INFLUENCE OF IMPURITIES ON OPTICAL QUALITY OF FLAME FUSED SILICA GLASS PRODUCED WITH BRAZILIAN NATURAL QUARTZ

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ABSTRACT

Silica glass has been a key material for the optical industry due to its unique physical properties. In recent years, the high transmittance in the ultraviolet region also increased its demand for the manufacture of special lamps and tubes for UV disinfection and purification applications. Silica glass obtained by flame fusion of natural quartz is the best choice for these applications mainly due to its lower production costs. Brazil has the world's biggest reserves of natural quartz but lacks desirable skills to qualify the raw material for silica glass production. Natural quartz of different regions usually has distinct properties related to the impurities and inclusions, which have a great impact in the processed glass. This work aims a further understanding of the effect of quartz impurities on the optical quality of glasses produced with Brazilian quartz by the Verneuil method, as well as to identify the best quartz areas for producing silica glass.

KEYWORDS: Silica glass, fused quartz, Brazilian natural quartz, optical glass

INTRODUCTION

Naturally occurring quartz is a strategic mineral as raw material for production of high purity silica glass used in high-tech industry. Fused quartz is a particular denomination for silica glass produced by fusing quartz powder(1), which is highly cost-effective in terms of raw material and processing. The IOTA Quartz, a high quality processed quartz powder produced by Unimin Corporation in the USA, is the main source of quartz powder in the world for the production of fused quartz. In recent times, however, due to the short delivery of IOTA Quartz, most silica glass manufacturers in the world have been looking for alternative sources of quartz powders(2). Brazil has the largest reserves of natural quartz in the world, but does not qualify this material for the production of silica glass. One high demanding application for fused quartz is silica tubes applied in UV disinfection system of drinking water, which appears to be the best alternative to the use of chlorine as a disinfectant. Chlorine in its various forms is the most common disinfectant used worldwide, including Brazil. However, chlorine has the disadvantage of forming potentially toxic and carcinogenic by-products, such as trihalomethanes and haloacetic acids(3). Germicidal UV radiation is effective in the inactivation of a variety of micro-organisms by causing severe damage to the DNA, thus disabling it from replication and not producing undesirable by-products. The germicidal effect is most potent at a wavelength of 260 nm and low-pressure mercury arc puts out 95% of its energy at 254 nm, providing an extremely effective germicidal effect and environmentally clean water purification(4). Efficient lamp operation requires an envelope material and a protective silica tube (“quartz sleeve”) with a high transmittance in the UV spectral range(5). High transparency in the UV region are only achieved when low levels of trace impurities are present, which are the main source of absorption in the range 200–350 nm(6). The present study has the purpose of relating the impurities present in the natural quartz powder with optical transparency of produced silica glass by fusion in LPG/O_2 in visible and UV regions.

MATERIALS AND METHODOLOGY

Starting Raw Materials

Brazilian natural quartz and quartz sand extracted from mines located in states of Minas Gerais (MG), Tocantins (TO) and Sao Paulo (SP) were used as raw materials for silica glass production (Table 1). Commercial quartz powders processed by Unimin Corp., USA (IOTA-STD) and Kyushu Ceramics, Japan (Kyucera) were also used for comparison studies.

Table 1. Identification and origin of raw materials.

Quartz powder	Origin
QP.MG	Grinded lascas from Governador Valadares, MG.
QP.TO	Grinded lascas from Cristalandia, TO.
QP.SR	Processed quartz powder produced by Santa Rosa, MG.
QP.RC	Processed quartz sand from Rio Claro, SP.
QP.IT	Commercial powder IOTA-STD produced by Unimin Corp., USA.
QP.KY	Commercial powder produced by Kyushu Ceramics Kyucera, Japan.

Silica Glass Preparation

Flame-fused silica glasses were produced by Verneuil method by using a similar apparatus as described by Torikai et al.[7]. The quartz powder with granulometry in the range 80–120 mesh was fed on the LPG/O_2 flame provided by two premix metallic burners, directed to the ingot in rotation. Main processing parameters, such as gas ratio, position of burners relative to the ingot, temperature, translation and rotation speed of the ingots (Table 2) were adjusted and optimized case by case in order to maximize the glass transparency and to avoid bubble generation. The temperature was measured by an optical pyrometer. Powder QP.TO was also sintered by Spark Plasma Sintering (SPS) method, using a Fuji Electronic Industrial Co. equipment.

Table 2. Process parameters used for silica glass preparation.

