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Preparation and/or Recycling of Waste Glasses into Novel "Glass-Ceramic Stoneware"

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Soda-lime-silica scrap is a widely accepted sintering additive for the manufacturing of traditional ceramics, but this solution does not fully exploit the potentialities of glasses compared to feldspar fluxes. In fact, glasses soften and undergo viscous flow sintering at much lower temperatures than those required for feldspar melting. This could be useful to develop "environmentally friendly" ceramics, i.e. made with a reduced consumption of energy and natural raw materials, if glasses would not constitute only a simple additive, to be used in limited amounts, but the only flux, to be used in massive amounts.

This approach may be applied to a variety of waste glasses, including both recycled glasses, hardly re-used for the manufacturing of the original objects (i.e. fractions of recycled soda-lime-silica enriched in contaminants, or glasses used in articles that are being withdrawn from the market, like cathode ray tubes), and glasses from the melting of inorganic waste.

When glasses replace the common feldspar flux, the advantage of low firing temperatures, even below 1000°C, may be counterbalanced by the lacking of mullite precipitation, with consequent low mechanical properties and problems of excessive viscous flow and uncontrolled shrinkage.

This work is focused on a positive solution for limiting the viscous flow and obtaining strong ceramics, still fired at very low temperatures: the shrinkage may be controlled by the presence of crystals, increasing the apparent viscosity; the crystal phases come mainly from partial crystallization of the glass, leading to a "glass-ceramic stoneware". This phenomenon occurred for glasses of the CaO-

Al_2O_3-SiO_2 system, in the form of fine powders, obtained by melting several inorganic waste, such as mining residues, exhausted lime, municipal solid waste incinerator fly ashes, red mud from the Bayer process of alumina. By optimizing the glass/clay ratio, the obtained “glass-ceramic stoneware” samples, sintered at temperatures ≤1000°C, exhibit mechanical properties (bending strength approaching 90 MPa, fracture toughness exceeding 2 MPa $m^{0.5}$) similar to those of conventional porcelain stoneware, essentially due to the formation of different crystal phases upon sintering: some crystals, corresponding to Ca-silicate and alumino-silicates, precipitated by surface nucleation, some others, i.e. Ca-rich feldspars, were due to chemical interaction between glass and clay.

The present approach is particularly significant for the absorption of inorganic waste, since pollutants may be permanently embedded in glasses, with a very simple process, resembling that of ceramic frits; in addition, the transformation in new products follows the low cost and well established manufacturing procedures of traditional ceramics, avoiding the quite complex techniques for glass-ceramics (currently the only significant application of glasses from waste).

Secondary crystal phases were obtained also in glass/clay formulations based on glasses which do crystallize, such as soda-lime-silica glass and cathode ray tube glasses, by the usage of suitable additives: in the first case some wollastonite precipitation was due to the use of a low amount of calcium hydroxide, acting as “devitrification promoter”; in the second case the crystal phase was due to the inclusion of a low amount of alumina platelets.

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