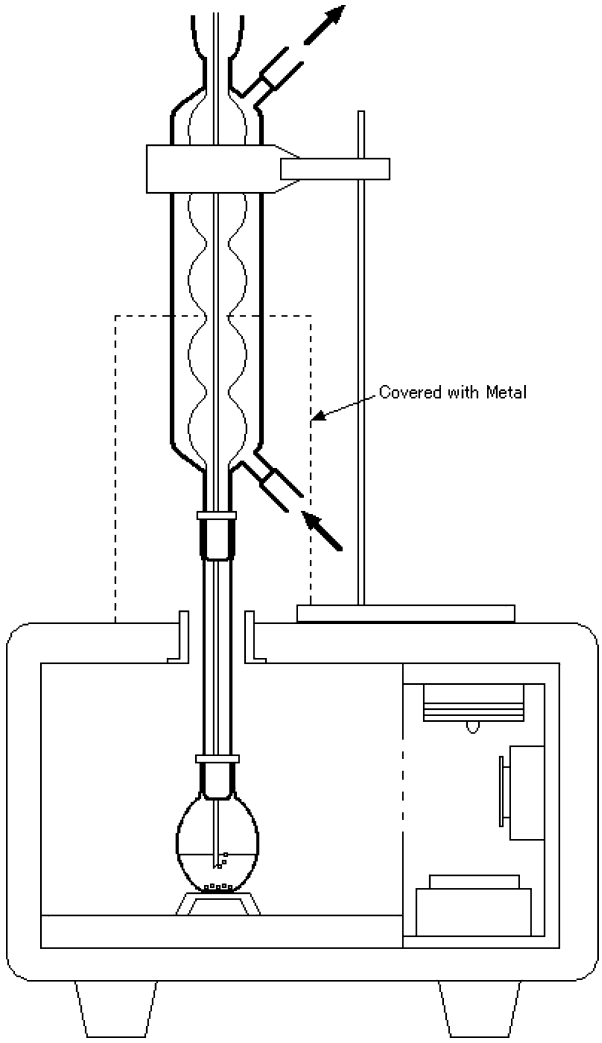

Figure 1. Typical microwave reactor for organic and/or organometallic synthesis.

generalization of data on the MW-obtaining and further MW irradiation of glasses and related materials that are based on them.

Microwave Heating of Glass: Classic Investigations

As it will be shown below, MW heating provides an extremely easy and automatically temperature-controlled route to synthesize glasses and change/improve the properties of glasses already fabricated by conventional methods. Among some classic research works on the MW irradiation of glasses or glass precursors, we note a detailed study of the microwave heating of different glasses by Kolberg et al.[25] The results showed a strong correlation between electrical conductivity and microwave absorption of different glasses. It was concluded that glasses with high alkali concentration could be heated very effectively, whereas glasses without alkali are difficult to heat with microwave energy. In another work, glass-forming compounds of several glasses were melted in a kitchen microwave oven, typically within 5 min, and quenched into glasses.[26] The rapid melting minimizes undesirable features such as the loss of components of the glass, variation of the oxidation states of metal ions, and oxygen loss leading to reduced products in the glass such as metal particles.

Strong absorption of the radiation was achieved by *preheating* the silicate glasses, or by the application of *microwave absorbing*

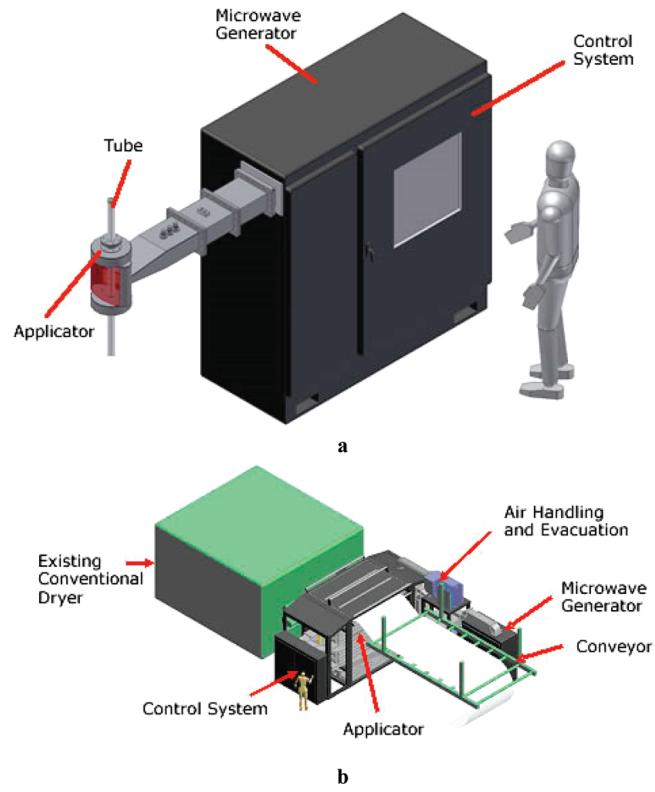

Figure 2. Elements of (a) cylindrical and (b) planar microwave heating systems. (Reproduced with permission from Industrial Microwave Systems, L.L.C.)

Figure 3. Microwave drying machine for medicine. (Reproduced with permission from the GS Enterprises.)

coating, or via *hydration*.[27] Experiments in melting, refining, reheating for forming, thermal toughening, and surface ion exchange showed that the principal advantages of microwave radiation are rapid heating and a capability to heat hot areas of the glass selectively while leaving the cooler areas unaffected. Control of the uniformity and rate of heating were the principal difficulties. That is why it is still difficult to apply MW heating widely to the glass industry, because glasses will crack because of nonuniform glass temperature distribution that is caused by the thermal runway. To obtain a uniform heating of glass, the uniform irradiation of electromagnetic wave is required. Kato et al.[28] studied the *uniform heating* of glass sheets, using the 28 GHz multimode millimeter wave, and obtained good results using both polygonal reflection board and stirrer with optimized shape, size, and rotation speed. The temperature difference within a glass sheet is improved to 1/2 or less. *Repair of glass* by sol−gel coating, using either conventional or MW heating, was proposed by Boonyapiwat et al.[29] Some samples were dip-coated with silica sol; heat treatments were conducted in either a conventional furnace or a microwave oven. As a result, microwave hybrid heating had the same effect on the repair of

uncoated glass as conventional heating. Coating the glass with sol resulted in greater glass strength than that obtained via heat treatment alone. Microwave hybrid heating seemed to yield higher reliability in sol−gel-coated samples than conventional processing. The production process of the glass product, which is defined by preparing the heating process, starting the microwave generator, and heating the glass fluid, was patented by Hasunuma et al.[30] The method was composed of disposal of the microwave generator in the feed channel, in addition to heating of the glass fluid with a microwave generator, wherein the microwave can pass through the glass fluid to heat its bottom, which makes the entire glass fluid have an even temperature distribution.

Surface modification of a sodium aluminosilicate glass, using a slurry ion exchange, was conducted in both a conventional furnace and a MW oven, to draw parallels between the two processing methods.[31] Exchange of a larger K^+ ion for a smaller Na^+ ion in the glass was investigated. Results showed an increase in the hardness of the glass samples treated using microwave energy, when compared to conventionally processed samples. However, electron microscope analysis revealed a much larger depth of surface alteration for the MW ion-exchanged glass. Glass preforms made via the deposition of porous glass on glass rods were exposed to microwaves, whereby *moisture and bubbles* were thermally removed.[32] Several different procedures for glass decomposition were evaluated for arsenic speciation using, in particular, *glass dissolution* via the action of NaOH or HF with and without MW irradiation.[33] The results showed that decomposition via the action of HF, in association with MW irradiation, led to arsenic loss.