Sample	LPG/O_2	Temperature (ºC)	Translation speed (mm/min)	Rotation speed (RPM)
SG.MG	0.18	1550	0.95	2.8
SG.TO	0.28	1650	0.55	12.0
SG.SR	0.26	1750	0.74	12.0
SG.RC	0.24	1650	0.70	5.3
SG.IT	0.35	1500	1.00	10.4
SG.KY	0.34	1550	0.90	11.0

Quartz powder characterization

Impurities concentration of quartz powders was determined by ICP-MS (Inductive Coupled Plasma Mass Spectroscopy). Samples were diluted in fluoridric acid and the solution was heated to the vaporization of the solvent. The impurities were diluted in deionized water and analyzed for quantification of impurities in wt ppm level of Ag, Al, B, Ba, Be, Ca, Cd, Cs, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, K, La, Li, Lu, Mg, Mn, Na, Ni, Ne, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. However, only the more relevant impurities that absorb in the UV region (Al, Ca, Fe, K, Li, Na, and Ti) were taken into account. Together, those selected impurities account for over 90% of total impurities present in the quartz powder.

Optical Spectroscopy

Rod-shaped ingots with diameters of about 20 mm were sliced and polished to achieve a thickness of about 5 mm. CeO_2 was used for transparency finish. Before each spectroscopy measurement, samples were cleaned in accordance with a standard procedure in ultrasound with distilled water, dish washing liquid, and isopropyl alcohol to remove residues of the polishing process and samples handling.

Optical spectroscopy measurements were carried out in a Perkin Elmer Lambda 9 spectrophotometer in the range 190–3200 nm, with resolution of 1 nm. All transmittance spectra were normalized to a 5 mm thickness equivalent to compensate for small sample thickness variations. OH content was estimated by the absorption peak at 2.73 µm wavelength(8).

A commercial fused quartz (SG.REF), produced with IOTA-STD or equivalent raw material, was used as a reference glass for qualifying the optical quality of produced silica glasses.

RESULTS AND DISCUSSIONS

Main impurities for all powder samples are listed in Table 3. Total impurities differ a lot among Brazilian powder samples, sustaining the high variability of raw materials. Surprising high levels of impurities was found in IOTA quartz if compared to the levels provided by the manufacturer. This powder was the same one used in past works(7), so those additional impurities were attributed to the long time storage and handling.

Table 3. Main trace impurities of quartz powders in wt ppm.

Sample	Al	Ca	Fe	K	Li	Na	Ti	Others	Total
QP.MG	142	19.4	15.4	44.8	6.7	54.1	6.1	27.3	315.7
QP.TO	15.7	21.3	4.4	10.6	1.6	35.8	1.9	5.9	97.2
QP.SR	10.6	35.7	2.2	n/d[1]	1.3	n/d[1]	1.0	5.3	56.0
QP.RC	116	38.3	143	52.4	1.9	53.6	157	51.7	613.9
QP.IT	751	197	68.4	189	0.4	294	7.6	67.7	1575
QP.KY[2]	6.0	0.2	0.3	0.4	0.3	0.9	4.5	n/m[3]	n/m[3]

[1] Not detected.

[2] Impurities obtained from (7).

[3] Not measured.

Optical Transmittance

Transmittance curves for all samples are shown in Figure 1, and major discrepancies in the UV range were found at short wavelengths (~200 nm) and around 240 nm. No absorption peak at 2.73 µm was detected in sample SG.TO (SPS), indicating that OH groups are not incorporated by SPS.

