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Effect of time and furnace atmosphere on the sintering of glasses from dismantled cathode ray tubes

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Abstract

The dismantling of cathode ray tubes (CRTs) represents a pressing environmental problem. CRTs consist of three distinguished glass parts. The front part is a barium–strontium glass, while the parts hidden inside the TV sets consist of lead silicate glasses. The high quality standards in manufacturing new CRTs impose a very limited amount of glasses to be recycled in the production of the original components. In addition, the presence of easily reducible oxides (like PbO) in the chemical composition of CRT glasses causes the risk of dispersing poisonous substances during remelting. Sintering of powdered glass could be a profitable way to produce new dense glass based materials without remelting. CRT glasses were found to be strongly susceptible to both the duration of the firing at the sintering temperature and the furnace atmosphere (oxygen, air, nitrogen). The evolution of the relatively large amount of dissolved oxygen, typical of CRT glasses, is found to contrast densification. Very short firing times (up to 15 min) are found to limit gas evolution. In addition, oxidative atmospheres lead to high quality sintered materials, capable of optical transparency comparable to that of pristine glasses.

Keywords: Sintering; Glass

1. Introduction

The production of innovative glass based materials may be considered as a promising way for the treatment of various types of wastes.[1,2] Glass fibres,[3] glass–ceramics,[4] foam glasses[5,6] and, mainly in the last 10 years, glass or glass-ceramic matrix composites[7,8] are the main examples of such approach. Glass generally possesses a high chemical stability, so that the obtained products can be safely employed.

It must be noted, however, that a fundamental distinction between the different starting wastes is needed. In fact, only in certain cases a vitrification treatment, i.e. the formation of a glass by melting a selected mixture of wastes is strictly necessary for the manufacturing of glass based products. When recycled glasses are employed as the starting wastes, the remelting of glass may not be advantageous from economical and environmental points of view: vitrification treatments are particularly energy consuming and glasses may be subjected to inappropriate chemical and physical reactions upon remelting (for example, the volatilisation of some constituents).[2]

A particular type of glasses for the manufacturing of new glass based articles are those coming from dismantled cathode ray tubes (CRTs). Such glasses are properly waste materials and represent a pressing environmental problem, since their recycling is very complicated. In a CRT different types of heavy metal containing glasses, lead- or barium-based, are employed.[9] The usage of heavy metal oxides in the chemical formulation of CRT glasses is necessary for the UV and X radiation, escaping from the electron gun, to be absorbed. The front part, commonly known as panel, is made of a barium-strontium glass, practically lead free, very homogeneous and thick. Expensive barium is chosen, instead of lead, in order to prevent the browning of the front part due to easily reducible oxides (like PbO) caused by high-energy electrons. Such effect is known as "solarization".[10] Lead is used in the parts hidden inside the TV set, commonly known as funnel (the cone part behind the screen) and neck (the tube enveloping the electron gun), in which no particular optical quality is needed. The closed-loop recycling of CRT glasses, i.e. the direct employment in the manufacturing of new CRTs, could be profitable only in the case of an absolute separation of the glass components: the introduction of a small percentage of

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funnel or neck glass in panel manufacturing is not acceptable for the solarization effect; on the other hand, the addition of panel glass to funnel or neck glasses generally lowers the mechanical properties.[9] Even if some improvements in the separation of the components are expected, the replacement of standard-definition television with high-definition television (without CRT) dramatically limits the suitability of closed-loop recycling.[11] On the other hand, the open-loop recycling, i.e. the utilization of CRT glasses as raw materials for applications independent from CRT manufacturing, such as laboratory equipment for radiation protection (containers, glass fibre textiles[12,13] etc.), may absorb only a small volume of CRT glasses, with the addition of the risk of PbO volatilisation upon remelting (such phenomenon causes CRTs to be banned from waste combustors, as reported in the literature).[14]

The complexity of the recycling of CRT glasses may be successfully solved by a sintering approach. It has been already demonstrated the feasibility of innovative glass-based products, like glass matrix composites,[15–19] and glass foams,[20,21] by a simple and cost-effective powder technology route. The fundamental remark of such approach is that CRT glasses possess a relatively low softening temperature, which is particularly profitable in viscous flow sintering, i.e. in achieving highly dense glass samples from the firing of powder compacts. Since relatively low processing temperatures are employed, the volatilisation of PbO is thought to be prevented.

