Journal of the Ceramic Society of Japan 116 [11] 1175-1181 2008 Review

Eco-friendly processing and methods for ceramic materials – A review

Cihangir DURAN,[*,] Kimiyasu SATO,[*] Yuji HOTTA,[*] Takaaki NAGAOKA[*] and Koji WATARI[*]**

[*]**National Institute of Advanced Industrial Science and Technology (AIST), 2266−98, Anagahora, Shimoshidami, Moriyama-ku, Nagoya-shi, Aichi 463−8560**

[**]**Gebze Institute of Technology, Department of Materials Science and Engineering, P. K. 141, 41400, Gebze-Kocaeli, Turkey**

Restrictions regarding waste disposal and strict environmental regulations require eco-friendly technologies. Organics such as binders are used extensively in green body fabrication but they must be eliminated and/or decreased due to global problems because during heat treatment carbon dioxide and other hydrocarbon emissions take place after organic decomposition. If it is possible to remove these polymers fully or partially before heat treatment, then harmful gas evolution to the atmosphere can be eliminated and/or controlled. In the cases where the organic usage is imperative, they must be replaced with the low-toxic or non-toxic ones because toxic substances pose the greatest threat to human beings and the environment. It is also important to recycle the wastes from various sources in order to save energy. This paper reviews the efforts to find or explore new eco-friendly processes, modifications and chemical methods in order to replace currently used ones from the viewpoint of sustainable development.

©2008 The Ceramic Society of Japan. All rights reserved.

Key-words : Eco-friendly processing, Organics, Toxicity, Inorganic binder

[Received March 31, 2008; Accepted September 11, 2008]

1. Introduction

Our world is experiencing tremendous environmental problems due to hazardous wastes, contaminated groundwater and air. Extensive research is carried out to discover new advanced analytical, biochemical, and physicochemical methods to characterize and eliminate hazardous chemical compounds from air, soil, and water.[1)] Restrictions regarding waste disposal and strict environmental regulations also require eco-friendly technologies.

Organic polymers (e.g., binders, dispersants, etc.) are used in green body fabrication and they must be removed prior to sintering. However, carbon dioxide and other hydrocarbon emissions take place after decomposition during heat treatment.[2),3)] CO_2 is believed to be one of the greenhouse gases responsible for global warming, while emitted hydrocarbons can be harmful. Current trend is to eliminate or decrease the amount of organic additives due to such global environmental problems. If strong bonding in the green state is achieved (by either interaction between polymers[4),5)] or development of organic binder-free methods[6)–8)]), then it may be possible to eliminate polymer pyrolysis stage. If organics (or inorganic) chemicals are to be used, they must be either low toxic or non-toxic, for example, replacing neurotoxin acrylamide monomer with a low-toxicity polyvinyl pyrrolidone in gel casting[9)] or usage of water in processing rather than organic-based solvents such as alcohols and ketones, etc.[10)–13)]

Large quantities of wastewater including dyes, detergents, and chelating agents are produced due to dyeing and finishing operations. Although these effluents can be treated by coagulation, adsorption on activated carbon, etc.,[14),15)] the method of Advanced Oxidation Processes (AOP's) was proposed to be a potential application for the removal of color, using TiO_2 and ZnO ceramics due to their photocatalytic ability under UV light irradiation.[1),16)–21)] In addition to the water contamination, huge amounts of domiciliary solid waste generated everyday and disposed mostly by dumping cause a serious environmental problem. Works have been carried out on the feasibility of reusing by recycling and recovering energy by incineration from the domiciliary and industrial wastes such as glasses and glass-ceramics[22)] and high-mullite refractory bodies.[23),24)]

Ceramic green bodies must be treated at high temperatures to facilitate bonding among the individual powders and to induce enough strength required during service. Low temperature sintering is a great asset particularly in controlling the microstructure evolution because physical properties are directly related to density and microstructure, and further in lowering the operational costs. Therefore, new methods based on powder synthesis, sintering, etc. were developed at aiming to lower the sintering temperature. For example, introduction of a simple ball milling step during hydrothermal reaction yielded powders which did not require the calcination/grinding steps for phase formation/particle size reduction and caused a significant drop as much as 400°C in sintering temperature of $BaTiO_3$ ceramics.[25),26)]

Eco-friendly methods must be sought in order to minimize and/or eliminate toxic materials and organic contents during processing to circumvent harmful gas evolution, to eliminate potential hazards of toxicity, to recycle the wastes generated everyday and also to save energy and time. In this review, novel and modified processing methods together with their results are presented. Our recent studies performed at AIST (Japan) as well as other representative studies in literature will be summarized.

2. Reducing or eliminating organics in green bodies

Polymers such as binders, dispersants, plasticizers, etc. are used in forming green bodies.[2),3)] However, the removal of the organics from green bodies requires heating for a long time due to very low heating rate not to cause cracking, which subsequently reduces the production rate. During heat treatment carbon dioxide and other hydrocarbon emissions take place after

organic decomposition. If it is possible to remove these polymers fully or partially before heat treatment, then harmful gas evolution to the atmosphere can be eliminated and/or controlled. Generally, polymers are preferentially used in order to form green body shape, as in the case of tape casting, slip casting, extrusion, etc. Therefore, in order for polymers to be removed from the system without using heat, powders in the green state must have some sort of a strong bonding to each other so as not to lose its shape and have enough strength for further processes. If strong bonding in the green state is achieved (by either interaction between polymers or development of organic binder-free methods), then it is possible to save energy by eliminating polymer pyrolysis stage, to eliminate harmful gas evolution and to lower operational costs down.

