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STRATEGIC HIGH QUALITY QUARTZ SUPPLY FOR FUSION INTO SILICA GLASS

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ABSTRACT

An extensive in loco survey of main quartz producing regions in Brazil integrated with physicochemical characterization studies of quartz lascas and their fusion into silica glass bring the possibility of obtaining high quality quartz powder supplies for various industrial applications. The advantage is the relatively simple, cheap and environmentally friendly processing due to the high quality huge reserve of quartz ores of hydrothermal geological origin. The possibility of using highly transparent first grade quartz lascas in conventional fusion processes allows the fabrication of nearly bubble free silica glass. Due to the increasing demand of silica glass for processing solar cells and other products, this material is certainly a strategic supply for the present and future scenarios.

INTRODUCTION

The advent of semiconductor industries in the 1960's and their rapid expansion in subsequent years demanded a large amount of silica glass[1] produced by fusion of natural quartz lascas* from Brazil, the only raw material available for this purpose at that time. Nevertheless, Brazilian miners and exporters were not able to improve quality control in terms of impurities and transparency to fulfill the rapid evolution of raw material specifications for fusion into silica glass.[2-4] With the advent of Iota high quality pure quartz powder[5] processed by Unimin in the United States, the share of Brazilian quartz lascas in the international market has decreased to almost zero. In recent times, however, due to the short delivery of Iota Quartz, most of the silica glass manufacturers in the world have been looking for alternative sources of quartz powders. This scenario has become critical due to the increasing demand of China, especially to process solar photo-voltaic cells. In addition, the perspective of solar electricity becoming one of the major energy sources by 2050 will also increase the demand for such material.[6]

Many countries have quartzite and quartz sand typically of pegmatite geological origin, but it is unusual to find large reserves of hydrothermal origin quartz, which is much purer in composition with higher transparency than most pegmatite ores.[7] Quartz resources in Brazil surprisingly present a huge occurrence of both pegmatite and hydrothermal quartz. The main quartz locations in Brazil were delineated during the Second World War as a result of an intense search of piezoelectric grade quartz for strategic use in radio communications. Quartz ores are distributed along large areas called quartz belts (Fig. 1.a), such as the Central belt in the states of Goias and Tocantins, the Coastal belt in the State of Espirito Santo, and the Minas-Bahia belt, which extends for approximately 1000 km along the Diamantina mountains. Motivated by the scenario of high demand, we have conducted a large scale survey extending from the southern region to the north of the country in Amazon, State of Para.

The project was conducted by UNICAMP-The State University of Campinas with the financial support of JICA-Japan International Cooperation Agency. Approximately two hundred quartz mines were surveyed to make a kind of quality mapping of quartz mines in various states: Minas Gerais, Bahia, Goias, Para, Tocantins, Ceara, Rio Grande do Norte, Sao Paulo, and Rio Grande do Sul.[8]

Extraction sites in the mine in Oliveira dos Brejinhos, State of Bahia, and mine in Diamantina, State of Minas Gerais, are shown in Figs. 1.b and 1.c; respectively. Fig. 1.d shows a giant piezoelectric grade single crystal.