Even if substantially successful, the sintering of CRT glasses undoubtedly needs further studies. Bernardo et al.[15,19] illustrated that the densification of CRT glasses may be altered by the development of a number of bubbles, in the manufacturing of Al and Al_2O_3 reinforced glass matrix composites, particularly detrimental to the mechanical properties. The formation of bubbles was attributed to the evolution of gasses, previously dissolved in the glass matrices; it is well-known that glasses containing significant amounts of heavy metals are formed under oxidative conditions and are not extensively refined, so that they contain some free oxygen. The introduction of metallic reinforcements[15] may result in the local lacking of oxidative conditions, with a dramatic decrease of gas solubility within glass. In the case of Al_2O_3 platelet reinforcement (an “inert” oxide reinforcement),[19] it was pointed out that the same gas solubility dramatically decreased with increasing sintering temperature and duration; very short firing times of 15 min, at low temperature (650 °C), were found to be advantageous in limiting the gas evolution, with a dramatic improvement of mechanical properties.

In this paper we present a more extensive study on the sintering of CRT glasses, with special regard to the duration and the processing atmosphere of sintering treatments, in order to recognize the optimum conditions for further applications in the field of glass matrix composites or other glass based articles. Different mixtures of Ba-based panel glass and Pb-based glasses were compared, in order to point out the effective role of the easily reducible PbO. The sintering behaviour was studied by means of both density and optical measurements. Short duration and oxidative environment had a synergic effect in promoting densification and contrast gas evolution, so that a remarkable degree of optical transparency was achieved in some sintered samples.

2. Experimental

The average chemical composition of the employed CRT glasses is shown in Table 1.[9]

All the glasses were available as granules with a diameter in the range 5–10 mm. The glasses were dry ball milled and sized in order to obtain grains <37 μm. The glass powders were ground in a tungsten carbide vibratory mill for 15 min, producing smaller glass particles (about <20 μm). In addition to pure panel glass, three different mixtures of panel and Pb-containing glasses were considered. Neck and funnel glass powders were mixed together in the dry ball mill for 1 h, with the proportions in weight reported in the literature,[20] thus generating a Pb-containing glass mixture. The panel glass powders were added with the Pb-containing mixture with different concentrations (10%, 20%, 34.27%, the last being the average concentration in a CRT,[22] so that it will be named “CRT” composition) and mixed together. The glass powders were uniaxially pressed in a cylindrical steel die (with a diameter of 31 mm) at room temperature, by using an hydraulic press operating at 40 MPa; no binder was added to the powders. The obtained discs were subjected to sintering treatments at 650 °C, with a heating rate of 5 °C/min, in a tubular furnace with different holding times, 15 min, 30 min and 1 h, and in different atmospheres, consisting of pure oxygen, air and pure nitrogen. The processing temperature was selected to be 650 °C, from other experiences:[19] it has been already reported[15,23] that the optimum sintering temperature is about 50 °C exceeding the dilatometric softening temperature, which is about 600 °C for panel glass (see Table 1).

