FABRICATION OF LEAD-FREE HIGH REFRACTIVE INDEX GLASS USING LOCAL RAW MATERIALS

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ABSTRACT

High refractive index glass can be made by adding a heavy metal ion such as lead into glass. Lead contained glass can be melt at low temperature. Due to the harmful effects of lead, there are several attempts on using other materials to replace lead as much as possible. In this study, the lead-free high refractive index glasses were made by using local raw materials and by adding barium carbonate to replace lead in a mixture with various contents. The main composition of the mixture consisting of glass sand, dolomite, feldspar, limestone, sodium carbonate and boron oxide was poured into the crucible and melted in an electric furnace, in the normal atmosphere at a temperature of 1250°C for 6 hours. The refractive indices of glass specimens were found to increase from 1.5602 to 1.6784 as the increase of the additional amount of barium carbonate from 24 % to 40%. Results from a comparison study in the 32% barium or lead contained glasses prepared from various places local sand was found that the average refractive index of the barium glass and lead glass were 1.63 and 1.67 respectively. The dwell time of the barium glass was found longer than that of the lead glass.

KEYWORDS: lead free, high refractive index, local raw materials, glass

1. INTRODUCTION

1.1 About Glass Archaeological findings indicated that glass was firstly found in the Middle East. In the beginning glass manufacturing was slow and costly. Glass melting furnaces were very small and hardly produced enough heat to melt glass properly. In the ancient time, glass was used for a gem substitution in decoration of the ancient place and objects. For house ware, glass was a luxury item and only few people could afford it. However, the demand was still as high as gemstone. The physical definition, glass is a uniform amorphous solid material and can be produced when the viscous molten material was cooled down very rapidly, thereby not giving enough time for a regular crystal lattice to form. In its pure form, glass is transparent, relatively strong, hard-wearing, inert, or inactive material and can be formed to be very smooth surface. These desirable properties lead to a great interest to use glass. Most common glass is the soda lime silica glass and in the high refractive index glass is the lead contained glass.

1.2 Glass making The process for production of all glasses can be prepared by mixing of the starting materials into the glass batch and then melted. The mixture composes of silica obtained from beds of fine sand or from pulverized sandstone, an alkali such as soda or potash, lime or dolomite.

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The U.S. Bureau of Standard appointed the Sand Class Conditions for glass making that contained 95 wt.%SiO_2 (min.), 4 wt.%Al_2O_3 (max.), 1 wt.% Fe_2O_3 (min.), and 0.5 wt.% CaO+MgO (max.).

1.3 High Refractive Index Glass Glass is known as transparent clear materials, therefore, refractive index is the important parameter for glass. Light can be bended well by the high refractive index glass and it is largely depended on the density of the material. In the lead contained glass which is known as crystal glass shows the refractive index higher than 1.52. Most of lead glass contains lead oxide approximately 12-28 % by weight. Even though glass is very stable and inert, the lead contained glass seems harmful. Therefore, the high refractive index glass contained with no lead becomes interesting topics for researchers to investigate. Adding barium to replace lead in the crystal glass was found to be able to increase the refractive index.

1.4 Local Raw Materials Thailand is rich in many kinds of quality materials for glass making processing; sand, dolomite, feldspar, and limestone. The local glass manufacturing depends on the imported raw materials, especially the lead crystal glass that imported sand from Europe sites.

1.5 Objective The aim of this study was to fabricate a lead-free high refractive index glass. The lead-free high refractive index glass with the addition of barium carbonate and with the local raw materials was prepared and the optical property was determined. The sand was taken from different sites such as Chantaburi, Chumphon, Nakhon Srithammarat, Pattani, Phuket, Ranong, Rayong, Songkhla, and Trad. The dolomite, feldspar, and limestone were taken from Kanjanaburi, Tak, and Phrae, respectively.

2. MATERIALS AND METHODS

The lead-free high refractive index glasses were prepared at the laboratory of the Glass and Glass Product Research and Development Laboratory, Institute for Research and Development Science and Technology, Chiang Mai University, Thailand. The composition and the structure of sand were determined by x-ray fluorescence spectrometer (Rigaku Model RIF-1000) and scanning electron microscope (Jeol Model JSM-840A), respectively. The grain distribution of sand was analyzed by particle size analyzer (Malvern Instrument Model Master Sizer). The 18 glass samples with 120 grams weight in each sample were made. The primary mixture contained 50 wt% sand, 25 wt% (dolomite+feldspar+limestone), 20 wt% Na_2CO_3, and 5 wt% B_2O_3 and was divided into two set of samples. The first set was glass mixtures that used sand from Chumphon added with various concentration of $BaCO_3$ ranging from 24, 26, 28, 30, 32, 34, 36, 38, and 40 wt%. The second set, the content of $BaCO_3$ was fixed at 32 wt% and prepared with the local sand taken from Chantaburi, Chumphon, Nakhon Srithammarat, Pattani, Phuket, Ranong, Rayong, Songkhla, and Trad. All mixtures were melted in an electric furnace, in a ceramic crucible, in the normal atmosphere at 1250 °C with dwell time of 6 hours. All specimens were prepared in parallel with the normal lead crystal glass and with the same concentration. After cooling, the glass samples were polished for measuring refractive index with an electronic Abbe refractometer (Finemech Model AR 2008).