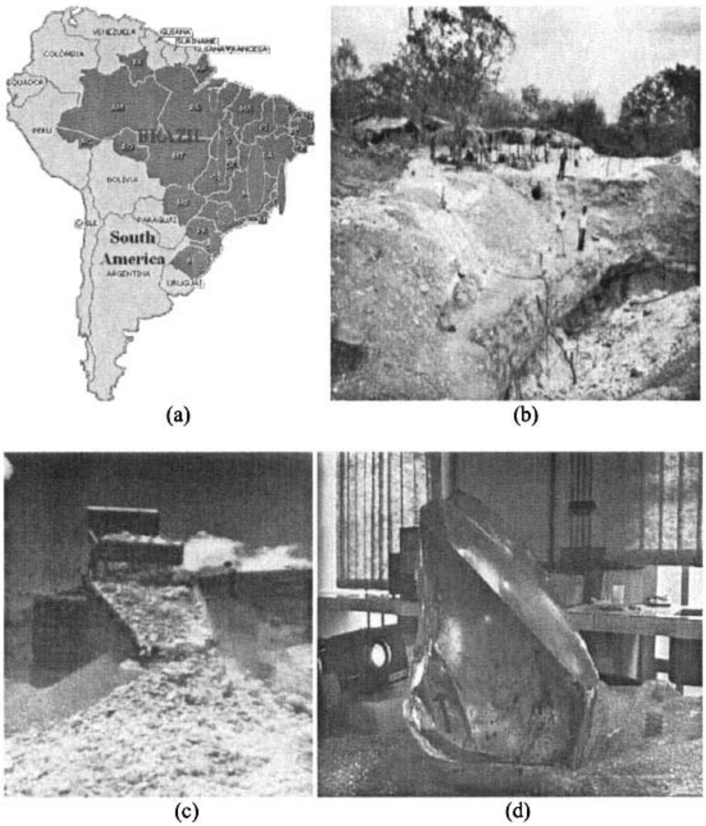
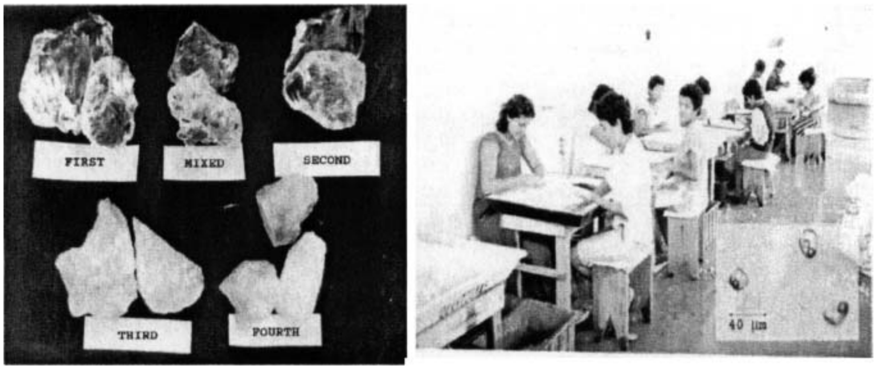


Figure 1. (a) Main quartz belts in Brazil; (b) mine in Oliveira dos Brejinhos, State of Bahia; (c) extraction in Diamantina, State of Minas Gerais; (d) giant piezoelectric grade single crystal quartz.

Graded Lascas and Fluid and Solid Inclusions

The degree of transparency of natural quartz varies according to the concentration of fluid inclusions and the number of small cracks. Depending on the type of lasca, it is possible to observe in the same lasca, parts of high transparency and different degrees of opacity. Therefore, for controlling transparency of quartz lascas, quartz ores are classified into graded lascas, denominated as first, mixed, second, third, and fourth (Fig. 2.a), and also to control eventual solid inclusions and large fluid inclusions by observation inside water (Fig. 2.b). Such a classification procedure can also be made by an automation system using a high resolution CCD camera.[9]



(a) (b)

Figure 2. (a) Graded lascas based on transparency degree. (b) Naked eye visual quality control of lascas in water tank. Inset shows optical microscopic image of solid and large fluid inclusions in lascas.

Silica Glass

Unique characteristics are found in silica glass, such as optical transparency and high resistance to corrosion, making it the only usable material for high temperature thermo-chemical treatment of semiconductors. However, physical properties of silica glass, such as viscosity, density, acoustic wave propagation, thermal conductivity, index of refraction, etc., depend on the fusion method and the metallic impurities contained in the raw material. In general, the silica glass manufacturers specify their products in various types according to the raw material, method of fabrication, and the type and concentration of impurities.[10]

Usual classification of silica glass based on natural quartz is:

(i) Type I, by fusion of natural or synthetic quartz powder in electric furnace in vacuum or in inert atmosphere at low pressure using plasma. Some of type I commercial products are Vitreosil, Infrasil, GE124, KI, KS4V, Puropsil A, Pursil, and T2030.

(ii) Type II, silica glass obtained by flame fusion, in general using hydrogen-oxygen flame. The OH content is ~120 ppm and metallic impurities are less than the initial raw-material by the effect of vaporization in high temperature flame. Some examples of type II products are Armesil T08, Heralux, Herasil, Homosil, KU-2, KV, OG Vitreosil, Optosil I, T-1030, and Ultrasil.

The present research aimed to obtain high quality and low cost quartz supplies for silica glass manufacture for various industrial applications, in particular, to fulfill the strong demand for processing solar photo-voltaic cells.

COMPARISON WITH IOTA QUARTZ AND DISCUSSION

Impurities content in natural quartz shows a good correlation with geological formation but it is particularly dependent on the region and the mine itself. It is possible to find a very high purity material even though in-natura. Table I shows the result of impurities analysis of lascas (first, mixed, second and third) from the same mine and their comparison with quartz powders Iota Standard and Iota 4. Surprisingly, they are comparable, even though practically without any purification processing.

Table I. Impurity contents in natural Brazilian quartz lascas compared to IOTA quartz (ppm).