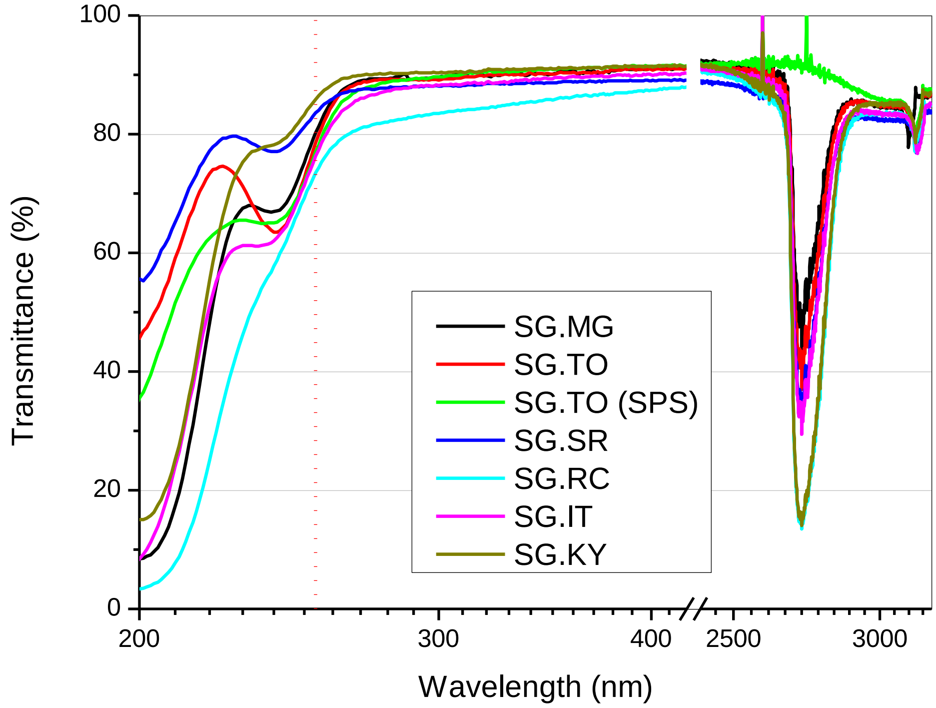


Figure 1. Transmittance of produced samples in UV-Vis-NIR regions.

As expected, best and worst transmittance in visible range and at 254 nm (Table 4) was achieved for samples produced with quartz powders with minor (SG.KY) and major (SG.RC) impurities, respectively.

Table 4. Optical transmittance in visible and UV range and estimate of OH^{-} content.

Sample	Tansmittance in Vis range (%)	Transmittance at 254 nm (%)	OH^{-} (ppm)
SG.MG	91.4	80.2	40
SG.TO	91.2	78.6	71
SG.SR	90.3	83.9	78
SG.RC	89.2	73.5	150
SG.IT	90.6	78.6	81
SG.KY	91.7	85.9	160
SG.TO (SPS)	91.3	77.0	n/d*

* Not detected.

The high absorption observed in SG.KY for shorter wavelengths (λ < 220 nm) was not expected. When compared to samples SG.SR and SG.TO (Figure 2), Ti is the only impurity that is greater in QP.KY, indicating a possible source of absorption.

In fact, absorption band of Ti^{4+} is located at 200 nm and increasing the Ti content in the glass causes a shift of the UV absorption edge position towards longer wavelengths(9). Alkali metal ions (Na, Li, K) also shift the UV cutoff to longer wavelengths, degrading the performance in VUV range by introducing nonbridging oxygen species. However, QP.MG, QP.IT, and QP.KY have a large difference in alkali content but similar transmittances for shorter wavelengths up to 220 nm. High purification of flame-fused bulk was observed by Torikai *et al.*, mainly for alkali metals(7), indicating a much lower level of alkali content in the glass.

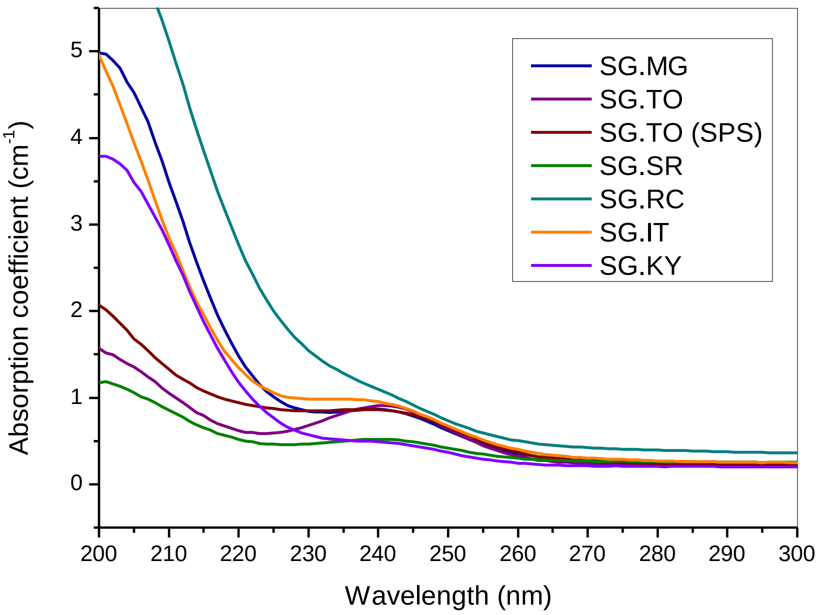
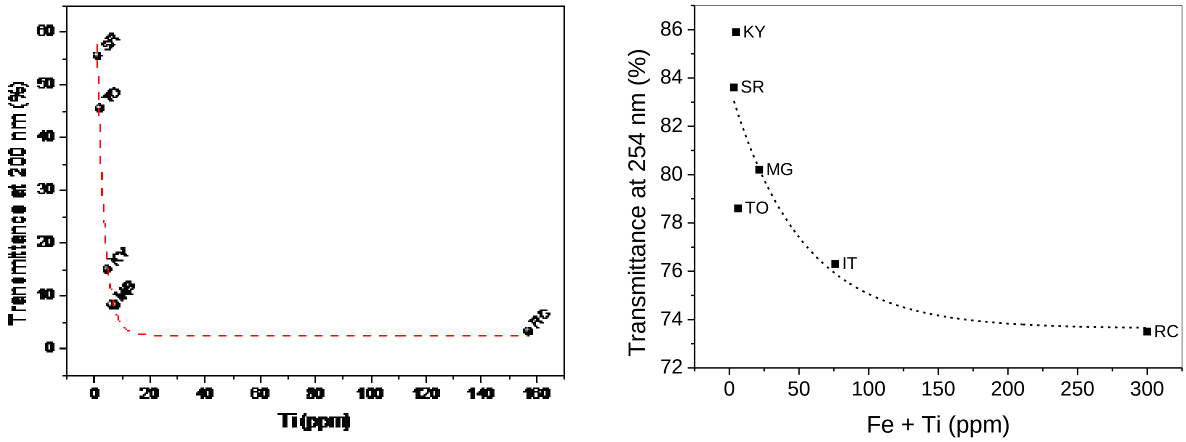