The total light transmittance in the visible wavelength range (380–780 nm), through the obtained sintered glasses, was measured by means of a double beam spectrophotometer (Perkin-Elmer mod. Lambda 900) equipped with an integrating sphere of 150 mm diameter. The total light transmittance is the sum of the direct and the scattered components of the transmitted light beam. The samples were also investigated by X-ray diffraction

Table 1
Chemical composition, physical properties and average weight proportions of CRT glasses

	Panel (Ba containing)	Funnel (Pb containing)	Neck (Pb containing)
Chemical composition in wt.% of CRT glasses (main oxides)			
SiO_2	60.70	54.10	38.00
Al_2O_3	1.70	1.80	0.90
Na_2O	7.50	6.20	2.00
K_2O	6.90	8.20	16.50
CaO	0.10	3.50	0.10
BaO	9.90	0.80	0.70
SrO	8.60	0.70	4.80
PbO	0.01	22.00	35.00
Thermal expansion coefficient (10^{-7} °C^{-1})	99.0 ± 0.5	99.0 ± 0.5	99.0 ± 0.5
Density (g cm^{-3})	2.71 ± 0.01	2.98 ± 0.01	3.08 ± 0.01
Dilatometric softening temperature (°C)	592.8	534.8	512.0
wt.% in a typical CRT	65.73	33.86	0.41

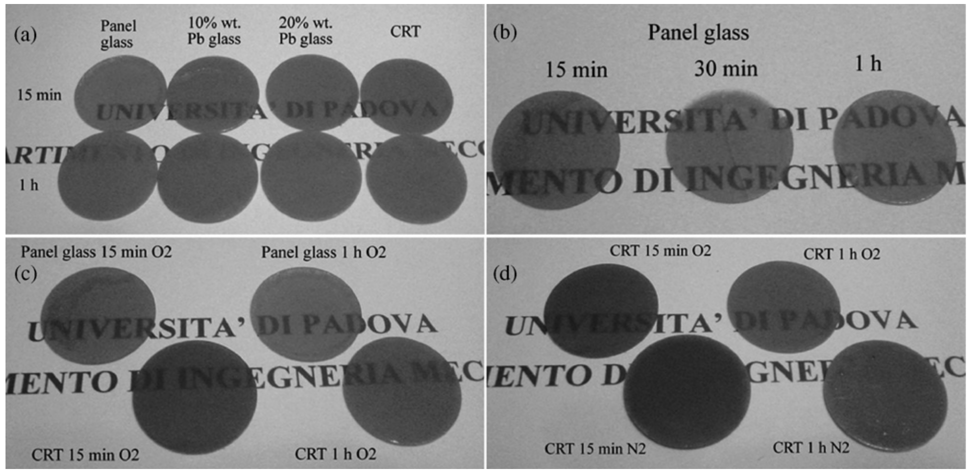

Fig. 1. Images of selected sintered samples (diameter of discs∼25 mm): (a) comparison between samples sintered in O_2 atmosphere for different times (15 min vs. 1 h); (b) comparison between samples from panel glass sintered in O_2 atmosphere for different times; (c) comparison between samples sintered in O_2 atmosphere for different PbO concentration; (d) comparison between samples sintered in different atmosphere (O_2 and N_2).

(XRD, Philips PW3710) by using Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The density of the sintered compacts was evaluated by means of the Archimedes' principle, on fragments cut from the obtained discs. Polished surfaces of selected samples were characterized by Scanning Electron Microscopy (JEOL-5900).

3. Results and discussion

The above described thermal treatments led to highly dense sintered samples, with a light grey colouration (due to the intrinsic colouration of the main glass component, i.e. panel glass, which usually contains traces of Ni, Co and Fe oxides).[9] A selection of sintered samples is shown in Fig. 1. The diameters of the samples were about 25 mm.

Samples sintered in an oxygen atmosphere revealed a drastically more pronounced optical transparency than the samples sintered in air or nitrogen. However, some important distinctions must be made, regarding both the duration of the sintering treatment and the starting glass composition, based on the simple observation of the samples reported in Fig. 1. Fig. 1a reveals that short treatments (15 min) in an oxygen atmosphere caused a remarkable transparency for all the compositions, while long treatments (1 h) caused a low transparency, practically not noticeable for the "CRT" composition. Fig. 1b shows that, for the same panel composition (practically lead-free), the transparency reaches a maximum, in an oxygen atmosphere, for an "intermediate" treatment of 30 min. Although exhibiting a notable transparency degree, the samples from "CRT" composition, as illustrated by Fig. 1c, revealed a darker colouration in the same oxygen atmosphere. This composition resulted in practically opaque samples for treatments in nitrogen atmosphere (see Fig. 1d).