Duran et al.[4] and Sato et al.[5] attempted covalently connecting SiO_2 powders in the green state using water-based colloidal methods. In those studies, SiO_2 powders were first coated with 3-aminopropyltriethoxysilane (3APS; $NH_2C_3H_6Si(OC_2H_5)_3$) and then connected each other using polycarbodiimide by means of organic covalent bonding upon heating to 100°C.[4),5)] **Figure 1** shows attachment of amino groups onto the SiO_2 surfaces.[4] They reported that 3APS reacted with silanol groups (–Si–OH) on the surface of SiO_2 particles because the silanol groups acted as reaction sites to anchor other organic molecules.[5] The polycarbodiimide has reactive carbodiimide segments (–N=C=N–) and water-attracting oxyethylene segments ($–C_2H_4O–$). A carbodiimide can react with an amino group ($–NH_2$) to form guanidine structure upon heating.[27] **Figure 2** shows FTIR spectra of the samples dried at 100°C for 1 d and 6 d. The binding mechanism upon heating between –N=C=N– and $–NH_2$ already attached on SiO_2 is also depicted. Presence of a sharp carbodiimide band at 2117 cm^{-1} indicated that the covalent bonding between SiO_2 particles was not complete after drying for 1 d (Fig. 2a). However, this band totally disappeared after drying for 6 d (Fig. 2b), stating that organic covalent bonding was complete. Then, shape stability and the degree of polymer dissolution in water were tested by keeping the green samples in water for 1 week. They observed that the sample without heat-treated at 100°C was totally disintegrated very quickly in water, while the sample kept for 6 days at 100°C retained its original shape without any disintegration or peeling off. The sample dried at 100°C for 1 d, however, had some peeling off from the sharp edges and disintegration from the top layers due to incomplete covalent bonding. Thermogravimetric analysis revealed that the sample without water-soaking had 14% relative weight lost as compared to 11% for the water-soaked sample.[4] They concluded that this new water-based approach helps eliminate the usage of organic solvent during processing and decreases the emission of harmful gases evolved during polymer pyrolysis by dissolving excess polymers into water in the green state.

Shirai et al.[6] reported a novel binder-free formation method to manufacture mechanically strong Al_2O_3 green bodies with excellent shape retention. Calcination and grinding steps may induce irregular crystal structure phases on the surface of α-alumina powders, which can generate surface hydroxide species as a mixture of aluminum trihydroxide polymorphs such as bayerite, gibbsite, and nordstrandite.[28)–32)] Microwave irradiation was applied to a green body to enhance strong hydration reaction between water and particle surfaces, which, then, resulted in creation of surface aluminum trihydroxide structures of adjacent particles bounded together tightly. Aluminum trihydroxide behaved as an inorganic binder. They proposed that this new technology makes it possible to fabricate mechanically strong

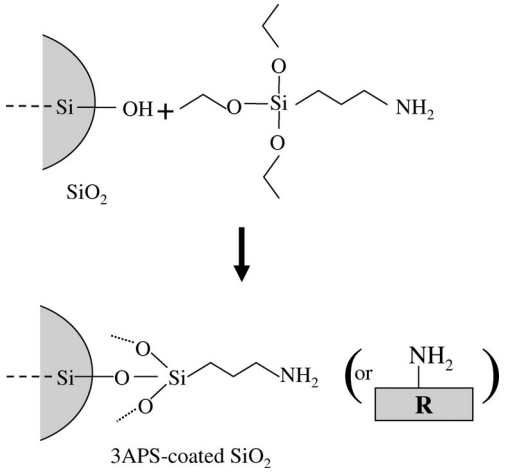

Fig. 1. Attachment of amino groups onto the SiO_2 surfaces.

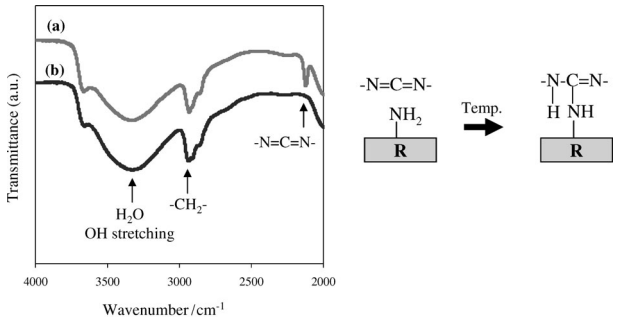

Fig. 2. FTIR spectra of the samples dried at 100°C for (a) 1 d and (b) 6 d. Binding mechanism between –N=C=N– and $–NH_2$ on SiO_2 upon heating is also depicted.

compacts with excellent shape retention without an organic binder and to produce a high-quality sintered ceramics.[6]

Conventional extrusion technique requires the use of organic substances to impart flowability and rigidity during the fabrication of green ceramics.[33)–35)] Ceramic bodies with inorganic binder boehmite had suitable flowability and rigidity for extrusion.[36)–38)] Boehmite has good compatibility with the alumina but it requires complicated processes such as adjusting the pH for dispersion and centrifugation and/or filtration to remove excess water. Hydraulic alumina was recently proposed as an inorganic binder for extrusion.[7),8)] It has unique properties such as rehydration and self-binding.[39)–41)] Nagaoka et al.[7),42)] studied extrusion of Al_2O_3 ceramics without using an organic binder. They used hydraulic alumina (HA) (mixture of ρ-Al_2O_3 and χ-Al_2O_3 powders) as an inorganic binder and α-alumina. Organic binder methyl cellulose (MC) was also used for comparison. The ratio of 80:20:35 by weight for α-Al_2O_3:HA:Water system and 100:2:22 by weight for α-Al_2O_3:MC:Water was determined to be the conditions for crack-free extrusion process.[7),42)] The curing period for HA-containing pastes was found to be important because composition and state of paste (e.g., softness/hardness of the green paste) changed with time.[8),42)] The main phase of HA is ρ-Al_2O_3 and its hydration yielded the formation of bayerite ($Al_2O_3.3H_2O$) and boehmite gel ($Al_2O_3.1–2H_2O$) as determined by XRD after 4 d curing period. Boehmite gel formed a three dimensional network during hydration and this network become more densely packed with the curing time, which resulted in the