Silica Glasses

MW irradiation has been used for preparation of a small number of glass types with distinct compositions (in particular, common silica glasses). Frequently, the data on the conventional heating of precursors were compared with the still "non-standard" MW irradiation. Thus, dehydrated silica-based glass for photomasks, which contains SiO_2 (90%), Al (<1%), H_2O (<100 ppm), and Cl (<100 ppm) and has an annealing point of 1150 C, was obtained by dehydrating a bubble-free SiO_2 glass by MW induction heating with other auxiliary heating means.[34] Glass bodies (pieces, samples, or parts) were manufactured[35] via a series of steps including the use of microwave treatment (2.5 GHz), as well as sonic or ultrasonic (20−200 Hz or 20−50 kHz respectively) treatments, of intermediate phases from SiO_2 suspension and NH_4F. The resulting 14- mm-diameter bubble- and striation-free glass rod with a density of 2.20 g/cm^3 and $n = 1.4592$ contained <50 ppb H_2O and transition metals. Sandy and foamed glass with a zeolitic surface, possessing excellent absorption and ion-exchange performances, was prepared via the reaction of sodium aluminate with Si and Na on the glass surface through irradiation of the base glass with microwaves under its immersion in an aqueous sodium aluminate solution.[36] Among other studies of MW-fabricated silica glasses, the luminescence of SiO_2 glasses, doped with Er^{3+}, containing germanium, aluminum, potassium, nitrogen, and fluorine additives and synthesized by a reduced-pressure plasma chemical method in a MW-induced discharge, was studied by Kholodkov et al.[37] It was shown that Er^{3+} luminescent properties in the glass, obtained by melting techniques, and similar glass, synthesized via plasma chemical deposition at low temperatures, were different. A model was proposed for physicochemical kinetics of synthesis and deposition of undoped silica glass in low-pressure microwave discharge.[38]

Phosphate Glasses

Phosphate glasses were prepared by melting batch materials in electric furnaces, induction furnaces, and in microwave ovens from the mixtures of $(NH_4)_2HPO_4$ and Fe_3O_4 or Fe_2O_3 as precursors; the results of these three routes were compared.[39] All the glasses were subjected to heat treatments for crystallization presented the $FePO_4$, $Fe_3(PO_4)_2$, $Fe(PO_3)_3$, $Fe(PO_3)_2$, and $Fe_7(PO_4)_6$ crystalline phases, whose amounts were dependent on the glass composition and preparation procedure. MW heating allowed melting temperatures to be reached at high heating rates, making the procedure easy and economical, but care should be taken concerning the final $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio. The unique MW-absorbing ability of $NaH_2PO_4 \cdot 2H_2O$ was determined to be very useful for the preparation of crystal and glassy sodium superionic conductors.[40] Thus, $NaPO_3$ glass was prepared by microwave heating from $NaH_2PO_4 \cdot 2H_2O$ as a starting material. Na^+ ion behavior was studied in $SnO \cdot NaPO_3$ glasses, which were prepared similarly.[41] The studies on the phosphate glass melted by microwave irradiation were performed by Wang et al.,[42] using $NH_4H_2PO_4$, Li_2CO_3, and $Ca(OH)_2$ as raw materials, mixed with and without adding water or pressing pressure. It was observed that, with the addition of water, the particles changed from irregular to aggregated; in addition, the existence of H_3PO_4 and an increase in hydroxyl groups in moist mixtures is due to the decomposition of $NH_4H_2PO_4$, which could promote microwave absorption. Dense mixtures could change into glass after MW irradiation with increasing pressing pressure.

The $15BaO-10PbO-5SrO-70P_2O_5$ phosphate glass was obtained via 2.45 GHz microwave heating by changing the glass-formation temperature and their physical properties were investigated by ^{31}P and ^{1}H MAS NMR.[43,44] The four bands—named band A, band B (both originate in protons in the glass), band C, and band D (originate in protons in adsorbed water on the surface of glass)—were observed in ^{1}H MAS NMR spectra. By changing the holding temperature (700, 800, and 850 C) and holding time (0 and 10 min), it was observed that the glass prepared at 700 C for 0 min showed the highest AC condition of 1.7×10^{-4} S/cm at 200 C.[45] The presence of branching PO_4 points, confirmed by the strong Q3 band in the ^{31}P MAS NMR spectra, which means that the glass prepared via the MW procedure had a three-dimensional (3D) polymer structure, which gave the higher stability of the glass, in comparison with those prepared by conventional electric furnace heating.[46]

The optical and semiconducting properties of Ca−Cu-phosphate glasses were determined by Romanova et al.[47] under the action of temperature and electromagnetic ultrahigh frequency (UHF) radiation. It was established that UHF radiation facilitates the formation of highly crystalline polymorphic modifications of phosphates and their transition into the amorphous phase. Niobium phosphate glasses were produced via the MW heating of a mixture of Nb_2O_5, $(NH_4)_2HPO_4$, KOH, PbO, and $BaCO_3$.[48] Note that not all tried compounds were melted during the microwave irradiation; in addition, the presence of KOH is indispensable in the mixture to allow microwave coupling. Glasses produced by microwave heating showed Al concentrations lower than those for glasses melted in electric furnaces. The chemical durability of glasses increases as a function of the amount of PbO. Among other related investigations on phosphate glasses, the MW melting of iron-containing phosphate glass materials, under wind cooling of the

container (without corroding the containers), was patented by Fukui.[49] Phosphate glass for proton conductive materials was manufactured via the MW process described by Imaeda et al.[50]

Optical Glasses

Few reports on the MW-irradiation use for the preparation and further improvement of optical glasses are available. Thus, shaped articles of high-quality quartz glass parts with fine-grained particles were sintered by MW heating, preferably at frequencies of <18−60 GHz. When the heating process was conducted under a fluoride-containing atmosphere, the thus-prepared glass is resistant to ultraviolet (UV) excimer lasers.[51] A nonstandard method for obtaining optical glass was offered by Saito,[52] where oxides that were used as precursors of optical glasses (B_2O_3, Ta_2O_5, La_2O_3, and ThO_2) were *vaporized individually* in sealed microwave-heated containers; the vapors were mixed and deposited onto a substrate that was kept at a temperature below the melting point of the optical glass in a vacuum container to obtain optical glass to form a 2-mm-thick glass layer. Ultrafine CeO_2 powder, which can be used for *polishing* the optical glass, was prepared via a microwave-assisted heating process and high-temperature calcination, starting from $Ce_2(CO_3)_3$ as the precursor.[53] Atomic force microscopy (AFM) microscopy proved that the polishing effect of CeO_2 prepared by microwave-assisted heating is better than that of CeO_2 synthesized via high-temperature calcination. In addition, the apparatus for *drying* glass lenses, using MW irradiation, was proposed by Lee et al.[54] The apparatus can be used to dry the glass lenses after the washing processes of the glass lens manufacturing method (which is comprised of the mold frame manufacturing process, the lens material injecting process, the hardening process (based on heat treatment), washing/drying processes, etc.).

Glasses Reinforced with Metals

Among previously reported fundamental studies, we focus on study of the application of MW radiation as the heating source for the processing of glass-matrix composites based on borosilicate glass powders that contain metallic (10 vol % of Mo, W, Al, Ti, Ni, and Fe) particles or fibers (2−50 μm).[55−57] The MW-processed samples had densities ≤96% of that of the conventionally processed samples and were obtained in significantly shorter times (7 min vs ∼7 h). The authors proposed that porosity formed during microwave heating is a consequence of localized glass-matrix overheating, in correspondence with the presence of metal fibers, which is caused by the preferential MW absorption exhibited by the Hastelloy X fibers themselves and by the microregions of the matrix heated well above the glass softening temperature. In the case of sintering porous borosilicate glass-matrix composites that have spherical porosity and molybdenum particle inclusions,[58,59] it was established that the inverse thermal gradient typical of MW heating and the presence of molybdenum particles led to the development of a layered porous structure of the compacts, which consists of a highly porous core and a relatively dense outer shell (which remained at lower temperature and is sintered by viscous flow with minimal distortion). Such a layered porosity was not observed in glass compacts without molybdenum particles. Microwave heating of soda−lime glass via the addition of iron powder was studied by Yoshikawa et al.,[60] intending to obtain fundamental knowledge for vitrification solidification and for the fabrication of metal-reinforced glass-matrix composites. A single-mode MW applicator was used to clarify the electric-field (E) and magnetic-field (H) contributions to the heating of each material and their mixtures. It was shown that the addition of iron powder (with an average size of 70 μm, and a volume fraction of 18%) made it possible to heat the glass beads at >700 C within 60 s.

Glasses Containing Other Elements

Ionic conducting glasses in the $AgI-Ag_2O-B_2O_3-SiO_2$ system (e.g., $2AgI-Ag_2O-2(0.95B_2O_3 \cdot 0.05SiO_2)$) were prepared by fast melting (2.5 min) in a domestic multimode MW oven operating at 900 W and 2.45 GHz.[61,62] Homogeneity in the quenched glasses was equivalent to or better than glasses obtained by conventional melting at 730 C. MW-processed glasses were reddish while the same composition prepared in a conventional furnace was yellow, possibly due to the structural changes and/or differences in Ag^+ mobility. Surface modification of the sodium aluminosilicate glasses, using microwave energy, was demonstrated.[63] *Ion exchange* of Ag^+ and K^+ for Na^+ was performed in a series of glasses. The extent to which microwaves affected the ion exchange reactions was dependent on the glass compounds and on the type of heating used to perform the reactions. Far-reaching penetration depths of Ag^+ were achieved in the glasses, while no significant interdiffusion increase was observed for K^+. *Superconducting* oxide compounds in vitreous matrixes can be formed, not only by copper oxide, but also by oxides of other transition metals (e.g., nickel oxide).[64] The superconducting structures in macroscopically nonsuperconducting silicoborate, phosphate, and germanate glasses doped with NiO were studied by magnetosensitive microwave absorption. It was shown that the dependence of concentration of superconducting structures on the NiO content in glasses had a maximum whose value and location was dependent on the composition and structure of the vitreous matrix.