The qualitative remarks from the direct observation of the sintered samples were confirmed by the results of the spectrophotometric tests. Each sample was positioned against the entrance port of the spectrophotometer integrating sphere and lighted by a perpendicular monochromatic beam. The spectrophotometer records the ratio "signal-through-sample/signal-through-air" versus the selected wavelength, producing the transmitting spectrum of the sample in the range of interest (UV, VIS, or NIR). The total light transmittance, corrected for sample thickness of 1 mm, was calculated with the weighting function according to the literature,[24] under standard illuminant C and 2° standard observer (1931). In Fig. 2 the total transmittance in the visible range is plotted against the percentage in weight of Pb-containing glass.

As a general trend, samples sintered in oxygen showed an almost double transmittance when compared to analogous samples sintered in air; the sintering in a nitrogen atmosphere caused

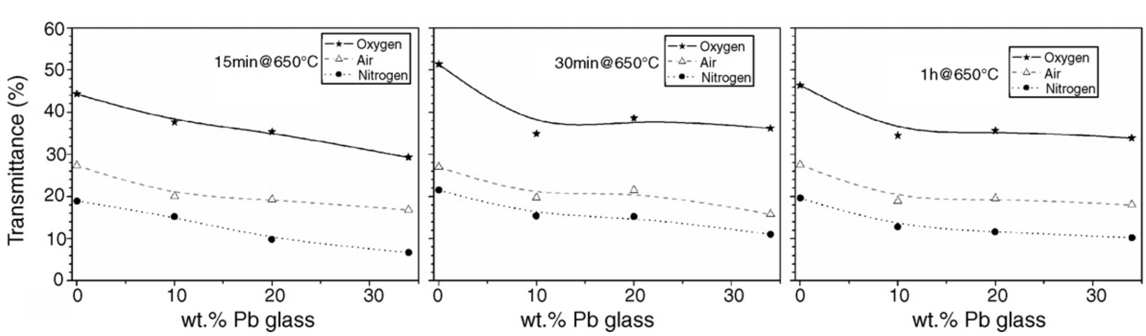

Fig. 2. Total transmittance in the visible range (380–780 nm) of the sintered samples.

an even more pronounced decrease. It must be noted the effect of the firing duration is particularly notable only for oxygen and nitrogen atmospheres, but it is practically absent for the treatments in air. In both oxygen and nitrogen, the best results were achieved for treatments with a 30 min duration; as already observed (Fig. 1b), the best transparency degree is that of the sample sintered in oxygen for 30 min consisting of pure panel glass. In this case the transmittance of the sintered samples reached more than a half of the transmittance of pristine panel glass (which was measured to be 88.1% on a 1 mm thick sample): a precise selection of the sintering conditions, in practice, caused a drastic approaching of sintered objects to the optical properties of conventionally produced glasses, as already demonstrated for the mechanical properties.[19] A further comparison between sintered panel glass and pristine panel glass is illustrated in Fig. 3.

The spectra plotted in Fig. 3 show a relatively flat trend throughout the visible interval, confirming the grey colouration of the samples. The pristine glass curve features a plateau between 450 and 650 nm probably due to a superposition of Fe, Co and Ni weak absorption bands.[9] The sintered panel glass curve seems to have no single absorption band, but a constant decrease of spectral transmittance towards lower wavelengths. The gap between the two curves indicates a difference in transparency of about 37%. Its actual value is probably lower due to incomplete collection of the entire beam scattered by the sample. Scattering occurs when a sample has rough surfaces (i.e. not polished) and/or some structural inhomogeneity (for example gas bubbles). An integrating sphere with a larger diameter would probably collect a larger fraction of the scattered beams and reduce the gap. Some experiments in the literature demonstrated that the gap is about 6%.[25] The addition of the Pb-containing glass to panel glass had a similar effect for all the sintering conditions, consisting in a remarkable decrease of transparency (the lines reported in Fig. 2, representing the same sintering condition, are all descending with an almost parallel trend).