Table 1. Physical Properties as a Function of Composition and Sintering Temperature

Sample composition	Sintering conditions	Relative density, %	Young's modulus, GPa	Hardness, H_V
α-Al_2O_3:MC:Water = 100:2:22	1500°C -2 h	96	368	1731
	1525°C -2 h	97.4	379	1893
	1550°C -2 h	98.7	388	2045
α-Al_2O_3:HA:Water = 80:20:35 (cured for 2 days)	1550°C -2 h	95.8	–	–
	1600°C -2 h	97.5	381	2012
α-Al_2O_3:HA:Water = 80:20:35 (cured for 4 days)	1500°C -2 h	89.8	–	–
	1550°C -2 h	93.7	332	1552
	1600°C -2 h	97.2	383	2050

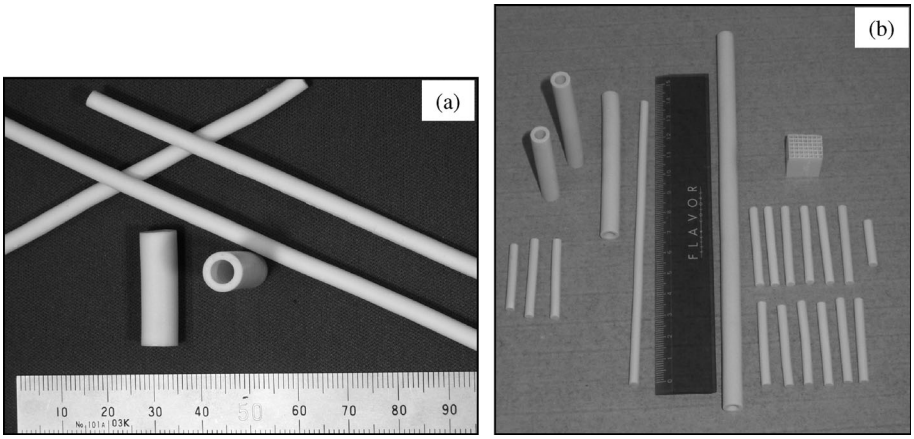

Fig. 3. Al_2O_3 rods and tubes fabricated using (a) inorganic binder HA (sintering condition is 1600°C for 2 h) and (b) organic binder MC (sintering condition is 1550°C for 2 h).

hardening of the green paste.[42] **Table 1** summarizes some physical properties of the ceramics as a function of composition and sintering temperature. For each set, density increased with increasing sintering temperature and reached ≥ 97% density. However, γ-Al_2O_3 formation in the HA samples[43),44] increased the temperature at which ceramics densify. Mechanical properties of the samples increased parallel with the densification. The Young's modulus and Vickers hardness values are almost the same, that is, Young's modulus > 380 GPa and H_V > 2000 are obtained regardless of the use of organic or inorganic binder.[7] **Figure 3** shows Al_2O_3 rods and tubes fabricated using inorganic binder HA and organic binder MC. They proposed that crack-free ceramics could be fabricated at any length and thickness by extrusion without using organic binder.

3. Organic and inorganic substances with low toxicity or non-toxic

Restrictions regarding waste disposal and strict environmental regulations require eco-friendly technologies. As explained above, organics used in green body fabrication must be eliminated or decreased due to global problems. However, in some applications, organic usage is imperative. Therefore, if organics (or inorganic) chemicals are to be used, they must be either low toxic or non-toxic. By this way, one can still have a chance to decrease the potential hazards. Cai et al.[9] searched for a low or nontoxic gel-forming system which yields rheological (i.e., low-viscosity slurry with high solid loading) and mechanical properties (i.e., high green strength) similar to the acrylamide-based system. Gel casting is a novel green body formation technique consisting of in-situ polymerization of acrylamide monomer. This technique offers near-net-shape forming, high green strength and low binder concentration.[45] However, acrylamide monomer is a neurotoxin which limits its wide-spread use. Therefore, Cai et al.[9] reported HEMA (2-hydroxyethyl methacrylate) as a new monomer. In order to ensure high green strength and reliability, the system was modified with a low-toxicity polyvinyl pyrrolidone (PVP). HEMA-PVP system was found to improve microstructure and strength homogeneity together with the elimination of surface exfoliation. **Figure 4** shows that there happens peel off from the top section as well as shape distortion in the absence of PVP (Fig. 4a), while, in the of PVP-HEMA case, there is no exfoliation with very good shape retention (Fig. 4b).

Another important issue is to establish water-based methods rather than organic-based ones such as alcohols, ketones, or hydrocarbons during processing because of the volatility and toxicity of organic solvents. For example, thin ceramic sheets are extensively fabricated by tape casting to be used in solid oxide fuel cells and multilayer capacitors.[46),47] In the production of these technologically important ceramic sheets, it is also imperative to prepare agglomerate-free slurries because they are produced at large volumes. Although water-based slurries have some drawbacks such as lower particle settling rate, difficulty in attaining higher solid loadings and higher crack sensitivity, aqueous processing is safe, eco-friendly and cost-effective.[48),49] Isobe et al.[10] prepared water-based casting slurries containing nano Al_2O_3 powders. They used wet-jet milling to efficiently disperse the flocculated particles, which resulted in attainment of low viscosity at high solid loadings (e.g., 30 vol%) as compared to the