Magnetite (Fe_3O_4) is a strong absorber of microwave energy, which can be used to enhance heating in microwave-transparent or low-absorbing matrixes.[65] To examine the heat generation of magnetite for ultimate use in materials consolidation, magnetite was dispersed in relatively low-absorbing soda−lime glass particles. The effects of magnetite weight fraction, microwave power, and sintering time on temperatures and bulk properties of the sintered specimens were reported. For a PbO-containing glass, crystallization behavior of $PbTiO_3$ from a $PbO-B_2O_3-ZnO-TiO_2$ glass system was studied by Park et al.,[66] who varied heating times and temperatures under MW processing and compared those results with those from conventional thermal processing. As a result of this comparison, it was concluded that the crystallization of $PbTiO_3$ by MW heating was faster, in comparison with conventional heating, and the alumina sheets were joined by MW processing, resulting in higher bending strength and shorter time. In a related work with PbO use, the characteristics of microwave direct coupling in the PbO, V_2O_5, TeO_2, and $V_2O_5-PbO-TeO_2$ compounds were investigated[67] at a MW input power of 600 W. It was found that $V_2O_5-PbO-TeO_2$ glass samples were directly coupled with microwaves, then heated to the given temperature, because of the high microwave coupling of V_2O_5 compound. Also, PbV_2O_6 and $Pb_4V_2O_9$ crystalline phases existed in the microwave heat-treated samples, but not in the conventional one; in addition, the electrical conductivity of microwave heat-treated samples was relatively higher than that of the conventional one. Se−Te-based chalcogenide glasses can be rapidly prepared through MW irradiation without the help of metal powders.[68] It was confirmed that the T_g values of the samples are comparable to the already-

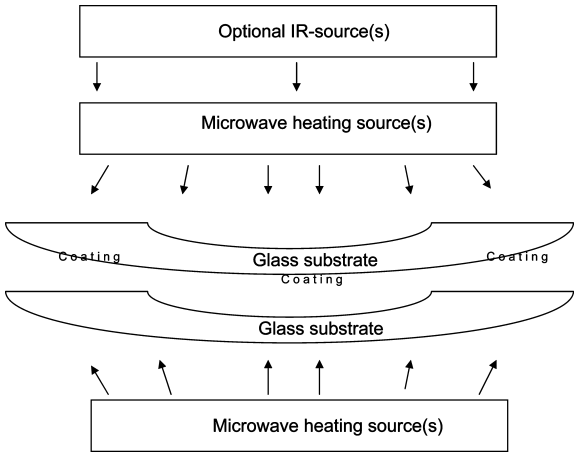

Figure 4. Bending glass using MW heating.

reported T_g values for samples prepared via conventional methods. This type of fast synthesis may replace the more time-consuming prolonged conventional procedures for the preparation of these glasses.

Coating Glasses with Inorganic and Other Films

The MW-applied coatings can be divided in elemental substances (such as metals or carbon), metal oxides, and organic paints. Thus, silver aggregates (100−500 nm in size) were obtained on glass substrates[69] via MW irradiation of glycerol solution of $AgNO_3$. The increase in reaction temperature above the boiling point of glycerin (which is an efficient reductant for Ag^+, under the MW-heating conditions) was observed during MW heating. The resulting fine silver particles were crystalline. A MW-assisted method for the fast deposition of continuous gold films on glass substrates was developed by Huang et al.[70] Under MW irradiation, gold nanoparticles in colloidal solutions were able to assemble on the naked substrates to form a gold monolayer within minutes. The prepared gold films were continuous and can be used as stable electrodes able to sustain several hundreds of redox circulation. Nanocrystalline diamond thin films were grown on glass substrates by microwave plasma chemical vapor deposition (MPCVD) from a gas mixture of methane and hydrogen at low substrate temperatures.[71] The initial stages of diamond growth are the growth of individual nanometer-sized crystals and clusters, and coalescence into a continuous layer. Grown nanocrystalline diamond films are optically transparent in a wide spectral range, and they exhibit a high refractive index of 2.34. A Sn/C composite thin film was synthesized from a solid organic precursor Sn(IV) *tert*-butoxide via the same technique.[72]

Titanium(IV) dioxide is the metal oxide most used as a coating for MW-prepared glasses. Thus, TiO_2 layers obtained by MW-activated chemical-bath deposition (MW-CBD) were proposed to improve the TiO_2 contact to the conducting glass. Spectra of the incident photon to current conversion efficiency showed higher values when TiO_2 double-layer photoelectrodes were used.[73] In a related work, the MW-born TiO_2 nanoparticles, prepared from the MW-induced thermal hydrolysis of a titanium tetrachloride aqueous solution in the presence of HCl, showed good affinity to glass and silicon substrates; thin films 10−50 nm thick, with the absorption edge blue-shifted, compared to bulk anatase, were obtained through a simple process without the need of heat treatment for crystallization purposes.[74] The behavior of TiO_2 film on glass substrates was studied under MW irradiation.[75] The results showed that all treated films were amorphous anatase and oriented on a glass slide with [101] anatase. Low-temperature MW irradiation is suitable when substrates cannot tolerate high temperatures, which means that the use of microwaves can replace the traditional heating methods. The deposition of TiO_2 thin films from solution on conducting glass for solar cells using a MW reactor at low MW power and short deposition time was reported by Vigil et al.[76] The substrates were immersed in a diluted homogeneous aqueous solution, which was prepared by mixing equal volumes of a fluorine-complexed titanium(IV) solution ([Ti] = 3.4×10^{-2} M) and a 6.8×10^{-2} M boric acid solution. The TiO_2 layers (100−500 nm; particle size is dependent on MW power and deposition time) obtained were well-adhered and homogeneous, with good specularity, and were colored by the interference of reflected light.

MW and conventional heating processes were utilized to achieve adequate crystallization in $MgO-Al_2O_3-TiO_2$-based glass coatings with identical compositions.[77] The studies showed that the misfit strain in the lattice of conventionally heat-treated coating was higher than that in the corresponding MW-processed coating. MW heating generated finer crystallites in the glass coating than those obtained in the coating processed by conventional heating. DSI results confirmed that the MW-processed coating possessed a much-greater hardness (∼6 GPa), compared to that of the conventionally processed coating.[78] A MW-radiation method for coating glass slides with ZnO particles with an average size of 200 nm and two main morphologies ((a) a very dense coating of ZnO hexagonal rods growing perpendicular to the glass surface and (b) ZnO flowerlike particles) was proposed by Irzh et al.[79] The apparatus used for the MW deposition of ZnO on glass substrates was proposed by Takizawa et al.[80] Si−Al−O-N films on glass molding dies for the direct molding of aspheric lead silicate glass lenses were obtained by microwave plasma-assisted chemical vapor deposition (CVD), using a $SiH_4-AlBr_3-H_2-N_2-N_2O-Ar$ gas mixture. The structure of these films remains stable at 900 C.[81] A nonstoichiometric semiconductive indium oxide (InO) film was prepared on glass via magnetron-sputtering deposition synchronously enhanced by microwave electron cyclotron resonance (ECR) plasma source ion-implantation.[82] This InO film had better adhesion to glass substrates and greater surface hardness, because of high implantation energy, compared to film prepared via reactive sputtering or reactive evaporation deposition. Water-thinned paint compositions that had excellent adhesion to glass and formed glass sheets for automotive and architectural windows painted with the compositions were patented by Boaz.[83] One of the last steps was the heating of the painted glass sheet via MW or IR radiation to a temperature that was below the softening point of the glass but sufficiently high to drive off the water that was present in the paint and cure the paint to obtain a glass sheet with an adherent coating.

