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DEVELOPMENT OF TRITAN CRYSTAL GLASS USING LOCAL PROCESSED SILICA SAND FOR TABLEWARES

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ABSTRACT

Crystal glass is a popular item among most people because of its brilliance and aesthetic appearances. In this study, silica sand obtained from Syarikat Sebangun Sdn. Bhd., Bintulu, Sarawak. It was to study the suitability of the local silica sand as raw materials for the preparation of the tritan crystal glass. In the present work, two equipments employed in upgrading the silica sand namely attrition scrubber and wet high intensity magnetic separator. In this study some mineral based additives such as titanium oxide, potassium oxide, calcium oxide, sodium oxide, zirconium oxide, etc. were used in the tritan crystal glass formulation. The glass formulation was melted in a front loading furnace at approximately 1450 ^{o}C. The resulting products were tested according to and compared with BS 3828:1973, the specification for crystal glass standards. Some of the parameters stipulated under the Standard are refractive index, density and hardness. The resulting properties will be elaborated in the forthcoming paragraphs.

Keywords: Silica sand; refractive index; density and hardness;

INTRODUCTION

In line with the Minerals and Geosciences Department's objective to value add local minerals, Mineral Research Centre has embarked on a research project that is to use locally processed silica sand for making tritan crystal glass products. This effort is not only to optimise the usage of local mineral but also to provide opportunities for the development of other spin off industries. Crystal glasses are heavy, durable glasses prized for their brilliant, glimmering and sparkling appearances. They are very exclusive and expensive. According to ASTM C162-56, Standard Definition of Terms Relating to Glass and Glass products, crystal glass is defined as colourless, highly transparent, frequently used for art and tablewares. Crystal glass technologies are dominated by the European countries particularly Germany, Czechoslovakia and Britain. The Bohemia from Czechoslovakia and English crystal from Britain are well known throughout the world. Nevertheless, most of the commercial crystal glasses contain lead oxide (PbO) and Barium oxide (BaO). It has been a tradition that PbO and BaO are added into the crystal glass formulation. PbO and BaO are toxic even in small amounts. They pose a danger to human health since lead and barium can be leached out after a short time from objects manufactured from such crystal glass.

For this reason, there is increased interest in lead and barium free crystal glass. In order to replace PbO and BaO, which are present in crystal glass, potassium oxide (K_2O), Titanium oxide (TiO_2) and Boron oxide (B_2O_3) are added. While replacing them with the new materials in the crystal glass composition, the properties of glass should comply to US patent [1]. The use of unique ingredients like titanium combined with an advanced manufacturing process has created an incredibly pure, hard and clear crystal glass. The definition of tritan crystal glass produced from above mentioned are as follows:

- Having an optical transmission of at least 85%;
- Having a refractive index of greater than 1.52;
- Having a density of at least 2.45 g/cm^3; and
- Having good solarisation.

Thus, due to the increasing awareness towards health and environment, elimination of lead and barium from crystal glass composition has currently become the main issue for the research and development (R&D) in the crystal glass industry. Therefore, the objective of this paper is to study lead and barium free crystal glass for tablewares purposes. Even though, it is known that the crystal glass technology and industry are well established throughout the world but they are not well known in Malaysia. Apart from that, this R&D intends to acknowledge that local silica sand is suitable for crystal glass making especially crystal glass products.

EXPERIMENTAL DETAILS

Silica sand

Silica sand was obtained from Syarikat Sebangun Sdn. Bhd., Bintulu, Sarawak. In the present work, as shown in Figure 1, some of the equipments employed in upgrading the silica sand were attrition scrubber and wet high intensity magnetic separator (WHIMS). The purpose of attrition scrubbing was generally to clean the surface of silica sand grains. It was very effective in removing ion staining material. The process was followed by separation using the WHIMS. Its role was to separate magnetic minerals that exist in silica [2]. Finally, after processing, the sample was sent to X-ray fluorescence (XRF). The main purpose of the sample being analyzed using XRF is to identify the element composition such as SiO_2, Fe_2O_3, Cr_2O_3 and Al_2O_3. According to Malaysian standard, MS701:1981, Table 1, the specification for crystal glass making should be silica sand of grade B [3]. The chemical content of B grade is as follows; 99.5% SiO_2, 0.015%Fe_2O_3, 0.05% Al_2O_3, 2 PPM Cr_2O_3 and 0.05% TiO_2.