Lascas	Fe	Al	Na	K	Li	Ti	Ca	Cu
First	0.2	9.7	0.3	0.2	1.2	0.5↓	0.1↓	0.02↓
Mixed	0.4	10.1	0.5	0.9	1.0	0.5↓	0.1↓	0.02↓
Second	0.4	8.3	0.4	0.2	0.9	0.5↓	0.2	0.02↓
Third	0.4	11.0	0.3	0.2	1.1	0.5↓	0.4	0.02↓
IOTA Standard	0.2	16.2	0.9	0.6	0.9	1.3	0.5	0.05↓
IOTA 4	0.3	8.0	0.9	0.35	0.15	1.4	0.6	0.05↓

Understanding the incorporation of different types of impurities in SiO_2 structure is of fundamental interest for the effective purification of natural quartz lascas. Particularly, it is important to understand how Al impurity behaves in quartz as it forms Al-related centers in conjunction with other types of impurities, e.g., Li^+, H^+, Na^+. Al impurity can enter the SiO_2 lattice as interstitial or substitutional. Interstitial Al can usually be removed by leaching, but substitutional one is quite stable by chemical leaching and remains even after fusion into silica glass. It is then essential and strategic to know a priori such characteristics in the quartz ores before spending time and energy for extraction and processing. The form of Al incorporation can be estimated by the correlation of Al and Li concentrations, which shows the tendency to form Al-Li in a larger or smaller scale. For example, in the material of mine 1 (Table II), the ratio Al/Li is about 1. It increases to 1.4 and 6.1 for mines 2 and 3, respectively. γ-ray irradiation causes the dissociation of Al-Li centers and formation of Al-hole and Al-OH centers[11-12] inducing the darkening effect by color centers related to the form of Al incorporation in the lattice. Higher the concentration of substitutional Al, more intense the effect of darkening, that can be quantified by the darkening factor (D), which corresponds to the quantity of Al-hole centers defined as:[8]

$$D = \alpha_\gamma - \alpha_0, \tag{1}$$

where, α_0 and α_γ are the absorption coefficients in 470 nm, before and after the irradiation, respectively.

Based on this method, it is possible to predict a priori that lascas from mine 1 are not suitable for purification treatment, as the main part of Al-content is substitutional.

Table II. Al incorporation in natural quartz as a function of Al/Li ratio in ppm and the darkening effect by γ-ray irradiation as adapted from Iwasaki et al.[8]

Natural quartz	Al	Li	Al/Li	Na	OH	Darkening degree by irradiation (cm^{-1})	Form of Al aggregation
Mine 1	282	284	1.0	1	32	5.9	Mostly substitutional
Mine 2	34	24	1.4	3	42	1.8	Part substitutional and part interstitial
Mine 3	55	9	6.1	0.3	67	0.4	Mostly interstitial

As aforementioned, the degree of transparency of lascas depends on the content of cracks and fluid inclusions. Parts of the fluid inclusions are eliminated by powdering, but another portion remaining in the grains can generate bubbles in fused materials. High viscosity of silica glass does not allow the elimination of bubbles, particularly in the case of flame fusion in air (Verneuil method). Therefore it is necessary to control good transparency of quartz ores in order to manufacture transparent silica glass. Strict selection of first grade lascas allows the manufacture of nearly bubble free silica glass by the Verneuil method (Fig. 3).

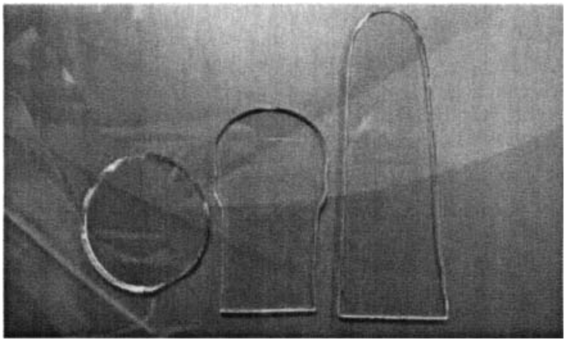


Figure 3. Silica glass of optical fiber cladding grade by flame fusion obtained from first grade lascas.

CONCLUSIONS

Characterization studies of Brazilian quartz extracted from various regions and their powdering and fusion into silica glass revealed technological and economic advantages of using quartz lascas for fusion into silica glass to fulfill the increasing demand for solar cells processing, optical fiber industries in terms of cladding and dummy rods, and other applications. Significant benefit to the environment can result by obtaining high purity quartz powder with a smaller quantity of energy, chemicals and infrastructure in comparison with the usual quartz ores; quartz sand or pegmatite origin quartz containing much higher concentrations of impurities.

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FOOTNOTES

*lascas are small natural quartz fragments of 20-200g classified according to their transparency degree.[13-11]

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