Glass-Ceramics and Composites

Glass-ceramic materials are generally prepared via conventional heating methods.[84−86] In addition, some studies on their MW sintering have been reported. Thus, polymer-net gel process for preparing ultrafine powder of Li−Al−Si glass-ceramics was described,[87] starting from tetraethylorthosilicate, with lithium and aluminum salts as precursors, comprising a series of steps, including drying the wet gel at 120 C for 12 h or in a microwave oven for 15−30 min to get dried gel before calcination at 600−1200 C to obtain an ultrafine powder of Li−Al−Si glass-ceramics. As has been shown, the MW method is faster and low in cost, yielding highly pure powder with small

particle diameters. A magnetic glass-ceramic containing ordered M-type strontium hexaferrite grains was obtained via crystallization induced by microwave heating, using the $SrO-Fe_2O_3-B_2O_3$ system as a glass-forming system. The resulting glass-ceramic contains two major crystalline phases: $SrFe_{12}O_{19}$ and $Sr_2B_2O_5$. It has a magnetization of 10.3 A m^2/kg (at a magnetic field strength of 720 kA/m) and a coercive force of 296 kA/m, indicating that a major part of the iron oxide is incorporated in the magnetic hexaferrite phase.[88] Dense yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) + 28 vol % alumina nanocomposite ceramics with and without 17 vol % oxynitride glass were fabricated at 1380 C using MW sintering.[89] It was established that plastic deformation at lower temperatures in glass-containing materials occurred via cooperative grain-boundary sliding. The changes in the deformation behavior at higher temperatures were related to crystallization of the glass and simultaneous plastic deformation by grain-boundary sliding. Densification and microstructural evolution of a $CaO-ZrO_2-SiO_2$ glass powder were studied during MW heating (2.45 GHz) or conventional heating to produce a glass-ceramic material.[90] The effect of microwaves was to accelerate the sintering process, but they did not affect the crystallization evolution of glass-ceramic materials differently, when compared to the conventional sintering. Remarkably different crystallization paths were observed, depending mostly on the composition of the glass and especially in the MW route.[91] *Color changes* during devitrification in $Li_2O-ZnO-Al_2O_3-SiO_2$ glasses with varying ZnO/Li_2O ratios under conventional and MW heating were studied by the same researchers.[92] The base glasses, which were yellowish in color, turned violet at 700−800 C. The glass remains transparent and the obtained color is stable during cooling. When heated at >800 C, the samples became opaque violet and finally opaque white at 900 C. The effect of the heat treatment on the physical and chemical properties of these materials was explained on the basis of changes in the composition and morphology of the residual amorphous and crystalline phases.

The MW sintering of hydroxyapatite-glass composites (HAP-G) was previously studied,[93] based on the $R_2O-Al_2O_3-B_2O_3-SiO_2$ system glass powder and hydroxyapatite, mixed in specific proportions and sintered by exposure to MW radiation at temperatures of 1150, 1200, and 1250 C. It was established that the sample structures gradually became compact as the sintering temperature increased, but the main crystalline phase in the ceramics did not change remarkably when the sintering temperature was <1200 C. The method and device used to make heat-insulating fire-resistant plates from perlite/glass fiber composites were patented by Viessmann.[94] His reported method included a series of steps, such as mixing the perlite granules with waterglass aerosol, forming triple-layer dry sheets containing a glass fiber layer between two perlite layers, densification of the obtained structure leading to the formation of a plate, and its drying under microwave action. A calcium magnesium aluminosilicate-based glass that contained 10 wt % of silicon carbide whiskers (SiC_w) as reinforcement was prepared by tape casting, followed by sintering either in a conventional furnace or in a MW oven.[95] As a result, the sintering at temperatures of >800 C did not improve the densification but rather resulted in severe whisker oxidation; in contrast, in the microwave oven, almost-full densification for the glass and ~95% of the theoretical densification for the composite were obtainable at 850 C for 15 min (10 h reduction of the total processing time). Porous glass-matrix composites thqat contain well-defined spherical porosity were fabricated by employing MW-assisted densification of powder compacts.[96] A high concentration of spherical pores in the central region of the sample and a relatively dense outer shell were observed, by applying the inverse thermal gradient that is typical of MW heating. Pores in the central region were formed in the molten glass phase, exploiting gas evolution and entrapment; the outer region, being at a lower temperature, was sintered by viscous flow. The present approach is advantageous because of the high heating rates of MW heating, resulting in time and energy savings. Among other reported glass-ceramics, multilayer ceramic substrates that contain crystallizable glass particles selected from borosilicate glass, lead glass, and precursors of the crystalline particles were studied in detail.[97] Thus, for example, an abnormally high mass transport of metals inside the volume of oxide glass-ceramics with a strongly pronounced nonmonotonic characteristic distribution of Cr, Al, Si, and other ions in the interface zone of metal-ceramic structures, and also the phenomenon of essential increase of adhesion of ceramics with a metal substrate at their synthesis in the fields of MW power radiation, were described by Ravaev et al.[98] Among other glassy composites, MW irradiation was applied in an improved process for the sintering of silicon carbide composites with a ceramisable glass powder additive by mixing silicon carbide powders of various fineness[99] and for the MW homogeneous curing of large-sized glass fiber−epoxy resin (DGEBA-3,3′-dimethyl-4,4′-diaminodicyclohexylmethane system).[100]

Other Microwave Applications

It is known that the nuclear industry generates contaminated burnable wastes, most of which are incinerated for the purpose of volume reduction. An incineration ash melting process using MW heating with a vitrification additive was designed and developed by Vincent et al.[101] The *vitrification of pulplike radioactive materials* with the production of borophosphate and borosilicate glasses, using MW energy at 2375 MHz and an output generator power of 5 kW, was studied by Vasil'ev et al.[102] As a result of these investigations, the permittivity and dielectric loss tangent angle of a pulp simulator, evaporated conglomerate (calcinate), and samples of glasses obtained from this pulp, among other characteristics, were measured. In another related work, Otsuka et al.[103] proposed a method that solved the radioactive Zircaloy waste disposal problem and the sodium waste problem at the same time, producing a glass with little Na leaching. Thus, waste sodium compound (as Na_2O), SiO_2 (glass-forming material), ZrO_2 (obtained from waste Zircaloy), and B_2O_3 were mixed and melted in a microwave furnace, cooled, and solidified to give a stable glass with little Na leaching. In addition, powdery waste glassy-black fused materials that were based on SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, and Na_2O were reported to be utilized by MW irradiation.[104]

A series of methods has been offered to *affix/seal* glasses and other materials/elements, which are difficult to be strongly contacted. Thus, elements that are difficult to attach, e.g., vehicle glass panes (aluminum or hard plastic to glass), were affixed to each other using polymer adhesives via MW irradiation to achieve polymerization.[105] Two elements, among which the first partially surrounds the second element, were brought into contact with the opening of a microwave guide, which is arranged at an angle with respect to the opening in the first element, so that the microwaves are directed toward the polymer to be heated and positioned in a space within the opening between the two elements. MW heating was also used to produce ceramic−glass−metal seals from a slurry of glass-sealing material and a coupling agent, which is applied to the ceramic

Table 2. Summary of Main Applications of Microwave Irradiation in Glass Fabrication and Improvement

process/study	description/observations	reference
	Physical Treatment of Glass	
bending of glass to obtain curved glass	two MW sources were used; sometimes, conventional heating was used before MW treatment	108
lamination of glass	a film covered the glass and was subjected to further MW heating	113, 114
sealing of glass	This was used, in particular, to seal glasses to aluminum or hard plastics in vehicles. "Ceramic−glass−metal" and "ceramic−glass−ceramic" MW techniques were reported.	105
vitrification of hazard wastes, in particular radioactive waste	a composite of a borophosphate or borosilicate glass with wastes was MW-formed	102, 103
MW-heating studies for various types of glasses	High concentrations of alkali metals contributed to MW-heating glasses. Preheating, films on glasses, and MW melting of glasses were studied. Uniform MW heating was developed.	25
glass repair	the glass was covered with a protective sol−gel precursor and MW-heated	29
glass layers deposition	glass layers were MW-deposited on a preformed glass	116
modification of glass surface	interchange of K by Na in glasses with the use of microwaves	31
studies of color changes	MW devitrification of $Li_2O-ZnO-Al_2O_3-SiO_2$ glass at 700−800 C led to color changes from yellow to violet	92
luminescence studies in glasses	Luminescence in MW-obtained glasses based on SiO_2, doped with Er^{3+} and containing additives of Ge, Al, K, N, F, was studied.	37
elimination of bubbles and humidity	MW irradiation allowed their elimination	32
superconductivity/ionic conduction	Local superconductivity in MW-obtained glasses was studied. Ionically conducting glass $2AgI-Ag_2O-2(0.95B_2O_3 \cdot 0.05SiO_2)$ was MW-synthesized.	61, 62
	Sinterization of Various Types of Glasses	
common alumosilicate and phosphate glasses	a series of glasses (for instance, $15BaO-10PbO-5SrO-70P_2O_5$, $PbO-B_2O_3-ZnO-TiO_2$) were MW-obtained from their precursors	34, 43, 66
optical glasses	MW irradiation was applied for fabrication of an optical glass by individual MW evaporation of Ba_2O_3, Ta_2O_5, La_2O_3, and ThO_2 and further mixing the formed vapors. MW-drying and polishing techniques for optical glasses were proposed.	52−54
	Preparation of Metal-Reinforced Glasses	
metal-reinforced glasses	borosilicate glasses, reinforced with 10% Mo, W, Al, Ti, Ni, and Fe (2−50 μm in size), were MW-fabricated	55−57
	Film Deposition on Glass Surfaces	
metals and nanodiamonds	elemental Cu, Ag, Au, Sn/C, nanodiamonds were MW-deposited on glasses	69−72
oxides	various oxides, such as TiO_2, $MgO-Al_2O_3-TiO_2$, ZnO, Si-Al-O-N, and InO, were MW-deposited on glasses	73−76
paints	MW-deposited paints for use in vehicle and architectural glass	83
	Sinterization of Glass Ceramics	
obtaining glass ceramics	MW heating was used to prepare a host of glass-ceramics, based on Li−Al−Si, $SrO-Fe_2O_3-B_2O_3$, $CaO-ZrO_2-SiO_2$, $R_2O-Al_2O_3-B_2O_3-SiO_2$ hydroxyapatite, perlite/glass, Ca−Mg-alumosilicate with SiC	87−89