Figure 2. Absorption coefficient in the UV spectral range.

Few ppm of iron as 4-coordinated Fe^{3+} induces a very strong UV absorption. Pearson's correlation coefficient between Fe and Ti indicates a strong and positive linear correlation so that the transmittance at 254 nm seems to be ruled mainly by Fe and Ti impurities (Figure 3).



(a) (b)

Figure 3. Effect of main metallic impurities on transmittance: (a) Ti at 200 nm and (b) Fe + Ti at 254 nm.

For achieving a transmittance higher than 40 % at 200 nm, based on sample SG.REF in Figure 4, Ti content in quartz powder should be lower than approximately 2 ppm, by interpolating data shown in Figure 3(a). In the same way, for a transmittance higher than 77.4 % at 254 nm, Fe content should be lower than 48 ppm. Based on these criteria, QP.SR and QP.TO are qualified quartz powders for silica glass production, with no need of additional purification processing. Sample QP.MG also presented a high transmittance at 254 nm, with potential to be used as an “ozone-free” fused quartz, since it presents a “naturally-doped” Ti that prevents ozone and UV stress generation. Silica glass production with Brazilian natural quartz powder by SPS method also showed good optical transmittance, mainly in the NIR region with no OH absorption.

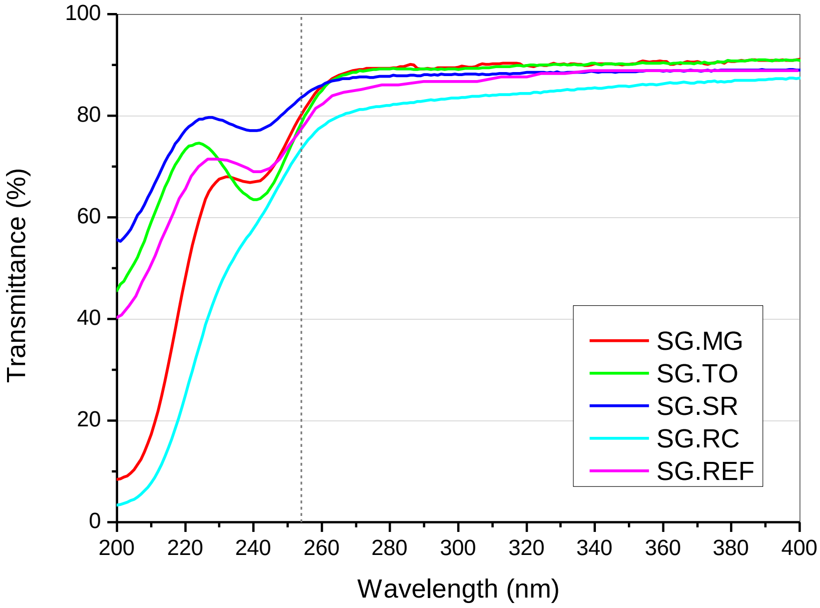


Figure 4. Comparison of optical transmittance of Brazilian quartz produced silica glasses with a commercial silica glass (SG.REF).

CONCLUSIONS

Brazilian natural and beneficed quartz were used as raw material for silica glass production by flame fusion to evaluate the feasibility for UV applications. Despite a large amount of alkali metal ions, Fe and Ti transition metals were found as main deleterious for transmittance in the UV range, causing a major impact on the optical transmittance at 254 nm. Quartz powders of Santa Rosa and from Cristalandia are qualified to be used, with no needs of additional purification.

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