It is well-known that glass tubes with a remarkable content of PbO are employed as photomultipliers by the formation of a metallic layer on the inner surface, due to the reduction of the same PbO to metallic lead.[26,27] Extensive reduction of PbO,

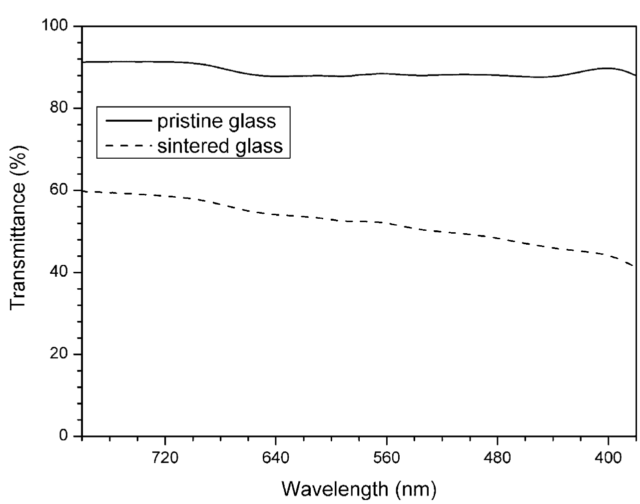

Fig. 3. Transmittance vs. wavelength plots for sintered and pristine panel glass.

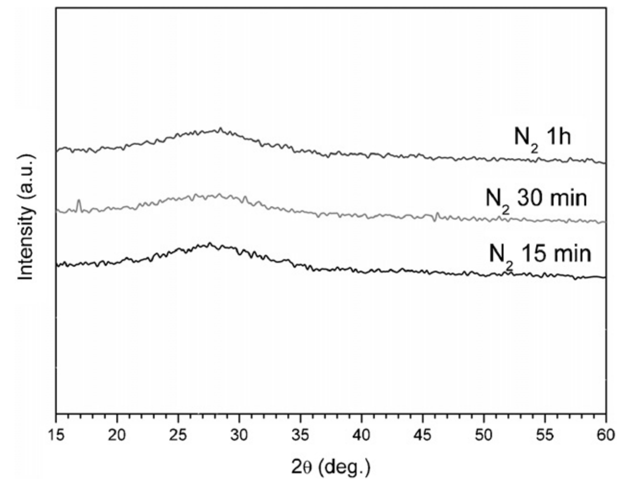

Fig. 4. XRD spectra of selected sintered glasses ("CRT" composition, N_2 atmosphere).

however, was not revealed in the present investigation, like in the previous experiences[19]: as illustrated by Fig. 4 for the samples with a "CRT" composition sintered in nitrogen, the sintered samples were all X-ray amorphous.

The observed phenomenology may be attributed to a complex of physical and chemical interactions. It has been widely reported that glasses containing heavy metals are characterized by a large amount of gasses dissolved,[28] directly from the manufacturing process, such glasses being not extensively refined. In particular, with regard to the raw materials for lead glasses, it is well known the usage of minium (Pb_3O_4), instead of PbO (that incorporated in the glass network), in order to introduce some "extra" oxygen, which could be useful for maintaining lead as lead oxide, as follows:

$$2Pb_3O_4 \rightarrow 6PbO + O_{2(g)}$$

In practice, glasses containing high percentages of heavy metal oxides are "oxidized" glasses.[28] The gas solubility in the glass mass is thought to become less and less with the increase of the sintering temperature[19] or with the introduction of reducing agents like metallic inclusions,[15] with the formation of bubbles, which contrast densification and are detrimental to both the mechanical and optical properties of the sintered materials, by acting as stress concentrators and causing the dispersions of light upon glass/pore interfaces, respectively. In the present case, the employed atmospheres resulted in different transparency degrees because of their different "oxidizing" character: the desorption of oxygen from glass is thought to be less and less probable with increasing oxygen content in the surrounding atmosphere, with a reduction of bubbles. As illustrated by Fig. 2, the addition of Pb-based glasses to panel glass resulted in the enhancement of the susceptibility of the glass mass to the desorption of gasses.