and metal workpieces.[106] The power, time, and frequency of the microwave energy used were sufficient to cause a liquid-phase reaction in the slurry. Thus, an Al_2O_3 ceramic was MW-joined to a workpiece of alloy containing 17% Co, 54% Fe, and 29% Ni (using a glass that was composed of 9.4 wt % B_2O_3, 2.4 wt % SiO_2, 14.4 wt % ZnO, and 64.9 wt % PbO) for 99 min, resulting in hermetically tight-sealed finished products. In a similar process ("ceramic-glass-ceramic"),[107] Al_2O_3 ceramic substrates were MW-joined to the same glass. The glass-sealing material completely reacted with the Al_2O_3 ceramic, forming a lead aluminoborate glass phase and an Al_2O_3-ZnO phase between the Al_2O_3 substrates. The authors emphasized that sealing via this method requires $^1/_{16}$ as much energy and $^1/_{14}$ as much time as does that using conventional heating.

The *bending* of glass using microwaves was described by Vandal.[108] Two sources of MW radiation were used to heat the glass substrate for bending (see Figure 4); a coating supported by a substrate is not heated as much during the MW-bending process, in comparison with conventional IR heating, so coating damage was reduced. The method for making *curved glass sheets* with an applied opaque layer was proposed.[109] The sheet was passed through a tunnel furnace and at least two MW-beam heating sections, each of which was provided to accomplish firing or curing of the opaque layer. Glass sheets can also be formed by MW irradiation,[110] according to the following series of steps: heating of a glass sheet to at least a first predetermined temperature (482−510 C), application of microwave energy to at least a second predetermined temperature (621−676 C), the cooling of an outer surface of the glass sheet to at least a third predetermined temperature (482 C), and the formation of the glass sheet (using forming rollers) to a predetermined configuration. A similar procedure was patented by the same inventor in ref 111. The combined MW thermal treatment of any type of glass and glasslike materials (preferably in a sheet form) for shaping, bending, tempering, annealing, coating, and float processing resulted in the processing of glass without cracking.[112] The glass, treated with MW radiation according to the proposed technique, can be used as car windows and architectural window glass and so on. Moreover, the glass can be MW-*laminated*,[113,114] using a laminating film placed over one surface of a first glass sheet and the film is heated with MW radiation to the bonding temperature and thereafter cooled,

whereby an appropriate bond was obtained between the film and the second glass sheet to provide glass lamination. The laminating apparatus for MW irradiation was patented by the same authors.[115] *The deposition of silica glass layers* on the external surface of a rodlike glass preform was reported by Van Stralen et al.[116] The process was performed by placing the preform between two MW generators in an enclosed chamber. The generation of a plasma zone in the chamber led to the deposition of silica glass layers on the preforms.

The main applications of MW irradiation in glass production, and its improvement, are given in Table 2.

Conclusions

Microwave (MW) irradiation of glass and/or its precursors is not widely applied on an industrial scale, despite a certain number of articles and patents reporting a critical comparative analysis of conventional and MW glass processing. Almost always, the MW heating of glass precursors is much faster (minutes versus hours), yielding good product quality, in comparison with the classic thermal treatment of glass precursors. Distinct types of glasses and glass-ceramics can be MW-sintered, devitrified, repaired, sealed, laminated, curved, and coated with films of a series of metals, their oxides, paints, and even nanodiamonds, as well as being deposited by glass layers, reinforced with metals, and improved via the elimination of bubbles or humidity. MW processing can lead to luminescent, locally superconductive, and optic glasses. Glass precursors can be evaporated individually and further deposited; nonuniform heating problems can be resolved using two or more MW sources. Generally, according to ref 117, it can be concluded that the "microwave processing of materials is a technology that can provide the material processor a new, powerful, and significantly different tool with which to process materials that may not be amenable to conventional means of processing or to improve the performance characteristics of existing materials", which would require, however, a good understanding of the processes prior to attempting their use.

Literature Cited

(1) Clark, D.; Folz, D. Microwave processing of materials. *Adv. Sci. Technol.* **2003**, *31*, 367. (10th International Ceramics Congress, 2002, Part B.)

(2) Clark, D. E.; Sutton, W. H. Microwave Processing of Materials. *Annu. Rev. Mater. Sci.* **1996**, *26*, 299.

(3) Das, S.; Mukhopadhyay, A. K.; Datta, S.; Basu, D. Prospects of microwave processing: An overview. *Bull. Mater. Sci.* **2009**, *32* (1), 1.

(4) Available via the Internet at http://eprints.usq.edu.au/2390/1/Ku_Siores_Ball_Publ_version.pdf.

(5) Kharissova, O. V.; Castanon, M. G.; Hernandez Pinero, J. L.; Mendez, U. O.; Kharisov, B. I. Fast Production Method of Fe-Filled Carbon Nanotubes. *Mech. Adv. Mater. Struct.* **2009**, *16* (1), 63.

(6) Kharissova, O. V.; Osorio, M.; Garza, M.; Kharisov, B. I. Study of Bismuth Nanoparticles and Nanotubes Obtained by Microwave Heating. *Synth. React. Inorg., Met.−Org. Nano-Met. Chem.* **2008**, *38* (7), 567.

(7) Kharissova, O. V.; Cardenas, J. R. Advance in methods of forming vertically aligned carbon nanotubes by microwave. *Phys. Status Solidi C* **2005**, *2* (8), 3063.

(8) Rodriguez, M. G.; Kharissova, O. V.; Ortiz-Mendez, U. Formation of boron carbide nanofibers and nanobelts from heated by microwave. *Rev. Adv. Mater. Sci.* **2004**, *7* (1), 55.

(9) Kharissova, O. V. Fabricating multilayer carbon nanotubes by microwave irradiation, which are aligned with encapsulated iron particles, Mex. Pat. Appl. MX 2006-10 20060213, 2007, 21 pp. (CODEN: MXXXA3 MX 2006NL00010 A 20070813 (patent written in Spanish). Priority: CAN 149:246654. AN 2008:273690.)

(10) Katz, J. Microwave sintering of ceramics. *Annu. Rev. Mater. Sci.* **1992**, *22*, 153.

(11) Rao, K. J. *Structural Chemistry of Glasses*; Elsevier Science B.V.: Amsterdam, 2002; 584 pp.

(12) Tiegs, T. N. Comparison of Properties of Sintered and Sintered Reaction-Bonded Silicon Nitride Fabricated by Microwave and Conventional Heating. *Mater. Res. Soc. Symp. Proc.* **1994**, *347*, 501.

(13) Tiegs, T. N.; Kiggans, O.; Ploetz, K. L. Application of Microwave Heating for Fabrication of Silicon Nitride Ceramics. In *Proceedings of the 17th Annual Conference on Composites and Advanced Ceramic Materials, Part 2 of 2*: Wachtman, J. B., Jr., Ed.; Ceramic Engineering and Science Proceedings 14; Wiley: New York, 2008; Issue 9/10.

(14) Stitch, M. L. Microwave Interaction with Matter. Proc. IRE 1962, *50* (5), 1225. (Available via the Internet at http://ieeexplore.ieee.org/xpl/freeabs_all.jsp?arnumber=4066843.)

(15) Kenkre, V. M.; Kus', M.; Katz, J. D. Explanation of the Barrier Depression Effect in Ceramics undergoing Microwave Heating. *Phys. Rev. B* **1992**, *46* (21), 13825.

(16) Stennett, M. C.; Hyatt, N. C. Microwave processing of glasses for waste immobilization. In *Scientific Basis for Nuclear Waste Management XXXII*, Materials Research Society Symposium Proceedings 985; Materials Research Society: Warrendale, PA, 2009; Paper No. 1124-Q03-05.