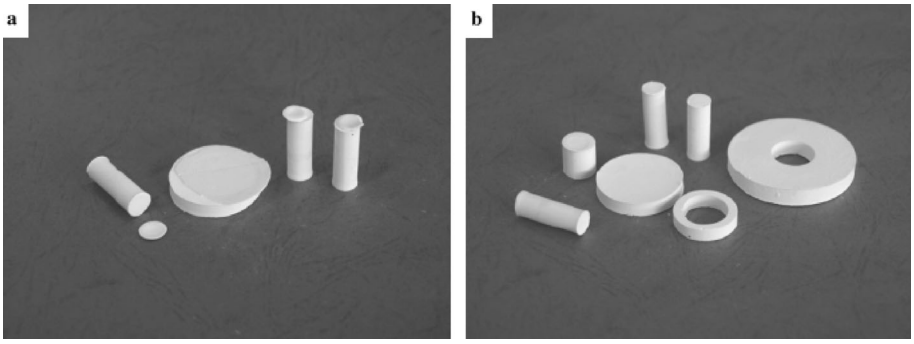

Fig. 4. Green alumina ceramics prepared by two different systems (a) acrylamide and (b) HEMA–PVP.

one prepared by ball milling. The resulting sheets were fabricated to be crack-free without any warping in the case of wet-jet milling method. Zhang et al.[49] studied aqueous processing of SiC green sheets and reported successful preparation of slurries with high solid loadings up to 50 vol%. Luo et al.[11] prepared AlN green sheets by aqueous tape casting. AlN is a very important advanced material due to its high thermal conductivity, high electrical resistivity, low dielectric constant, non toxicity and close thermal expansion coefficient to silicon.[12] However, it is very difficult to make aqueous processing of AlN due to hydrolysis reaction of aluminum nitride.[13] Therefore, AlN surface must be modified such that this hydrolysis reaction can be prevented. Luo et al.[11] applied a kind of ester of polyacrylate both to modify the powder surface and have a good dispersion for a stable tape casting slurry. Similar water-ceramic interaction is observed in aqueous processing of $BaTiO_3$ powders because Ba^{2+} dissolves towards the acidic region.[50] Therefore, well-dispersed powders in water were prepared by carefully selecting the dispersant and adjusting pH towards the alkaline region such that Ba^{2+} dissolution and stoichiometry change were successfully eliminated.[51]

Lead-containing compounds, as cited by the Environmental Protection Agency (EPA) of the US, is one of the top 17 chemicals posing the greatest threat to human beings and the environment.[52] Lead oxide is one of the main constituents of well-known piezoelectric ceramics such as $Pb(Zr,Ti)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$. These ceramics are the most important piezoelectric materials that are being widely used in various fields for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric and electromechanical properties.[53)–56] However, the toxicity of lead oxide and its high vapor pressure during powder synthesis and heat treatment causes environmental pollution. This necessitates that eco-friendly lead-free piezoelectric materials are urgently demanded to replace currently used ones from the viewpoint of sustainable development. Therefore, manufacturers are more and more compelled to decrease and/or eliminate the lead in their compositions. Research on lead-free piezoelectric materials has been mainly focused on alkali niobates, modified alkali bismuth titanates, and systems with a morphotropic phase boundary (MPB) (e.g., a boundary where two phases occurs simultaneously).[53),57)–60] Importance of the presence of a MPB is that dielectric and piezoelectric properties are enhanced considerably near MPB due to increased numbers of available polarization directions.[55] Therefore, solid solutions comprised of tetragonal titanates such as $PbTiO_3$, $BaTiO_3$ or $K_{0.5}Bi_{0.5}TiO_3$ to make MPB's has been suggested as excellent candidates for low-lead or lead-free piezoelectric materials.[61)–65] Recently, Saito et al.[66] reported that a high piezoelectric charge coefficient ($d_{33} = 416$ pC/N) constant was obtained in textured $(Na,K)NbO_3$-based ceramics close to a MPB. This value is comparable to extensively used $Pb(Zr,Ti)O_3$ ceramics. This work again confirmed the potential of $(Na,K)NbO_3$ ceramics as a promising candidate for lead-free piezoelectric ceramics. Pursuits to fabricate lead-free piezoceramics are note-worthy, but, in some of the critical applications such as underwater acoustic devices like sonars and transducers, lead-based ceramics are still dominantly used. Therefore, studies on lead-free piezoelectric ceramic must continue to eliminate the lead totally in the end-products.

4. Cleaning of wastewater by semiconductors

Large quantities of wastewater including dyes, pesticides, detergents, and organic compounds, chelating agents and other contaminants are produced due to dyeing and finishing operations, which can be categorized as high levels of total organic content and color. These effluents can be treated such methods as coagulation, adsorption on activated carbon, chemical oxidation, and biological treatment.[14),15] The method of Advanced Oxidation Processes (AOP's) was proposed to be a potential application for the removal of color. Among AOP's, heterogeneous metal oxide semiconductors such as TiO_2 and ZnO have been applied to a variety of environmental problems due to their photocatalytic ability under UV light irradiation.[1),16)–21] Most of the time, metal oxides are used in powder form rather than monolithic ceramics, but it requires separation from the bulk fluid after treatment by filtration, centrifugation, or coagulation and flocculation, which decreases economical viability due to additional operation and causes powder loss as well. Therefore, researchers have focused on immobilization of semiconductor powders on a self-supported substrate so as to use them in consecutive multiple photodegradation processes.[67),68] This process has some drawbacks, most notably, low surface area-to-volume ratio as compared to the direct usage of powders. Yassitepe et al.[67] fabricated self-supported semiconductor ZnO plates by tape casting method and adjusted specific surface area (or porosity) of the plates by changing the sintering temperature (i.e., 700°C vs. 1050°C). Efficiency of the plates were tested for Remazol Brilliant Orange 3R (RO 16, C.I. Reactive Orange 16) and Remazol Brilliant Red F3B (RR 180, C.I. Reactive Red 180) dyes. **Figure 5** shows that efficiency of the plates sintered at 700°C is about 95% for RR 180 and 88% for RO 16, as compared to about 8% for RR 180 and 10% for RO 16 for the plates sintered at 1050°C due to highly porous microstructure of the former. They concluded that semiconductor plates, rather than powders, prevented the costly and time consuming removal and recycling processes of the powders, and also gave the advantage of re-use of the plates repeatedly while eliminating the color and degrading the dye molecules.[67]

