VARIATION IN RAW MATERIAL IMPURITIES CONTENT AFTER SILICA GLASS MANUFACTURE BY FLAME FUSION

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ABSTRACT

The worldwide increasing demand for renewable energy sources has driven a significant raise in the production of photovoltaic solar cells. In order to manufacture such devices it is required high purity silicon material, which can only be processed using special tools made of high purity silica glass to avoid contamination of the final material. The most usual process to obtain such tools is to fuse natural quartz powders into $H_2\backslash O_2$ or LPG\O_2 torches. During this process, the level of impurities contained in the raw material suffers severe modifications, which will affect the overall quality of the fused silica glass obtained. The understanding of this technique is of high interest of Brazilian industry, once this country possesses large good quality quartz mineral deposits and very little know-how in fusion technology.

The present work investigates the variation of such impurities' level in different geological origins natural powder after they are fused into silica glass. All samples investigated were obtained using the Verneuil method of flame fusing, using a flame made of LPG and O_2, using different LPG\O_2 ratios. Regarding raw materials, four kinds of Brazilian natural powder were used, from Governador Valadares, MG; Rio Claro, SP; Tocantins State and São João del Rei, MG, regions. Both raw materials and produced glasses were powdered into 500 mesh powders for chemical analysis by ICP-MS technique.

Results showed that in all studied cases, flame fusion process provided impressive alkali purification. Na was the most purified material, which can be purified up to 96% during fusion. Also Li, which is usually one of the most difficult impurities to be eliminated in raw materials, showed high purification levels for all samples, reaching up to 86.7%. It was also observed that higher purification was obtained in oxidative flame ratios. Such results are very important in order to improve Brazilian fusion technology for high quality silica glass production.

Keywords: silica glass, quartz, Verneuil, SPS

INTRODUCTION

Silica glass is broadly used during the processing of both electronic and solar grade silicon(1). They are the key material for the crucibles that will receive melted silicon for purification(2), and therefore need to have high chemical purity levels, in order to avoid that eventual trace elements in its structure react with the silicon melt, affecting both silicon and silica glass quality(3).

There are several methods for obtaining high purity silica. Such methods involve both complex and expensive procedures that can produce silica glass with much less than 1 ppm of total trace elements (such as VAD or MCVD methods)(3), and simple methods that will result in larger trace element content (about 30 ppm total impurity)(5). Such methods are for example melting natural powders in flame torches ($H_2\backslash O_2$ or LPG$\backslash O_2$) or in electric furnaces, which are both the mostly used in the crucible industry(6).

During those processes, especially the flame fusion, several modifications in chemical composition of the raw material occur. There have been reported that Na and K amounts within the final fused silica as significantly lower than the one in the raw material(7). On the other hand, references for the behavior of other elements contents, such as Li, one major impurity in natural quartz, are lacking in literature.

This work therefore aims to further investigate the purification behavior of several elements during the flame fusion of different quartz powders. It is also aimed a higher understanding if specific characteristics within raw material, such as geological origin, affects the degree of purification.

EXPERIMENTAL PROCEDURE

Raw Materials

For raw material, it was used quartz obtained from 4 distinct occurrences. The first ore, called Rio Claro (RC) is a major sand deposit located in Rio Claro, SP. It has a pegmatite geological origin, and a large content of impurities, especially Fe and Al, as shown in Table 1. The second sample was also of pegmatite geological origin, located in Governador Valadares, MG and in this work it is called GV. There were also selected 2 samples of hydrothermal geological origin, from the state of Tocantins (called TO) and São Jõao del Rei, MG (called SR). The major chemical contaminants (more than 90% of total impurities) for all powders are shown in Table 1. Sample RC also presented some black spots on the final powder, being identified as other minerals, such as biotite and ilmenite, which make this sample presents Fe and Ti in much higher amounts.

All samples, both sand and stones were grinded using a silica glass mortar, in order to avoid contamination during the powdering procedure. The materials were all sieved using 80 mesh and 200 mesh sieves in order to achieve a final particle size distribution between 75 and 180 microns. All powders were then analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique, using a XSeriesII Thermo ICP-QMS equipment, with collision cells in accordance with usual procedures for quartz chemical analysis[(8)].

Table 1 – Major chemical contaminants in quartz raw powders.