(17) Available via the Internet at IndustrialHeating.com January 2005, 43. (http://www.ceralink.com/publications/Advancements-Jan2005.pdf.)

(18) Keyson, D.; Volanti, D. P.; Cavalcante, L. S.; Simoes, A. Z.; Souza, I. A.; Vasconcelos, J. S.; Varela, J. A.; Longoc, E. Domestic microwave oven adapted for fast heat treatment of $Ba_{0.5}Sr_{0.5}(Ti_{0.8}Sn_{0.2})O_3$ powders. *J. Mater. Process. Technol.* **2007**, *189*, 316.

(19) Kharisov, B. I.; Kharissova, O. V.; Jimenez Gomez, M.; Ortiz Mendez, U. Recent advances in the synthesis, characterization, and applications of fulleropyrrolidines. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 545.

(20) Luhken, A.; Bader, H. J. Fabrication of glass and enamel in the microwave oven. *Chem. Sch.* **2002**, *51* (2), 41.

(21) Available via the Internet at http://www.industrialmicrowave.com/products.htm.

(22) Available via the Internet at http://www.appliancessolution.com/products-2/industrial-microwave-equpment.

(23) Available via the Internet at http://www.microdry.com/art1.htm.

(24) Ross, C. P.; Tincher, G. L. Glass Melting Technology: A Technical and Economic Assessment. U.S. Department of Energy, Industrial Technologies Program: Washington, DC, 2004. (Available via the Internet at http://www.osti.gov/glass/Special%20Reports/Glass%20melting%20tech%20assessment.pdf.)

(25) Kolberg, U.; Roemer, H. Microwave heating of glass. In *Microwaves: Theory and Application in Materials Processing V*; Ceramic Transactions 111; American Ceramic Society: Westerville, OH, 2001; p 527.

(26) Vaidhyanathan, B.; Ganguli, M.; Rao, K. J. A novel method of preparation of inorganic glasses by microwave irradiation. *J. Solid State Chem.* **1994**, *113* (2), 448.

(27) Knox, M. P.; Copley, G. J. Use of microwave radiation for the processing of glass. *Glass Technol.* **1997**, *38* (3), 91.

(28) Kato, H.; Yuki, K.; Nakaoka, E. Improvement of heating uniformity of glass sheet on the millimeter-wave heating. In *International Congress on Glass, Proceedings, 20th*, Kyoto, Japan, Sept. 27−Oct. 1, 2004; Yoko, T., Ed.; 2004; 04.021/1−04.021/5.

(29) Boonyapiwat, A.; Fathi, Z.; Folz, D. C.; Clark, D. E. Repair of glass by sol−gel coating using either conventional or microwave heating. In *Microwaves: Theory Application in Materials Processing II*; Ceramic Transactions 36; American Ceramic Society: Westerville, OH, 1993; p 341.

(30) Hasunuma, I. A feed channel with microwave heater and the method for preparing glass product with this feed channel, Chin. Patent Application CN 2003-141483 20030709, 2005. (CODEN: CNXXEV CN 1566001 A 20050119 (patent written in Chinese); Priority: AN 2005:1117551.)

(31) Atong, D.; Clark, D. E.; Folz, D. C. Surface modification of glasses using microwave energy. In *Surface-Active Processes in Materials*; Ceramic Transactions 101; American Ceramic Society: Westerville, OH, 2000; p 75.

(32) Murata, H.; Yoshida, K. Heat treatment of porous glass, Jpn. Patent Application JP 91-126719 19910430, 1992, 3 pp. (CODEN: JKXXAF JP 04331730 A 19921119 Heisei (patent written in Japanese); Priority: CAN 118:108285 AN 1993:108285.)

(33) Cicero do Nascimento, P.; Bohrer, D.; Becker, E.; Machado de Carvalho, L. Comparison of different sample treatments for arsenic speciation in glass samples. *J. Non-Cryst. Solids* **2005**, *351* (14&15), 1312.

(34) Hachiuma, S.; Oota, Y.; Kikukawa, S. Dehydrated silica-based glass for photomask and its manufacture, Jpn. Patent Application JP 91-355031 19911220, 1993, 5 pp. (CODEN: JKXXAF JP 05097466 A 19930420 Heisei (patent written in Japanese).)

(35) Clasen, R. Extrusion of glass bodies, Dtsch. Patent Application DE 85-3511450 19850329, 1986, 14 pp. (CODEN: GWXXBX DE 3511450 A1 19861002 (patent written in German).)

(36) Shimamune, T.; Yoshikawa, A.; Hara, H. Method for treatment of glass for formation of zeolitic surfaces, Jpn. Patent Application JP 2003-418688 20031114, 2005, 9 pp. (CODEN: JKXXAF JP 2005145807 A 20050609 (patent written in Japanese); Priority: CAN 143:30709; AN 2005: 487856.)

(37) Kholodkov, A. V.; Golant, K. M. Er^{3+} ions luminescence in non-fused silicate glasses fabricated by SPCVD. *Opt. Mater.* **2005**, *27* (6), 1178.

(38) Denisov, A. N.; Biriukov, A. S.; Golant, K. M. Physicochemical kinetics of silica glass deposition in plasmachemical technology of optical fiber preforms. *Adv. Sci. Technol.* **2003**, *36*, 307. (Computational Modelling and Simulation of Materials II.)

(39) Almeida, F. J. M.; Martinelli, J. R.; Partiti, C. S. M. Characterization of iron phosphate glasses prepared by microwave heating. *J. Non-Cryst. Solids* **2007**, *353* (52−54), 4783.

(40) Sridarane, R.; Raje, G.; Shanmukaraj, D.; Kalaiselvi, B. J.; Santhi, M.; Subramanian, S.; Mohan, S.; Palanivel, B.; Murugan, R. Investigations on temperature dependent structural evolution of $NaPO_3$ glass. *J. Therm. Anal. Calorim.* **2004**, *75* (1), 169.

(41) Bhat, M. H.; Ganguli, M.; Rao, K. J. Conductivity studies in SnO−$NaPO_3$ glasses. *Bull. Mater. Sci.* **2003**, *26* (4), 407.

(42) Wang, J.-S.; Jeng, J.-S.; Ni, C.-T. The study on the phosphate glass melted by microwave irradiation. *J. Non-Cryst. Solids* **2009**, *355* (13), 780.

(43) Imaeda, K.; Minami, Y.; Sakurai, M.; Watanabe, M. Assignment of mobile proton in proton-conductive 15BaO−10PbO−5SrO−70P_2O_5 glass prepared by microwave heating. *Phosphorus Res. Bull.* **2008**, *22*, 22.

(44) Murase, I.; Imaeda, K.; Sakurai, M.; Watanabe, M. Formation mechanism of branching structure in phosphate glasses prepared by microwave heating. *Phosphorus Res. Bull.* **2005**, *19*, 65.

(45) Minami, Y.; Imaeda, K.; Sakurai, M.; Watanabe, M. Physical properties of phosphate glasses prepared by temperature-controlled microwave heating. *Phosphorus Res. Bull.* **2005**, *19*, 60.

(46) Imaeda, K.; Murase, I.; Sakurai, M.; Watanabe, M. Branching structure in BaO−PbO−SrO−P_2O_5 phosphate glass prepared by microwave heating. *Phosphorus Res. Bull.* **2006**, *20*, 185.

(47) Romanova, D. V. Influence of electromagnetic irradiation on the structure of semiconducting glasses. *Fiz.-Khim. Mekh. Mater.* **2000**, *35* (6), 890.

(48) Ghussn, L.; Martinelli, J. R. A novel method to produce niobium phosphate glasses by microwave heating. *J. Mater. Sci.* **2004**, *39* (4), 1371.

(49) Fukui, T. Method for stable melting of iron phosphate glass, Jpn. Patent Application JP 2002-253121 20020830, 2004, 11 pp. (CODEN: JKXXAF JP 2004091246 A 20040325 (patent written in Japanese).)

(50) Imaeda, K.; Watanabe, M.; Sakurai, M.; Takahashi, M.; Abe, Y.; Hayashi, M.; Iwamoto, T.; Washimi, H.; Mizutani, Y. Manufacture of phosphate glass for proton conductive materials, Jpn. Patent Application JP 2004-67536 20040310, 2005, 21 pp. (CODEN: JKXXAF JP 2005255443 A 20050922 (patent written in Japanese).).

(51) Uekatano, M.; Kashima, T.; Harada, K.; Moriyama, T. Manufacture of high-quality quartz glass for optical use, Jpn. Patent Application JP 2002-378405 20021226, 2004, 8 pp. (CODEN: JKXXAF JP 2004210548 A 20040729 (patent written in Japanese); Priority: CAN 141:127505; AN 2004: 605678.)