The effect of time (i.e. firing duration) is not univocal. Short treatments generally led to higher transparency, coherently with the hypothesis of reduction of gas desorption from glass, but the superposition of the sintering kinetics must be encountered. In fact, short treatments could lead to an incomplete densification,

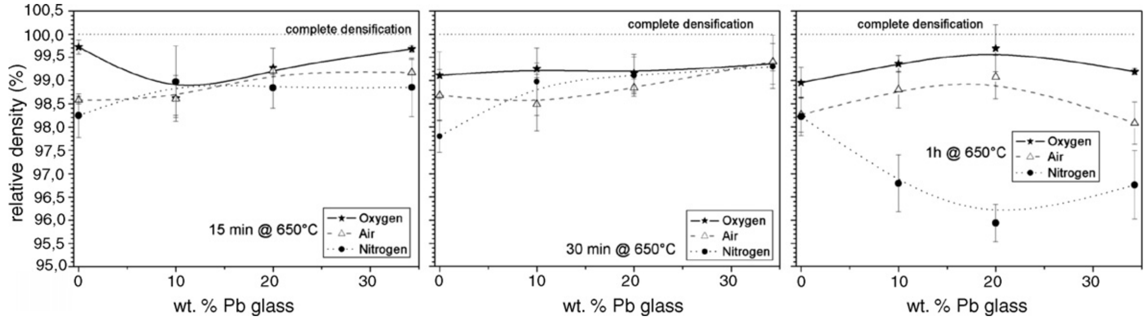

Fig. 5. Relative density of the sintered samples plotted against the wt.% of Pb-containing glass, as a function of the firing duration and the sintering atmosphere.

with the retention of the pores caused by the packing of glass powders upon pressing, prior to firing. Further information on the complexity of interactions occurring upon sintering results from densification measurements. In Fig. 5 the relative density (i.e. the ratio between the measured density and the expected density of the sintered samples, calculated from the density of the constituents in the hypothesis of full densification) is plotted against the wt.% of Pb-containing glass.

As observed in previous investigations,[19] the adopted processing temperature may be seen as the optimum sintering temperature for the employed glasses, since only in a few cases the relative density was lower than 98%. Unlike in several other viscous flow pressureless sintering experiences reported in the literature,[13,15,16] the densification was found to be almost complete for holding times shorter than 1 h. The sintering in oxygen caused the highest densification degree, the relative density being particularly close to unity, except for the treatment of 15 min with a 10% wt. Pb-containing glass. One likely reason for such anomaly might be the above mentioned superposition of gas desorption and sintering kinetics effects; the addition of lead-based glass on the one hand caused an enhanced susceptibility to gas evolution from the glass mass, contrasting densification, on the other caused an alteration of the sintering kinetics, since Pb-based CRT glasses possess a lower softening temperature (see Table 1) and consequently a lower sintering temperature,[15,16] favourable to densification. Such contrast is confirmed by the observation of the total transmittance in Fig. 2, where there is a dramatic decrease of transmittance from pure panel glass to 10% wt. Pb-containing glass. The promotion of sintering due to Pb-glasses probably becomes dominant for longer treatments, or higher percentages of Pb-containing glass.