3. RESULTS AND DISCUSSION

Determination of the composition shows that the sand from various sites mostly contain of more than 96 wt% silica (SiO_2), except sand taken from Nakhon Srithammarat and Ranong that not only the concentration of silica is low, but also the contamination of alumina (Al_2O_3) and iron oxide (Fe_2O_3) are high, as shown in Table 1. The morphology of sand from various sites, the grains are almost loose and finesse shape as shown in figure 1. The density of sand is 2.600 gm/m^3, the grain concentration, the specific area, and the grain size are between 0.1175 to 0.2120 %vol., 0.0309 to 0.0572m^2/gm, and 190.79 to 331.32 μm, as shown in table 2. From the study, the refractive indices were found to increase as the increase of the lead or barium content. In the specimen contained lead, the index of refraction increase from 1.525 to 1.702 and in the barium contained specimens the index of refraction increase from 1.5602 to 1.6754, details are indicated in table 3 and table 4. The refractive index of the barium glass increased linearly as the increasing of the concentration of barium is indicated in the figure 2. Comparison of glass melting processing between the barium and the glasses, it was found that the dwell time of the barium and the lead glasses were 6 and 4 hours, respectively.

Table 1 The composition of local sands analyzed by XRF technique

Site	Composition (wt%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
Chantaburi	98.840	0.770	0.050	0.010	n/a	0.040	0.180	0.180
Chumphon	99.140	0.570	0.030	n/a	n/a	0.020	n/a	0.170
Nakhon Srithammarat	75.240	13.200	1.130	0.060	0.070	6.060	0.290	3.860
Pattani	95.980	2.600	0.100	0.010	0.050	1.030	n/a	0.280
Phuket	97.040	0.850	0.370	0.010	n/a	0.030	n/a	0.860
Ranong	58.130	26.120	2.110	0.020	0.070	9.110	0.270	4.430
Rayong	97.470	0.950	0.310	0.030	n/a	0.140	n/a	0.750
Songkhla	96.920	1.850	0.120	0.010	n/a	0.570	n/a	0.350
Trad	98.850	0.560	0.050	n/a	n/a	n/a	n/a	0.230

Table 2 The distribution of local sand particle analyzed by particle size anlyzer

Site	Grain size (V,0.5) (mean diameter, μm)	Concentration (%V)	Specific area (m^2/gm)
Chantaburi	249.66	0.1376	0.0572
Chumphon	219.01	0.1456	0.0431
Nakhon Srithammarat	224.58	0.1175	0.0496
Pattani	241.23	0.1365	0.0481
Phuket	331.32	0.2120	0.0399
Ranong	224.51	0.1602	0.0309
Rayong	190.79	0.1476	0.0434
Songkhla	221.89	0.1194	0.0545
Trad	247.50	0.1661	0.0460

Table 3 The refractive index of glasses with various concentration of barium and lead

wt% Concentration	Refractive Index at 589.3 nm	
	Ba-glass	Pb-glass[1]
24	1.5602	1.525
26	1.5841	1.565
28	1.6084	1.622
30	1.6108	1.649
32	1.6234	1.660
34	1.6386	1.680
36	1.6421	1.686
38	1.6543	1.694
40	1.6784	1.702

Table 4 The refractive index of glasses prepared from various sites local sand, added 32 wt% $BaCO_3$

Local Sand	Refractive Index at 589.3 nm	
	Ba-glass	Pb-glass[1]
Chantaburi	1.6232	1.660
Chumphon	1.6234	1.660
Nakhon Srithammarat	1.6331	1.675
Pattani	1.6306	1.660
Phuket	1.6302	1.670
Ranong	1.6513	1.695
Rayong	1.6317	1.665
Songkhla	1.6323	1.665
Trad	1.6230	1.660