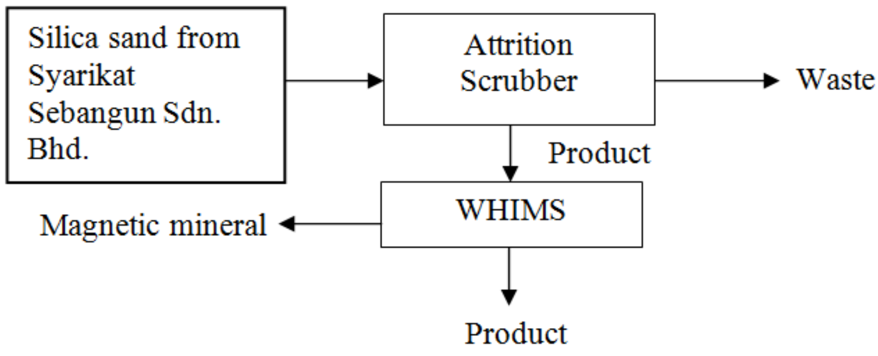

Figure 1: Flow process of upgrading silica sand

Table 1: Malaysian specification for glass sand

Grade	Usage	% SiO_2 min.	% Fe_2O_3 max.	% Al_2O_3 max.	Cr_2O_3 ppm max.	% TiO_2 max.	% CaO+ MgO max.	Loss on ignition % max.
A	Optical glassware	99.80	0.008	0.05	2	0.03	0.05	0.20
B	High grade domestic and decorative glass	99.50	0.015	0.05	2	0.05	0.05	0.20
C	Colourless glass including containers	98.50	0.03	0.10	6	0.10	0.10	0.50

Glass composition

The compositions of tritan crystal glass used in the study are as shown in Table 2. Glass system is based on an alkali-lime-silicate glass. In glass composition TriPPM-1, the amount alkali metals can be greater than 25% by weight and the amount of TiO_2 and ZrO_2 can be between 1% and 3%. In glass composition TriPPM-2, the amount of TiO_2 + ZrO_2 can be between 0.5% and 1% by weight while quantity of alkali metals can be between 25% and 30% by weight. In TriPPM-3 formulation the quantity of TiO_2 + ZrO_2 and alkali metals are between 2.5% - 4% and 25% - 30% by weight respectively.

SiO_2 functions in glass as a network former. It is the backbone for the glass besides increasing chemical durability. Alkali metals such as K_2O and Na_2O were used to lower the melting temperature. The impurities such as Fe ions could be effectively suppressed by K_2O. Al_2O_3 increases the chemical stability and stabilises the network while the use of TiO_2 and Li_2O is to increase the refractive index of the glass. Sb_2O_3 is added as refining agents to reduce bubble in the glass melting [4].

Table 2: Crystal glass composition

Components	TriPPM-1 wt%	TriPPM-2 wt%	TriPPM-3 wt%
SiO_2	68.30	67.30	66.00
Al_2O_3	0.68	0.86	2.00
Li_2O	-	0.84	0.62
Na_2O	7.50	7.35	8.75
K_2O	12.08	10.10	10.40
CaO	8.98	12.25	9.20
TiO_2	2.12	0.95	1.22
ZrO_2	-	-	1.48
Sb_2O_3	0.34	0.35	0.34

Glass melting and glass characterization

Melting is the thermal process by which the components are completely converted into molten glass. The melting temperature and time for melting depend on the type of glass to be melted. In this study the time taken for melting was around 10 hours. In theory, the melting process can be divided into three stages namely melting and dissolving of the batch materials, fining of the glass and getting it free from bubbles and seeds, and homogenizing the glass and getting it ready for forming [4]. Figure 2 shows the flow process of producing and characterisation of crystal glass. As recommended by patent no. US 6391810 B1 issued in 2002, the glass melting temperature is about 1450 ^{o}C for raw crystal glass and followed by annealing process. Annealing process occurs at around 620 °C. The aim of the annealing process was to remove internal stresses in the glasses and finally they would not crack or break when putting at room temperature [4]. In this study, front loading furnace was used for crystal glass melting as well as annealing process.