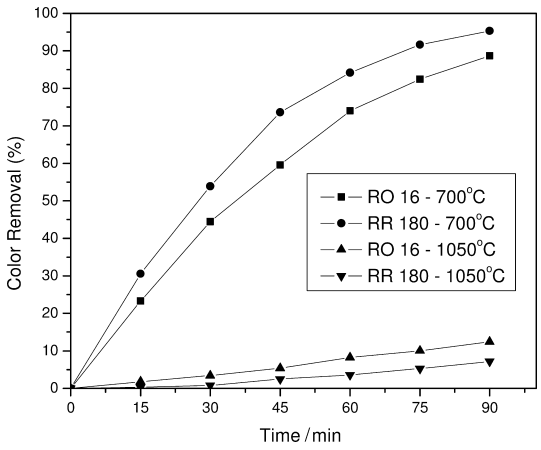

Fig. 5. Color removal efficiency of the plates sintered at 700°C and 1050°C. RO 16 and RR 180 stand for Remazol Brilliant Orange 3R (C.I. Reactive Orange 16) and Remazol Brilliant Red F3B (C. I. Reactive Red 180) dyes, respectively.

5. Low temperature sintering

Solid-state synthesis is mostly applied in powder synthesis, but it has some disadvantages such as a large particle size, wide particle distribution, agglomeration and high impurity content due to calcination and grinding steps.[69] Calcination can cause the formation of hard agglomerates with poor particle shape control. In such instances, grinding is required during which contamination may take place. In addition, calcination and grinding steps put additional costs. Chemical methods such as sol–gel, coprecipitation and hydrothermal, enable us to synthesize uniformly-sized powders with better particle shape control, but, most of the time, calcination step is again required except for the hydrothermal method. Elimination of calcination and grinding steps lower the processing costs, and at the same time, allows the possibility of lower temperature sintering. It is very important to sinter ceramics at temperatures as low as possible in order to control microstructural evolution such as attaining uniform grain size and to save time and energy.

Various studies were performed for low temperature processing of ceramics. Xu et al.[70] demonstrated that a nano-Si_3N_4/5 mass% nano-C composite could be fabricated by a novel method, that is, high-energy ball milling followed by spark plasma sintering. The milling promoted the amorphization of the starting powders, resulting in a low sintering temperature and a rapid densification rate. Milled powders were densified fully at 1600°C, as compared to 1780°C under a compressive stress of 30 MPa. The hardness was found to be comparable with that of conventional Si_3N_4 whereas Young's modulus was significantly decreased. Similar results were obtained in Si_3N_4-based ceramics using high energy milling.[71] Gravity of acceleration was set to 110 G during milling, which also resulted in the amorphization of the starting powder in a very short time. Highly dense ceramics sintered at a temperature as low as 1600°C for 1 h without applying any external force were obtained with comparable mechanical properties with the hot-pressed ones. These new processing methodologies using a simple milling step result in a huge temperature decrease (e.g., saving energy) and elimination of pressure during sintering.

Hotta et al.[25),26)] recently developed a novel method to perform low-temperature sintering of functional ceramics. They synthesized nano $BaTiO_3$ powders by a modified hydrothermal process. They introduced ball milling during the reaction to control the growth of solid phase by mechanical action. Ball milling during the reaction induced enhanced densification at 900°C[25)] as compared to the condition without ball milling (**Fig. 6**), due to the expanded lattice and strain formation in the synthesized particles (e.g., broken bonds caused by surface damage on each particle), which causes enhanced sinterability by introducing an additional driving force for sintering.[72)–74)] Besides, this temperature is much lower than that solid-state synthesized $BaTiO_3$ powders

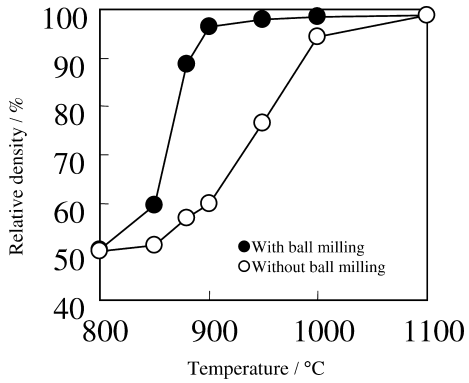

Fig. 6. Densification as a function of sintering temperature and synthesis condition.

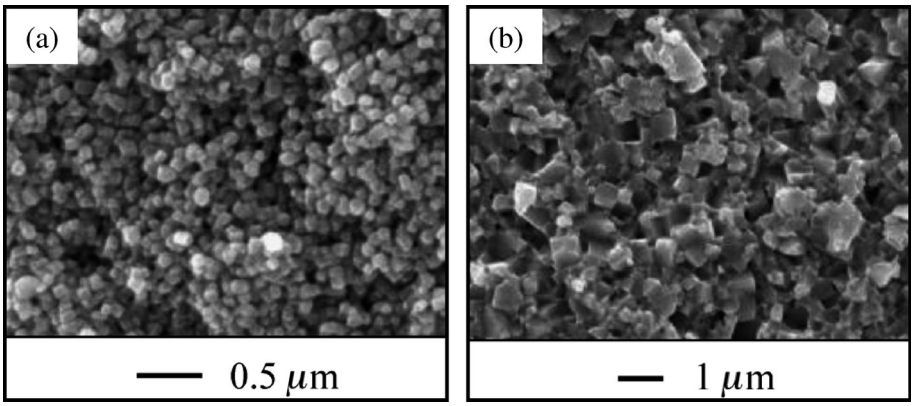

Fig. 7. Fracture surfaces of the samples sintered at 900°C; prepared using (a) without and (b) with ball milling system.