(52) Saito, S. Manufacture of optical glass, Jpn. Patent Application JP 85-221781 19851007, 1987, 4 pp. (CODEN: JKXXAF JP 62083324 A 19870416 (Showa Patent written in Japanese); Priority: CAN 107:45033; AN 1987:445033.)

(53) Hao, S.-Y. Synthesis of ultrafine CeO_2 by microwave-assisted heating and its polishing properties. *Wuji Huaxue Xuebao* **2008**, *24* (6), 1012.

(54) Lee, J. H.; Shin, D. S.; Seo, J. Apparatus for drying glass lenses by using microwave, Kor. Patent Application KR 2007-24014 20070312, 2008, 9 pp. (CODEN: KRXXA7 KR 2008083443 A 20080918 (patent written in Korean).)

(55) Minay, E. J.; Boccaccini, A. R.; Veronesi, P.; Cannillo, V.; Leonelli, C. Processing of novel glass matrix composites by microwave heating. *J. Mater. Process. Technol.* **2004**, *155−156*, 1749.

(56) Minay, E. J.; Veronesi, P.; Cannillo, V.; Leonelli, C.; Boccaccini, A. R. Control of pore size by metallic fibers in glass matrix composite foams produced by microwave heating. *J. Eur. Ceram. Soc.* **2004**, *24* (10−11), 3203.

(57) Veronesi, P.; Leonelli, C.; Pellacani, G. C.; Fiumara, V.; Barba, A. A.; D'Amore, M. Microwave assisted sintering of powder mixtures of glass and tungsten particles. *Mater. Eng.* **2002**, *13* (1), 65.

(58) Boccaccini, A. R.; Veronesi, P.; Siligardi, C.; Leonelli, C. Porous molybdenum particle reinforced glass matrix composites fabricated by microwave processing. *Key Eng. Mater.* **2002**, *206−213*, 317. (Part 1, Euro Ceramics VII.)

(59) Veronesi, P.; Leonelli, C.; Pellacani, G. C.; Boccaccini, A. R. Unique microstructure of glass-metal composites obtained by microwave assisted heat-treatments. *J. Therm. Anal. Calorim.* **2003**, *72* (3), 1141.

(60) Yoshikawa, N.; Wang, H.; Mashiko, K.-i.; Taniguchi, S. Microwave heating of soda−lime glass by addition of iron powder. *J. Mater. Res.* **2008**, *23* (6), 1564.

(61) Duval, D. J.; Terjak, M. J. E.; Risbud, S. H.; Phillips, B. L. Microwave melting of ion-conducting glasses. In *Microwave Processing of Materials V*; Materials Research Society Symposium Proceedings 430; Materials Research Society: Pittsburgh, PA, 1996; 125 pp.

(62) Duval, D. J.; Phillips, B. L.; Terjak, M. J. E.; Risbud, S. H. Reversible color changes and structural implications of microwave melting ion-conducting glasses. *J. Solid State Chem.* **1997**, *131* (1), 173.

(63) Fathi, Z.; Folz, D. C.; Clark, D. E.; Hutcheon, R. Surface modification of sodium aluminosilicate glasses using microwave energy: II. In *Microwaves: Theory and Application in Materials Processing II*; Ceramic Transactions 36; American Ceramic Society: Westerville, OH, 1993; p 333.

(64) Veinger, A. I.; Zabrodskii, A. G.; Tisnek, T. V.; Shchavelev, K. O.; Shchavelev, O. S.; Yakobson, N. A. Local superconductivity in nickel-containing glasses. *Fiz. Khim. Stekla* **1996**, *22* (6), 550.

(65) Kao, Y. H.; Mackenzie, J. D. Magnetite as a sintering aid for microwave consolidation of soda-lime glass. In *Microwaves: Theory and Application in Materials Processing*; Ceramic Transactions 21; American Ceramic Society: Westerville, OH, 1991; p 341.

(66) Park, S. S.; Jung, K. S.; Kim, B. W.; Lee, S. E.; Park, H. C. Microwave heating induced crystallization of $PbTiO_3$ from a PbO−B_2O_3−ZnO−TiO_2 glass joined to alumina. *Glass Technol.* **2002**, *43* (2), 70.

(67) Lee, S.-E.; Kim, B.-W.; Park, S.-S.; Park, H.-C. The study for the characteristics of microwave coupled V_2O_5−PbO−TeO_2 glass system. *Han'guk Seramik Hakhoechi (2000−2002)* **2001**, *38* (5), 438.

(68) Sivakumaran, K.; Nair, C. K. S. Fast synthesis of chalcogenide glasses of Se-Te-Sb system by microwave irradiation. *J. Phys. D: Appl. Phys.* **2005**, *38* (14), 2476.

(69) Honda, K. Formation of Ag aggregate on glass substrates using the microwave induction heating. *Trans. Mater. Res. Soc. Jpn.* **2006**, *31* (2), 303.

(70) Haowen, H.; Shufeng, Z.; Li, Q.; Xiao, Y.; Yi, C. Microwave-assisted deposition of uniform thin gold film on glass surface. *Surf. Coat. Technol.* **2006**, *200* (14−15), 4389.

(71) Kromka, A.; Rezek, B.; Remes, Z.; Michalka, M.; Ledinsky, M.; Zemek, J.; Potmesil, J.; Vanecek, M. Formation of continuous nanocrystalline diamond layers on glass and silicon at low temperatures. *Chem. Vapor Deposition* **2008**, *14* (7−8), 181.

(72) Marcinek, M.; Hardwick, L. J.; Richardson, T. J.; Song, X.; Kostecki, R. Microwave plasma chemical vapor deposition of nanostructured Sn/C composite thin-film anodes for Li-ion batteries. *J. Power Sources* **2007**, *173*, 965.

(73) Zumeta, I.; Ayllon, J. A.; Gonzalez, B.; Domenech, X.; Vigil, E. TiO_2 films obtained by microwave-activated chemical-bath deposition used to improve TiO_2-conducting glass contact. *Solar Energy Mater. Solar Cells* **2009**, *93* (10), 1728.

(74) Gressel-Michel, E.; Chaumont, D.; Stuerga, D. From a microwave flash-synthesized TiO_2 colloidal suspension to TiO_2 thin films. *J. Colloid Interface Sci.* **2005**, *285* (2), 674.

(75) Ren, C.; Zhong, B. Photocatalytic activity of nanometer TiO_2 thin films treated by UV light and microwave. *Huaxue Fanying Gongcheng Yu Gongyi* **2004**, *20* (4), 338.

(76) Vigil, E.; Saadoun, L.; Ayllon, J. A.; Domenech, X.; Zumeta, I.; Rodriguez-Clemente, R. TiO_2 thin film deposition from solution using microwave heating. *Thin Solid Films* **2000**, *365* (1), 12.

(77) Das, S.; Basu, D.; Datta, S.; Mukhopadhyay, A. K. Crystallization of glass coating by microwave heating. *Trans. Indian Ceram. Soc.* **2008**, *67* (3), 139.

(78) Das, S.; Mukhopadhyay, A. K.; Datta, S.; Das, G. C.; Basu, D. Hard glass-ceramic coating by microwave processing. *J. Eur. Ceram. Soc.* **2008**, *28* (4), 729.

(79) Irzh, A.; Gedanken, A. A microwave-assisted process for coating polymer and glass surfaces with semiconducting ZnO submicron particles. *J. Appl. Polym. Sci.* **2009**, *113* (3), 1773.

(80) Takizawa, I.; Nakayama, T.; Kashiwagi, K.; Sakamoto, Y. Thin film forming apparatus, JP 2005-267802 20050915, 2007, 10 pp. (CODEN: JKXXAF JP 2007077456 A 20070329 (patent written in Japanese).)

(81) Someno, Y.; Sasaki, M.; Hirai, T. Preparation and characterization of Si-Al-O-N protective films for a glass aspheric lens molding die. *Surf. Eng., [Pap. Int. Conf.]* **1993**, 115.

(82) Wang, C.; Wang, B.; Tao, Y.; Liu, H.; Ma, T. Preparation of indium oxide film on glass by sputtering deposition synchronously enhanced by microwave ECR plasma source ion-implantation. *Guisuanyan Tongbao* **2000**, *19* (2), 22.

(83) Boaz, P. T. Manufacture of water-thinned paint compositions having excellent adhesion to glass, and manufacture of formed glass sheets for automotive and architectural windows painted with the compositions. U.S. Patent Application 19971230, 1997, 7 pp. (CODEN: USXXAM US 5702520.)

(84) Ruiz Valdes, J. J.; Gorokhovsky, A. V.; Escalante García, J. I. Vitrification in the $BaO-B_2O_3-Al_2O_3-TiO_2$ system with small admixtures of PbO. *J. Non-Cryst. Solids* **2005**, *351* (24), 2036.