Sample	Al (ppm)	Ca (ppm)	Fe (ppm)	K (ppm)	Li (ppm)	Na (ppm)	Ti (ppm)	Others (ppm)	Total (ppm)
GV	142	19.4	15.4	44.80	6.70	54.1	6.1	27.3	315.7
TO	15.7	21.3	4.4	10.60	1.60	35.8	1.9	5.9	97.2
RC	116	38.3	143.0	52.40	1.90	53.6	157	51.7	613.9
SJ	26.4	27.1	3.7	10.4	5.07	34.5	1.4	7.2	110.7

Silica glass manufacture and analysis

All samples were fused using the Verneuil technique, in a furnace at Optron Micromecanica Ltd., in Campinas, SP. The furnace was equipped with 2 metallic burners and a metallic feeder. The parameters, such as flame ratio, ingot rotation, powder feeding, ingot translation, etc., were all optimized for each powder in order to achieve maximum transparency in the fused glass and to avoid bubble generation, as shown in Table 2 for each sample. Temperature was measured by using an optical pyrometer.

Table 2 – Fusion parameters.

Sample	LPG/O_2	Temperature (ºC)	Translation speed (mm/min)	Rotation speed (RPM)
GV	0.18	1550	0.98	0.95
TO	0.31	1650	0.55	0.55
RC	0.24	1650	0.7	0.70
SJ	0.21	1550	0.78	0.90

The post-fusion samples were grinded in the same silica mortar and analyzed by the same technique described in the powder analysis section.

RESULTS AND DISCUSSIONS

Among all materials, alkali elements, such as Na, K and Ca were the ones with higher purification, being Na the most purified element for all samples. Figure 1, 2 and 3 shows the evolution of Na, K and Ca, respectively, in all glasses.

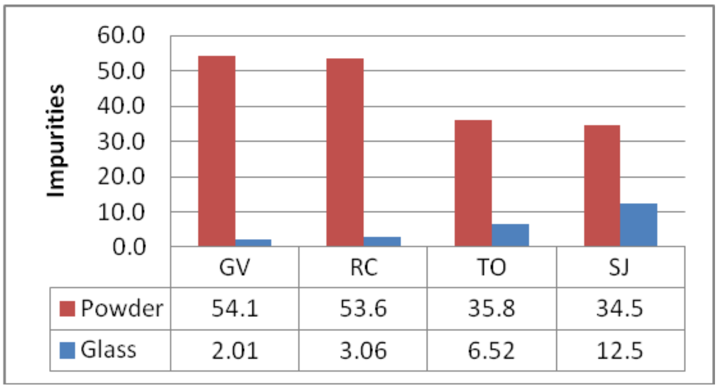

Figure 1 - Na content in all samples.

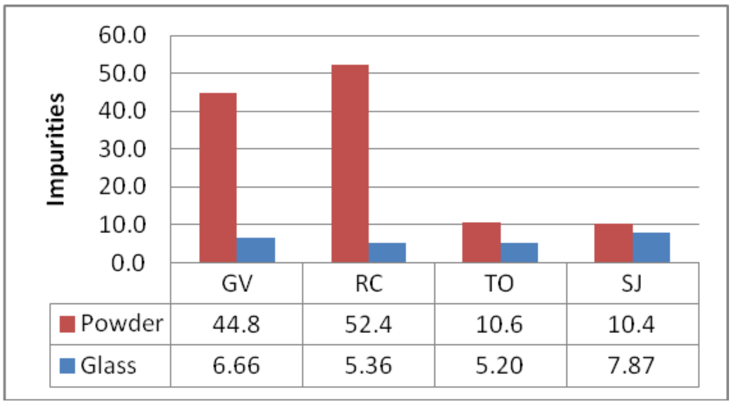

Figure 2 - K content in all samples.

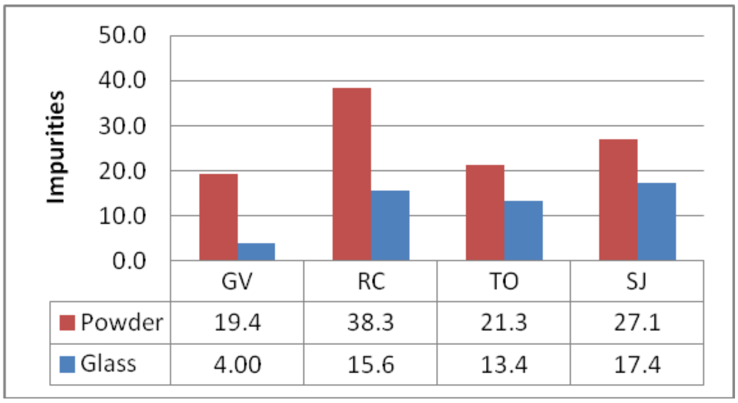

Figure 3 - Ca content in all samples.