densify (e.g., above 1300°C). **Figure 7** compares the fracture surfaces of the samples sintered at 900°C as a function of reaction condition. Enhanced densification due to ball milling during the synthesis allows achievement of uniform microstructure evolution (e.g., grain size is around 0.5 μm) (Fig. 7b). Smaller grain size and dense microstructure[73)–75)] resulted in enhanced dielectric properties such that the dielectric constant was found to be near 4500 at room temperature and 1 kHz, which is among the highest in the literature for a pure $BaTiO_3$ ceramics obtained by conventional sintering. Therefore, enhanced permittivity can be attributed to higher density and smaller grain size due to low temperature sinterability of $BaTiO_3$ powders. Low-temperature sintering of ferroelectric ceramics, particularly below 1000°C, yields economical benefits for the sake of saving energy (i.e., efficient use of resources) as well as some processing easiness such as co-firing of multilayer capacitors and piezoelectric ceramics, replacing platinum and palladium electrodes with the relatively inexpensive silver or copper ones.

6. Recycle and reuse of materials

Developed countries face with a major problem due to huge amounts of domiciliary solid waste generated everyday and disposed mostly by dumping, which causes serious environmental problem. Some amount of this waste can be re-used by recycling (e.g., selection and classification of the waste materials) and the other non-recyclable amount can be recovered as energy by incineration.[22)] Romero et al.[22)] studied the feasibility of recycling fly ashes from domiciliary waste incineration by producing glasses and glass-ceramics. They found that the main crystalline phase in the resulting glass-ceramic was $Ca_2MgSi_2O_7$ with some TiO_2 and $TiSi_2$ forming in the later stages of heat treatment. They suggested that mechanical properties and erosion resistance were superior to the other glasses produced from fly ashes, and thus could be used in applications such as tiles for the building industry and places where erosion resistance was required. Gorokhovsky et al.[76)] reported that combination of different industrial wastes can be used to produce high quality pyroxene glass-ceramics without the addition of any admixtures of nucleation agents. They have shown that oil shale ash from heat power stations consisted of the crystalline phases and the slurry from phosphorous fertilizer production behaved as nucleating agents. It is very important to convert industrial wastes into pyroxene glass-ceramics because these glass-ceramics are promising materials to be used in construction industry for facing materials due to its high mechanical and chemical properties and low manufacturing cost.[77)] Bossert et al.[78)] fabricated glass-ceramics using fly-ash from coal power stations and waste glass of TV monitors, windows and flask glass. They improved bending strength from 12 to 56 MPa and E-modulus from 6 to 26 GPa at 50% waste TV glass and 50% fly ash mixture. Barbieri et al.[79)] reported the possibility of recovering the steel ash both as a starting material in glass and glass-ceramic formulations and as coloring agent in place of a pure iron oxide into a colorless base system. Costa Oliveira et al.[23),24)] proposed economically feasible recycling of both slate sludge and aluminum-containing residues to produce high-mullite refractory bodies. Although the optimum sintering window was found to be narrow (± 25°C) within the range of 1425–1450°C and large shrinkage rate (up to 30%), recycling of such wastes was suggested as an environmentally friendly recycling method as well as low-cost ceramic products to be used in the construction or foundry sectors. There are some similar works reported in literature[80)–82)] regarding how to recycle or reuse the wastes from various sources towards a cleaner and safer world at the same time saving energy.

7. Conclusions

Many chemicals and organics with some degree of toxicity or hazard to our world were used in many processing. Researches were focused on eliminating or decreasing the toxicity because they pose the greatest threat to human beings and the environment, and thus must be either totally eliminated or replaced with the low-toxic or non-toxic ones. For example, neurotoxin acrylamide monomer commonly used in gel casting was replaced with low-toxic 2-hydroxyethyl methacrylate - polyvinyl pyrrolidone system. This new system was found to improve microstructure and strength homogeneity together with the elimination of surface exfoliation, resulting in very good shape retention.

Strong bonding, induced by using organic or inorganic binders, yields green compacts with excellent shape retention, which allows green machining, saves time and lowers the operational costs. For example, silanol groups on the SiO_2 surfaces were modified with 3-aminopropyltriethoxysilane and then polycarbodiimide bounded SiO_2 particles tightly by covalent bonding upon heating. Amount of polymers used in fabrication was decreased by water dissolution without distorting the shape, giving rise to a relatively lesser amount of organics to be removed during polymer pyrolysis. In extrusion of alumina bodies, organic binder was successfully replaced with inorganic binder. Samples fabricated using organic and inorganic binders reached relative density ≥ 97%, Young's modulus > 380 GPa and H_V > 2000.

Eco-friendly processing and energy-saving procedures (e.g., recycling) have been applied to various systems. This paper reviews the efforts to find or explore new eco-friendly processes, modifications and chemical methods in order to replace currently used ones. In summary, one must strive hard in order to find environmentally benign production technologies from the viewpoint of sustainable development and much safer world.