(85) Ruiz Valdes, J. J.; Gorokhovsky, A. V.; Escalante García, J. I.; Mendoza Suarez, G. Glass-ceramic materials with regulated dielectric properties based on the system $BaO-PbO-TiO_2-B_2O_3-Al_2O_3$. *J. Eur. Ceram. Soc.* **2004**, *24* (6), 1505.

(86) Gorokhovsky, A. V.; Escalante García, J. I.; Mendoza Suarez, G.; Ruiz Valdes, J. J. Synthesis of glass-ceramic materials in the system $BaO-PbO-B_2O_3-Al_2O_3-TiO_2$. *Glass Phys. Chem.* **2002**, *28* (6), 417.

(87) Wu, S.; Wang, F.; He, L. Chin. Patent Application CN 2004-10013562 20040218, 2005, 6 pp. (CODEN: CNXXEV CN 1559943 A 20050105 (patent written in Chinese).)

(88) Zaitsev, D. D.; Kazin, P. E.; Vanetsev, A. S.; Ivanov, V. K.; Tret'yakov, Yu. D.; Jansen, M. Synthesis of magnetic glass ceramics based on strontium hexaferrite by microwave heating. *Dokl. Chem.* **2005**, *402* (1), 69.

(89) Chaim, R.; Goldstein, A.; Eldror, I.; Gurman, A. Fabrication and plastic deformation of Y-TZP/alumina nanocomposite ceramics containing oxynitride glass. *J. Mater. Sci.* **2005**, *40* (1), 187.

(90) D'arrigo, M. C.; Siligardi, C.; Leonelli, C.; So, J. Y.; Kim, H. S. Evolution of Macropores in a Glass-Ceramic Under Microwave and Conventional Sintering. *J. Porous Mater.* **2003**, *9* (4), 299 Volume Date 2002.

(91) Siligardi, C.; D'Arrigo, M. C.; Leonelli, C.; Pellacani, G. C. Bulk crystallization of glasses belonging to the calcia−zirconia−silica system by microwave energy. *J. Am. Ceram. Soc.* **2000**, *83* (4), 1001.

(92) Siligardi, C.; Barbieri, L.; Corradi, A. B.; Leonelli, C.; De Sanctis, M.; Lazzeri, A. Color development during devitrification in $Li_2O-ZnO-Al_2O_3-SiO_2$ glasses under conventional and microwave heating. *Phys. Chem. Glasses* **2000**, *41* (2), 81.

(93) Wu, N.; Wang, Z.; Li, C.; Lu, G.; Lin, S. Microwave sintering of hydroxyapatite−glass composite ceramics. *Guisuanyan Tongbao* **2006**, *25* (4), 54–58.

(94) Viessmann, H. Method and device for making heat insulating fire-resistant plates from perlite/glass fiber composite. Eur. Patent Application EP 2001-116557 20010709, 2002, 9 pp. (CODEN: EPXXDW EP 1172346 A2 20020116 (patent written in German).)

(95) Chen, L.; Leonelli, C.; Manfredini, T.; Siligardi, C. Processing of a silicon-carbide-whisker-reinforced glass-ceramic composite by microwave heating. *J. Am. Ceram. Soc.* **1997**, *80* (12), 3245.

(96) Boccaccini, A. R.; Veronesi, P.; Leonelli, C. Microwave processing of glass matrix composites containing controlled isolated porosity. *J. Eur. Ceram. Soc.* **2001**, *21* (8), 1073.

(97) Lewis, D. A.; Shaw, J. M. Manufacture of multilayer ceramic substrates by microwave heating. Eur. Patent 538663, 1993, 11 pp. (CODEN: EPXXDW EP 538663 A1 19930428.)

(98) Ravaev, A. A.; Pan, E. G.; Khomenko, A. I.; Esakov, I. I.; Bogdanov, A. G.; Kolmakov, A. G.; Ivanov, V. A.; Konyzhev, M. E. Features of firing the metal-ceramics structures in fields of power microwave radiation. *Prikl. Fiz.* **2006**, (6), 108.

(99) Ghatak, S.; Mukhopadhyay, A. K.; Adikari, K.; Mandal, S.; Seal, A.; Samanta, A. K.; Phani, K. K.; Maiti, H. S. Microwave heating and nucleating agent-containing glass powder additive in improved process for making sintered silicon carbide composites. Indian Patent Application IN 2000-DE162 20000225, 2008, 12 pp. (CODEN: INXXBQ IN 2000DE00162 A 20080801 (patent written in English).)

(100) Outifa, L.; Jullien, H.; Delmotte, M. The microwave curing of large size epoxy-glass composite samples: How to make it homogeneous. *Polym. Mater. Sci. Eng.* **1992**, *66*, 424.

(101) Vincent, J. J.; Boen, R.; Cartier, R.; Silve, J. M.; Choudhary, M. K. In *Proceedings of the XVIII International Congress on Glass*, San Francisco, CA, July 5−10, 1998; 259 pp.

(102) Vasil'ev, A. V.; Sibirtsev, S. N.; Nazarov, A. V. Investigations of the microwave electromagnetic properties of pulp with fluxing additives. *At. Energ.* **2001**, *91* (6), 1003.

(103) Otsuka, K.; Aikawa, H.; Tamai, H. Solid glass disposal method for radioactive waste sodium compound, Jpn. Patent 61013196, 1986, 4 pp. (CODEN: JKXXAF JP 61013196 A 19860121.)

(104) Maeshima, T.; Mizuno, S.; Yoshihara, M.; Tamai, M.; Yamashita, N.; Sano, M.; Matsubara, Y.; Kawahigashi, T. Studies on the utilization of powdery waste materials. VI. Utilization of powdery waste material treated by microwave. *Kinki Daigaku Kankyo Kagaku Kenkyusho Kenkyu Hokoku* **1983**, *11*, 165.

(105) Forsstroem, W. Method and apparatus for affixing difficult to bond elements by irradiation with microwaves, PCT International Patent Application WO 90-EP2012 19901119, 1992, 26 pp. (CODEN: PIXXD2 WO 9208762 A1 19920529 (patent written in English); Priority: CAN 117: 152366; AN 1992:552366.)

(106) Meek, T. T.; Blake, R. D. Ceramic−glass−metal seal by microwave heating, U.S. Patent Application US 83-538889 19831004, 1984, 10 pp. (Avail. NTIS Order No. PAT-APPL-6-538 889. CODEN: XAXXAV US 538889 A0 19840914 (patent written in English); Priority: CAN 101: 196980; AN 1984:596980.)

(107) Meek, T.; Blake, R. D. Ceramic−glass-ceramic seal by microwave heating, U.S. Patent Application US 83-538890 19831004, 1984, 8 pp. (Avail. NTIS Order No. PAT-APPL-6-538 890. CODEN: XAXXAV US 538890 A0 19840914 (patent written in English); Priority: CAN 101:196979; AN 1984:596979.)

(108) Vandal, R. A. Apparatus and method for bending glass using microwaves, U.S. Patent 7,140,204 B2, 2006.

(109) Sklyarevich, V. E. Method of manufacturing curved glass using microwaves, PCT International Patent WO 2006/088892 A3, 2006.

(110) Boaz, P. T. Method for heating and forming a glass sheet. U.S. Patent 5,656,053, 1997.

(111) Boaz, P. T. Method for heating a glass sheet, U.S. Patent 5,782,947, 1998.

(112) Sklyarevich, V. E.; Shevelev, M. Method for rapid thermal treatment of glass and glass-like materials using microwave radiation. U.S. Patent 6,408,649 B1, 2002.

(113) Sklyarevich, V. E.; Shevelev, M. Method for laminating glass sheets by microwave radiation. PCT International Patent WO 2005/067527 A2, 2005.

(114) Sklyarevich, V.; Shevelev, M. Method for laminating glass sheets using microwave radiation. U.S. Patent Application 2004-802626 20040317, 2005. (CODEN: USXXCO US 2005150586 A1 20050714 (patent written in English); Priority: US 2004-536338 20040113.)

(115) Sklyarevich, V. E.; Shevelev, M. Method and apparatus for laminating glass sheets. PCT International Patent WO 2005/048464 A2, 2008.

(116) Van Stralen, M. J. N.; Swarts, M. J.; Marinus, J. Low-pressure plasma deposition of silica glass layers on the surface of rod-like preforms using two microwave generators. PCT International Patent Application WO 2002-NL610 20020923, 2003, 12 pp. (CODEN: PIXXD2 WO 2003029158 A1 20030410; Priority: NL 2001-1019076 20011001.)

(117) *Microwave Processing of Materials*, National Materials Advisory Board Publication NMAB-473; National Academy Press: Washington, DC, 1994; 164 pp.

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