The SEM observations yielded additional information about the previously reported optical and density measurements. Samples from panel glass, sintered in oxygen, actually demonstrated a particularly low residual porosity. Fig. 6a shows a sample sintered for 15 min: some pores are distinguished, and they may be related to the incomplete sintering; Fig. 6b reveals that, for a 1 h treatment, residual porosity is practically absent. The images in Fig. 6, achieved by collecting backscattered electrons, show that some structural inhomogeneity can be found also by considering only panel glass, since different tones are visible, due to different chemical compositions (backscattered electron emission is strongly susceptible to the atomic weight of the elements, since heavy atoms with a high atomic number are stronger scatterers than light ones).[29] Light grey zones were attributed (from EDS analysis) to a more pronounced strontium content than in the surrounding glass: Table 1[9] expresses an average chemical composition, so that some fluctuations may be found, for example due to the dismantling of cathode ray tubes with different dimensions and/or different origin. The structural inhomogeneity is likely the reason of the gap between pristine panel glass and sintered panel glass illustrated in Fig. 3, since variations in the chemical composition may cause variations of the refractive index through the sintered samples, with consequent scattering of light upon multiple internal reflections and refractions.

The samples sintered from a mixture of panel and Pb-containing glasses showed a more pronounced porosity, as illus-

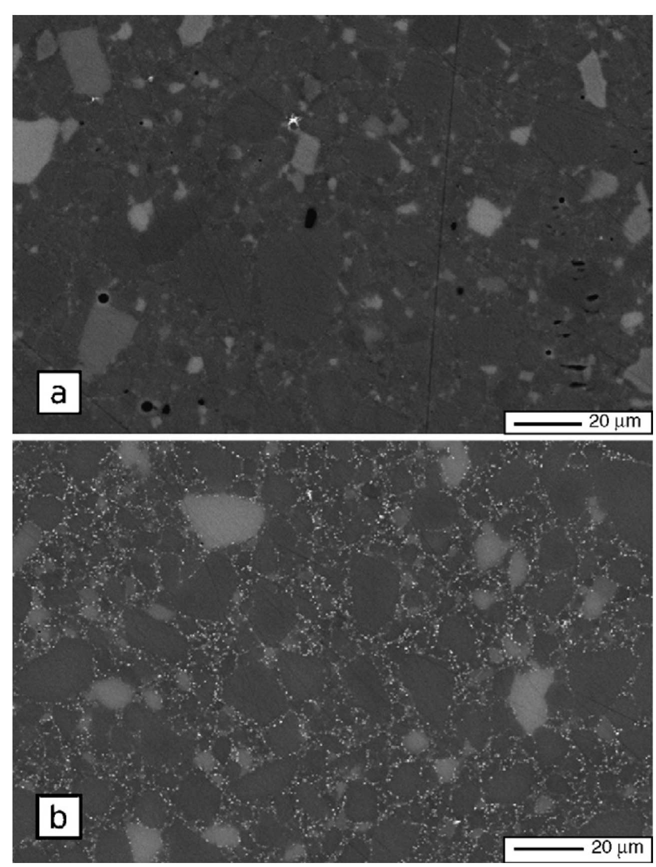

Fig. 6. SEM micrographs of sintered panel glass: (a) 15 min at 650 °C; (b) 1 h at 650 °C.