The characterisation of the tritan crystal glass produced were carried out and then compared with crystal glass standards, BS 3828:1973, specification for crystal glass, Table 3, [5].

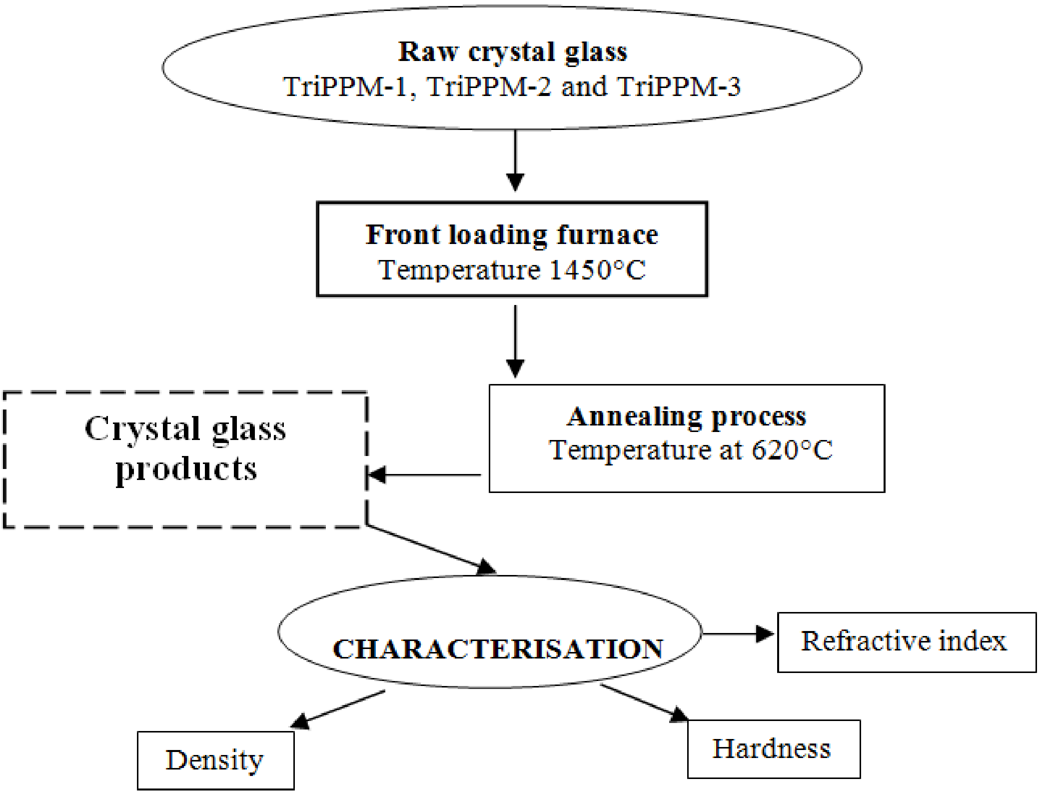

Figure 2: Flow process of melting and characterisation of crystal glass

Refractive index

Refractive index is the ratio of the velocity of light in air to that in the medium. The glass sample size required was 20-30 mm of length, 8-10 mm of width and 3-10 mm of thickness. The two sides of the sample were polished until we got a flat and mirror-like surface. Then, the refractive index of the sample was determined by using The Abbe refractometer 4T.

Density

The density is defined as the mass per unit volume. It was measured by weighing a glass sample in air and dividing this weight by the buoyancy (the reduction in weight) when the sample was suspended in water. The density balance used was Mettler toledo model AG 204. The formula used to calculate the density is as follows:

$$Density, \rho = \frac{W_a}{(W_a - W_b)}(\rho_o - \rho_L) \qquad (1)$$

where, ρ = density of sample, W_a = weight of sample in air, W_b = weight of sample in auxiliary liquid, ρ_o = density of the auxiliary liquid and ρ_L = density of air (0.0012 gcm^{-3}).