This high alkali purification can be explained by the way those impurities are present in the initial powders. Usually, such elements occur not in substitutional positions on quartz lattice, but on fluid inclusions or interstitial positions inside the crystalline structure [8]. Such interstitial positions would be severely modified during the glassy transformation that take place during the silica fusion, resulting in smaller spaces for those elements to fit, and consequently resulting in their vaporization high temperatures.

A similar behavior is observed regarding Li impurity content, another element traditionally thought to occupy interstitial positions (as shown in Figure 4), yet in a much lower degree than the alkali group elements. This lower degree can be explained by the fact that the ion Li^{+} preferentially compensates the charge of Al^{3+}, when this last occupy substitutional positions replacing Si^{4+} ions. This might result in a higher interaction between Li and the newly formed glassy structure, when compared with the alkali.

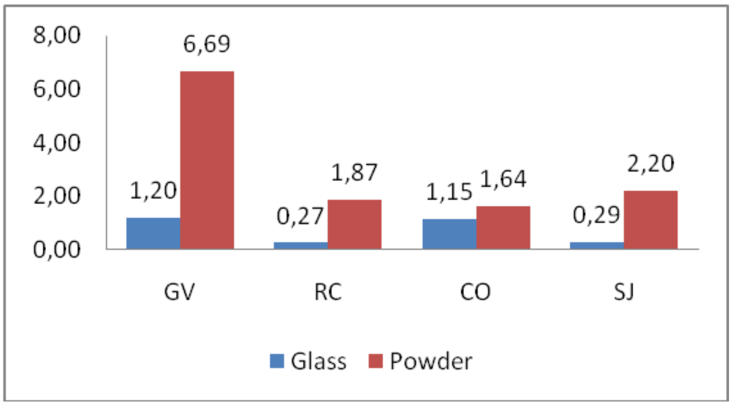

Figure 4 - Li content in all samples.

On the other hand, elements traditionally attributed to occur in substitutional positions, such as Al and Fe, show little purification, being always lower than 30% for Al and 50% for Fe. The only exception is sample RC, which shows a Fe purification of 70%. This result may be attributed to the fact that part of the biotite and ilmenite were eliminated during the fusion process, yet part was still present as little black spots on the formed glass. Other elements that showed little or no purification were Ti and Ge, also thought to be on substitutional positions.

One very interesting fact that can be noticed is the influence of process parameters on purification. Surprisingly, temperature did not affect significantly on purification behavior, as higher temperatures (on samples TO and RC) did not resulted in higher purification. Stoichiometry, on the other hand, seems to interfere in purification results. Stoichiometric LGP/O_2 ratio is about 0.2, sample GV, which was the most purified, had a lower ratio and therefore excess of oxygen on the fusion environment. Results suggest that this excess of oxygen might potencializate elements purification, especially for alkali elements and Li (for Li, TO sample with a high lack of oxygen showed the worse purification ratio). It is also important to notice that sample GV showed lower final impurities ratio than all others, evidencing the influence of flame ratio.

Regarding geological origins, samples with pegmatitic origin showed overall higher purification from ones with hydrothermal origin. This is probably due to the fact that hydrothermal quartz generally has a lower level of impurities. Final amounts, excluding sample GV, have very similar impurities levels, for both RC, SJ and TO samples.

CONCLUSIONS

The manufacture of silica glass using the Verneuil fusion was studied in order to analyze impurities variation during fusion. Several powders were used under diverse flame conditions and all of them showed a great deal of purification, especially for alkali and Li elements, reaching levels up to 96.3% of purification efficiency for alkali and 86.7% for Li. Fusion temperature seems not to influence on the purification behavior, at least within the studied conditions. Flame condition, driven by oxygen availability, on the other hand showed to be very important in order obtain a purer silica glass, once oxidative flames showed lower final impurities levels.

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