References

1) M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemannt, *Chem. Rev.*, **95**, 69–96 (1995).
2) R. Moreno, *Am. Ceram. Soc. Bull.*, **71**[10], 1521–1531 (1992).
3) R. Moreno, *Am. Ceram. Soc. Bull.*, **71**[11], 1647–1657 (1992).
4) C. Duran, K. Sato, Y. Hotta and K. Watari, *J. Am. Ceram. Soc.*, **90**[1], 279–282 (2007).
5) K. Sato, Y. Hotta, T. Nagaoka, K. Watari, M. Asai and S. Kawasaki, *J. Ceram. Soc. Japan*, **113**[10], 687–691 (2005).
6) T. Shirai, M. Yasuoka and K. Watari, *J. Am. Ceram. Soc.*, **90**, 4026–4029 (2007).
7) T. Nagaoka, C. Duran, T. Isobe, Y. Hotta and K. Watari, *J. Am. Ceram. Soc.*, **90**[12], 3998–4001 (2007).
8) T. Nagaoka, K. Sato, Y. Hotta, T. Tsugoshi and K. Watari, *J. Ceram. Soc. Japan*, **115**[3], 191–194 (2007).
9) K. Cai, Y. Huang and J.-l. Yang, *J. Am. Ceram. Soc.*, **88**[12], 3332–3337 (2005).
10) T. Isobe, Y. Hotta and K. Watari, *J. Am. Ceram. Soc.*, **90**[11], 3720–3724 (2007).
11) X.-J. Luo, B.-L. Zhang, W.-L. Li and H.-R. Zhuang, *Ceram. Int.*, **30**, 2099–2103 (2004).
12) L. M. Sheppard, *Am. Ceram. Soc. Bull.*, **69**[11], 1801–1812 (1990).
13) S. Fukumoto, T. Hookabe and H. Tsubakino, *J. Mater. Sci.*, **35**, 2743–2748 (2000).
14) J. M. Peralta-Hernandez, Y. Meas-Vong, F. J. Rodriguez, T. W. Chapman, M. I. Maldonado and L. A. Godinez, *Dyes and Pigments*, **76**, 656–662 (2008).
15) V. Augugliaro, C. Baiocchi, A. B. Prevot, E. Garcia-Lopez, V. Loddo and S. Malato et al., *Chemosphere*, **49**, 1223–1230