Hardness
In this study Digital Micro Hardness Tester Model MMT-3 was used for measuring of glass surface hardness. Vickers hardness equation is as follows:

$$VHN = \frac{1.8544 \times F}{D} \quad (2)$$

where, F = Load imposed on glass (kg) and D = Average diagonal length (mm)

Table 3: Crystal glass specification, BS 3828:1973

Category	% Metallic oxides	Density (g/cm^3)	Reftactive index (nD)	Surface hardness (Hv)
Full Lead Crystal 30%	PbO $\geq$ 30%	$\geq$ 3.00	nD $\geq$ 1.545	-
Lead Crystal 24%	PbO $\geq$ 24%	$\geq$ 2.90	nD $\geq$ 1.545	-
Crystal glass	ZnO; BaO; PbO; K_2O alone or together, $\geq$ 10%	$\geq$ 2.45	nD $\geq$ 1.520	Vickers 550 $\pm$ 20
Crystal glass	BaO; PbO; K_2O alone or together, $\geq$ 10%	$\geq$ 2.40	nD $\geq$ 1.520	Vickers 550 $\pm$ 20

RESULTS AND DISCUSSION

Characterisation of silica sand and tritan crystal glass
Table 4 indicates the quality of silica sand from Syarikat Sebangun Sdn. Bhd. Bintulu, Sarawak after undergoing upgrading process. The SiO_2 content has achieved category B silica sand, which is suitable for crystal glass making. Table 5 shows the properties of three tritan crystal glass.

Table 4: Result of silica sand quality

Components	Percentage
SiO_2	99.7
Fe_2O_3	0.01
TiO_2	0.03
MgO	< 0.01
CaO	< 0.01

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Table 5: Result of refractive index, density and hardness

No.	Designated of crystal glass	Refractive index (nD)	Density (g/cm^3)	Hardness (VHN)
1.	TriPPM-1	1.6221	2.490	494.78
2.	TriPPM-2	1.6220	2.489	526.30
3.	TriPPM-3	1.6218	2.510	531.06

Refractive index
As formulated in Table 5, the refractive index of the three tritan crystal glass namely TriPPM-1, TriPPM-2 and TriPPM-3 were 1.6221, 1.6220 and 1.6218 respectively. The readings were high and this means that the quality of the crystal glass products produced from processed silica sand is comparable with crystal glass standard as stipulated by BS 3828:1973. According to Shelby [6], the refractive index of glasses is determined by the interaction of light with electrons of constituent atoms of the glass. Increases in either electron density or polarizability of the ions increase the refractive index. As a result, low indices are found for glasses containing only low atomic number ions, which have both low electron densities and low polarizabilities.

Density
As indicated in BS 3828:1973, shown in Table 3, there are four values of density corresponding to the content of metallic oxides; the highest density is shown by full lead crystal containing equal or greater than (30% lead oxide) where its density is greater or equal to 3.00 g/cm^3 and the lowest is 2.40 g/cm^3 shown in crystal glass that contains ZnO; BaO; PbO; K_2O alone or together $\geq$ 10%.

Results of the density tests are summarised in Table 5. The readings of the density of tritan crystal glass were in the range of full lead crystal and crystal glass containing $\geq$10% of BaO, PbO and K_2O alone or together. In other word, tritan crystal glass produced from processed silica sand is comparable with crystal glass specification as above mentioned.

According to Shelby [6] and [7], the difference in value of density is contributed by many factors such as the structure, bonding and composition of glass material. Other contributing factor was the cooling rate of the glass. In general, a faster cooling rate yields a lower density because the melt has less time to densify its structure before freezing.

Hardness
Results of hardness tests of designated crystal glass are shown in the Table 5. It was concluded that all readings were lower compared with British standard. According to BS 3828:1973, the hardness of full lead and crystal glass is 550 $\pm$ 20 VHN. This means that tritan crystal glass produced from local processed silica sand was comparatively softer. This kind of crystal glass can be easily cut and engraved.

CONCLUSION

As a conclusion, based on the experimental works, the silica sands from Syarikat Sebangun Sdn. Bhd. is found to be suitable for making tritan crystal glass. Also, in this research work, it was found that the glass composition as designed by Mineral Research Centre can produce good quality crystal glass. The application of the right melting and annealing process plays an important role in determining whether the crystal glass produced is better or low in quality. Characterisation study showed that some properties of the crystal glass product were comparable with BS 3828:1973, specification for crystal glass.

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