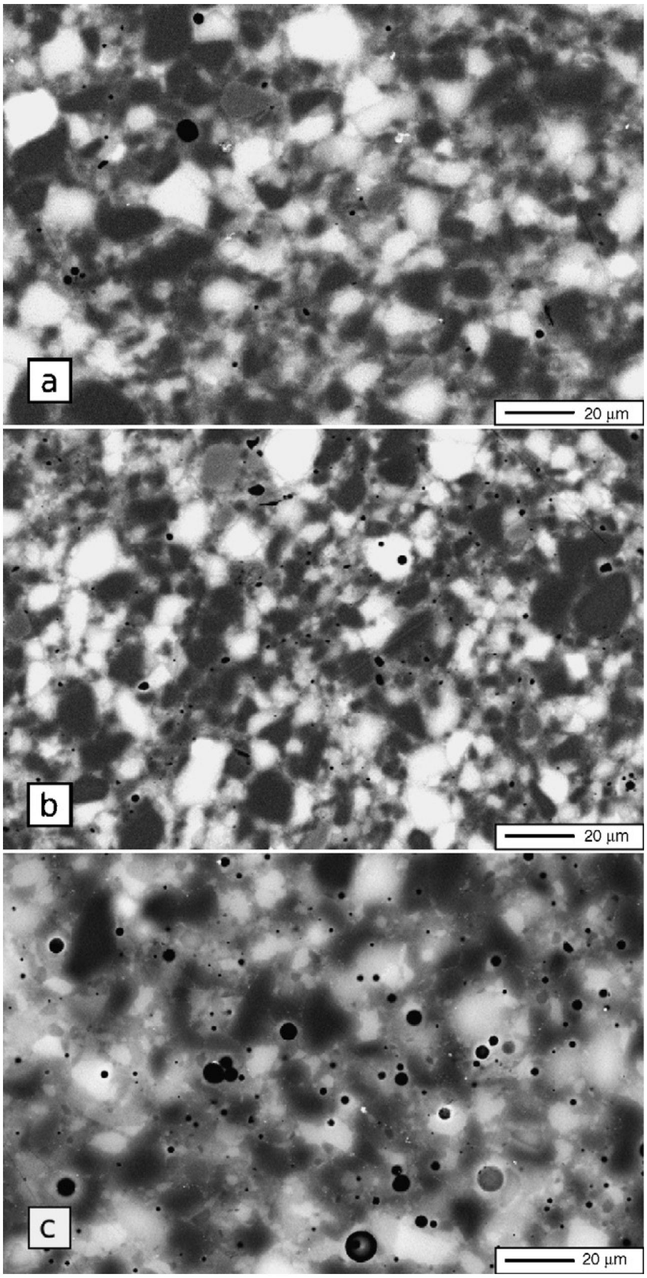

Fig. 7. SEM micrographs of sintered glass mixture ("CRT" composition): (a) 15 min in O_2; (b) 15 min in N_2; (c) 1 h in N_2.

trated by Fig. 7. As previously reported by Bernardo et al.[19] the shape of the porosity is particular: some "clusters" are clearly visible. The cluster shape suggests some gas evolution from the glass mass, since pores from incomplete sintering should be isolated. The sample from a "CRT" composition sintered in oxygen for 15 min showed a limited number of pores (see Fig. 7a) compared with the analogous sample sintered in nitrogen (Fig. 7b), thus confirming the role of the oxygen content in the furnace atmosphere. Extensive pore evolution was achieved for the treatment in nitrogen for 1 h (Fig. 7c). The enhanced porosity in the samples from "CRT" composition is consistent with the observed low transmittance. The scattering of light is likely due to the superposition of the presence of pores and chemical inhomogeneity from the employment of glasses with drastically different composition.

4. Conclusions

The reported experiences proved that sintering of powdered glass could be effectively a way to produce new dense glass based materials without remelting, since a precise selection of the sintering conditions led to samples with remarkable "optical quality", i.e. exhibiting a relatively high optical transmittance. The accurate selection of the sintering conditions could have several effects, as follows:

- CRT glasses could be employed with no need for an absolute separation of the different components (for example it could be mentioned that the transmittance of glasses sintered in oxygen was, for all the compositions, higher than that corresponding to pure panel glass in the other atmospheres);
- heavy metals containing glass could be employed for the manufacturing of new articles, like transparent or translucent panes for radiation protection or for other applications, like glazing of ceramics, by means of a sintering process applied to the glasses directly in the as received state, with no need for remelting;
- the conditions of high optical transmittance, causing a drastic reduction of pores, could be exploited for the manufacturing of highly dense and strong glass matrix composites, by the introduction of several reinforcements;
- an oxidizing atmosphere was found to grant the retention of gasses, useful for preventing the precipitation of heavy metals; even if an extensive precipitation of metals was not revealed even for long treatments in nitrogen, the selection of the sintering atmosphere and short firing times are thought to be useful for minimizing the chemical and physical alterations of glass upon sintering, which in turn could be useful for maintaining the original characteristics (chemical durability, thermal and electric properties etc.) in the successive employments.

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