(2002).
16) "Photocatalysis: Science & Technology," Ed. by M. Kaneko and I. Okura, Kodansha–Springer Berlin (2002).
17) A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobio. C: Photochem. Rev*., 1, 1–21 (2000).
18) D. S. Bhatkhande, V. G. Pangarkar and A. ACM. Beenackers, *J. Chem. Tech. Biotech*., 77, 102–116 (2001).
19) K. Pirkanniemi and M. Sillanpää, *Chemosphere*, 48, 1047–1060 (2002).
20) I. K. Konstantinou and T. A. Albanis, *Appl. Catal. B: Environ*., 49, 1–14 (2004).
21) C. Bauer, P. Jacques and A. Kalt, *J Photochem Photobiol A*, 140, 87–92 (2001).
22) M. Romero, R. D. Rawlings and J. M. Rincon, *J. Non-Cryst. Solids*, 271, 106–118 (2000).
23) F. A. Costa Oliveira, V. Livramento and F. Delmasm, *J. Mater. Proc. Technol*., 196, 101–108 (2008).
24) F. A. Costa Oliveira, V. Livramento and F. Delmasm, *J. Mater. Proc. Technol*., 195, 255–259 (2008).
25) Y. Hotta, K. Tsunekawa, C. Duran, K. Sato, T. Nagaoka and K. Watari, *Mater. Sci. Eng. A*, 475[1–2], 57–61 (2008).
26) Y. Hotta, C. Duran, K. Sato, T. Nagaoka and K. Watari, *J. Eur. Ceram. Soc*., 28, 599–604 (2008).
27) EU patent 0878496, JP patent 10316930, US patent 6124398, Y. Imashiro, I. Takahashi, N. Horie, T. Yamane, S. Suzuki, to Nisshinbo Industries Inc., 15 May (1998).
28) P. Raharjo, K. Tanamura, M. Matsuda and K. Ishizaki, *J. Ceram. Soc. Japan*, 106, 531–534 (1998).
29) T. Shirai, C. Ishizaki and K. Ishizaki, *J. Ceram. Soc. Japan*, 114, 286–289 (2006).
30) T. Shirai, *Mater. Japan*, 45, 131–134 (2006) [in Japanese].
31) T. Shirai, C. Ishizaki and K. Ishizaki, *Interceram*, 50, 176–181 (2001).
32) P. Raharjo, C. Ishizaki and K. Ishizaki, *J. Ceram. Soc. Japan*, 108, 449–455 (2000) [in Japanese].
33) J. E. Schuetz, *Am. Ceram. Soc. Bull*., 65[12], 1556–1559 (1986).
34) J. K. Wright, R. M. Thomson and J. R. G. Evans, *J. Mater. Sci*., 25, 149–156 (1990).
35) Y. Chen, A. Burbidge and J. Bridgwater, *J. Am. Ceram. Soc*., 80[7], 1841–1850 (1997).
36) C. S. Kumar, U. S. Hareesh, A. D. Damodaran and K. G. K. Warrier, *J. Eur. Ceram. Soc.*, 17, 1167–1172 (1997).
37) S. Ananthakumar and K. G. K. Warrier, *J. Eur. Ceram. Soc.*, 21, 71–78 (2001).
38) S. Ananthakumar, A. R. R. Menon, K. Parabhakaran and K. G. K. Warrier, *Ceram. Int.*, 27, 231–237 (2001).
39) Y. Hongo, *Taikabutsu*, 31, 647–653 (1979).
40) S. D. Vaidya and N. V. Thakkar, *J. Phys. Chem. Solid*, 62, 977–986 (2001).
41) T. Nagaoka, T. Tsugoshi, Y. Hotta, M. Yasuoka and K. Watari, *J. Mater. Sci*., 41, 7401–7405 (2006).
42) T. Nagaoka, T. Tsugoshi, Y. Hotta, K. Sato and K. Watari, *J. Ceram. Soc. Japan*, 113[1], 87–91 (2005).
43) S. J. Wilson, *J. Solid State Chem*., 30, 247–255 (1979).
44) M. Kumagai and G. L. Messing, *J. Am. Ceram. Soc*., 68[9], 500–505 (1985).
45) A. C. Young, O. O. Omatete, M. A. Janney and P. A. Menchhofer, *J. Am. Ceram. Soc*., 74[3], 612–618 (1991).
46) T. P. Hyatt, *Am. Ceram. Soc. Bull*., 74[10], 56–59 (1995).
47) C. T. Yang, W. J. Wei and A. Roosen, *J. Am. Ceram. Soc*., 87[6], 1110–1116 (2004).
48) P. Nahass, W. E. Rhine, R. L. Pober, H. K. Bowen and W. L. Robbins, *Ceramic Transactions*, 15, 355–364 (1990).
49) J. X. Zhang, D. L. Jiang, S. H. Tan, L. H. Gui and M. L. Ruan, *J. Mater. Res*., 17[8], 2012–2018 (2002).
50) Z.-G. Shen, J.-F. Chen, H.-K. Zou and J. Yun, *J. Coll. Inter. Sci.*, 275, 158 (2004).
51) W. Sakamoto, H. Nakaoka, T. Yogo and S.-I. Hirano, *J. Ceram. Soc. Japan*, 111[11], 811–814 (2003).
52) E. P. Wood and K. L. Nimmo, *J. Electron. Mater*., 23[8], 709–713 (1994).
53) T. Takanaka, *Ultrasonic Technology*, 8, 2–12 (2001).
54) J. W. Waanders, Piezoelectric Ceramics-properties and Applications, Philips Components, Eindhoven (1991).
55) B. Jaffe, W. R. Cook and H. Jaffe, "Piezoelectric Ceramics," Academic Press, New York (1971).
56) K. Uchino, "Ferroelectric Devices," Marcel Dekker, Inc., New York (2000).
57) R. Zuow, J. Rodel, R. Chen and L. Li, *J. Am. Ceram. Soc*., 89[6], 2010–2015 (2006).
58) J.-R. Gomah-Pettry, S. Said, P. Marchet and J.-P. Mercurio, *J. Eur. Ceram. Soc*., 24, 1165–1169 (2004).
59) E. Ringgaard, T. Wurlitzerand and W. W. Wolny, *Ferroelectrics*, 319, 97–107 (2005).
60) M. Kosec, V. Bobnar, M. Hrovat, J. Bernard, B. Malic and J. Holc, *J. Mater. Res*., 19, 1849–1854 (2004).
61) J.-R. Gomah-Pettry, S. Said, P. Marchet and J.-P. Mercurio, *J. Eur. Ceram. Soc*, 24, 1165–1169 (2004).
62) O. Elkechai, M. Manier and J. P. Mercurio, *Phys. Stat. Solid (a)*, 157, 499–506 (1996).
63) S. E. Park and K. H. Hong, *J. Appl. Phys*., 79[1], 383–392 (1996).
64) Y. M. Chiang, G. W. Farrey and A. N. Soukhojak, *Appl. Phys. Lett.*, 75[25], 3683–3685 (1998).
65) S. Said and J. P. Mercurio, *J. Eur. Ceram. Soc*., 21, 1333–1336 (2001).
66) Y. Saito, H. Takkao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, *Nature*, 432, 84–87 (2004).
67) E. Yassıtepe, H. C. Yatmaz, C. Öztürk, K. Öztürk and C. Duran, *J. Photochem. Photobio. A: Chemistry*, 198, 1–6 (2008).
68) X. Meng, B. Lin and Z. Fu, *J. Luminescence*, 126, 203–206 (2007).
69) C. G.-Yanez, C. Benitez and H. B.-Ramirez, *Ceram. Int*., 26, 271–277 (2000).
70) X. Xu, T. Nishimura, N. Hirosaki, R.-J. Xie and H. Tanaka, *J. Am. Ceram. Soc*., 90[4], 1058–1062 (2007).
71) S.-L. Ma łgorzata, H. Gocmez and C. Duran, unpublished work.
72) D. Hennings and S. Schreinemacher, *J. Eur. Ceram. Soc.*, 9, 41–46 (1992).
73) G. Art, D. Hennings and G. de With, *J. Appl. Phys.*, 58, 1619–1625 (1985).
74) O. S. Bergmann and J. Barrington, *J. Am. Ceram. Soc*., 49, 502–507 (1966).
75) W. R. Bussem, L. E. Cross and A. K. Goswami, *J. Am. Ceram. Soc*., 75, 2926–2929 (1992).
76) A. V. Gorokhovsky, V. A. Gorokhovsky, D. V. Mescheryakov, J. Mendez-Nonell, J. I. Escalante-Garcia, M. I. Pech-Canul and G. Vargas-Gutierrez, *Materials Letters*, 51, 281–284 (2001).
77) L. A. Zhunina, M. I. Kuzmenkov and V. N. Yaglov, Pyroxene Glass-Ceramics. BGU, Minsk (1974).
78) J. Bossert, E. Fidancevska, B. Mangutova, B. Panova, D. Milosevski and M. Milosevski, *Science of Sintering*, 36, 87–92 (2004).
79) L. Barbieri, A. Corradi and I. Lancellotti, *J. Eur. Ceram. Soc*., 22, 1759–1765 (2002).
80) A. Alvarez-Mendez, L. C. Torres-Gonzalez, N. Alvarez, L. M. Torres-Martınez, *J. Non-Cryst. Solids*, 329, 73–76 (2003).
81) A. Karamberi, K. Orkopoulos and A. Moutsatsou, *J. Eur. Ceram. Soc*., 27, 629–636 (2007).
82) M. T. Vieira, F. M. Barreiros and L. Catarino, *J. Mater. Proc. Technol.*, 143–144, 454–457 (2003).