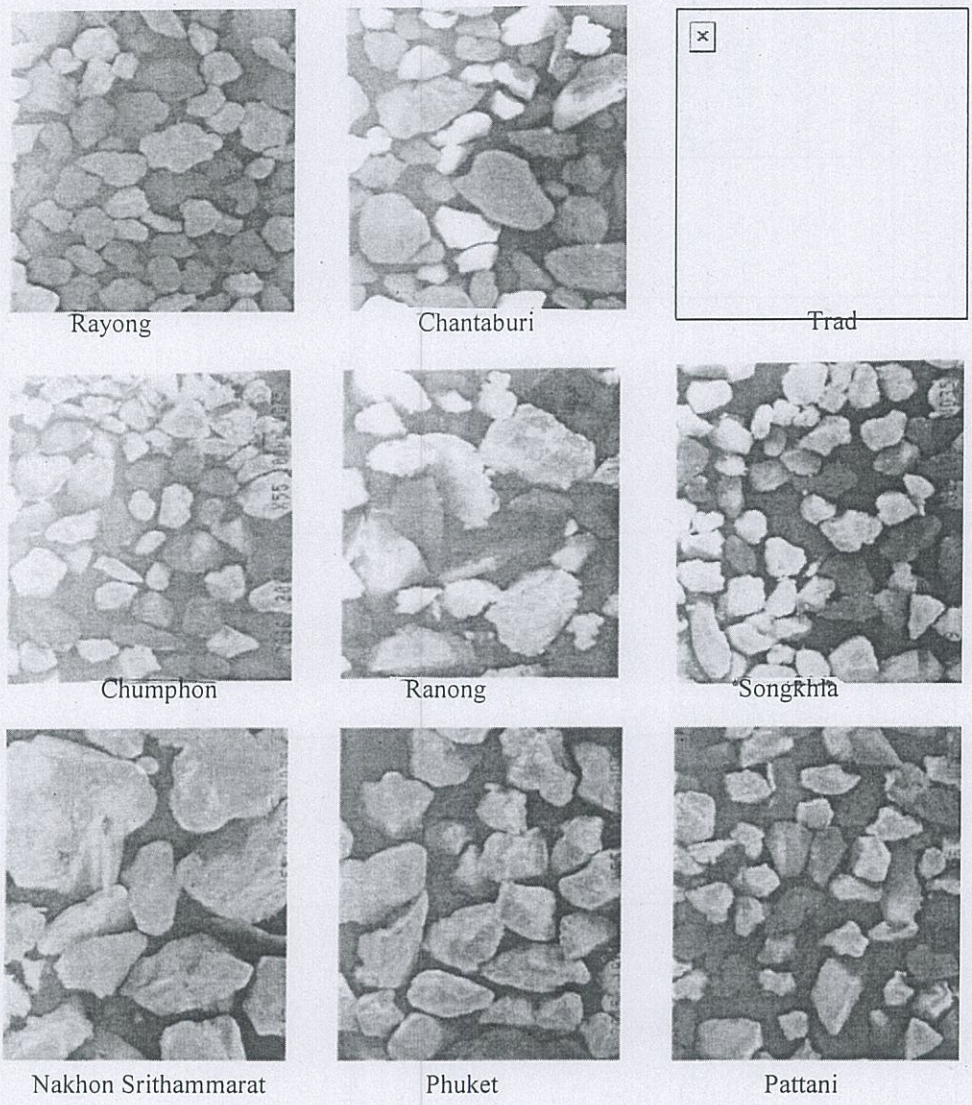

Figure 1 Morphology of local sand from various sites

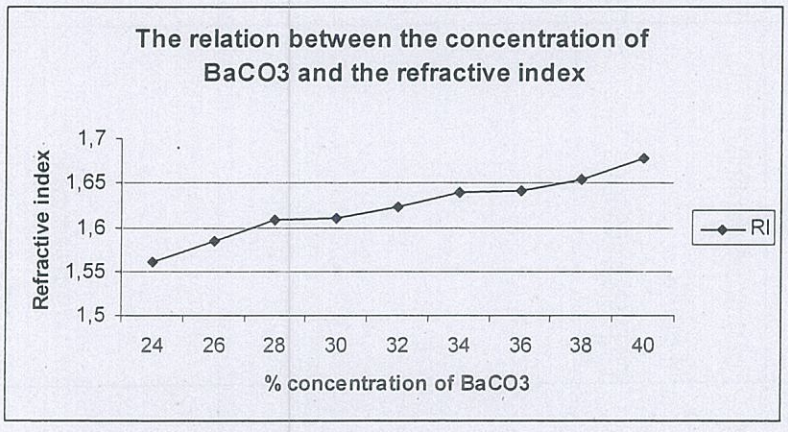

Figure 2 The relation between the concentration of $BaCO_3$ and the refractive index

4. CONCLUSIONS

The local sands were satisfactory for glass making processing. Compilation and distribution information of location and abundance showed that the sand from Chumphon is the best one, high silica content, low alumina and iron oxide impurities. The lead-free high refractive index glass can be fabricated by adding with barium carbonate in replacing lead oxide. The refractive indices of glass specimens were found to increase linearly from 1.5602 to 1.6784 as the increasing of the additional amount of barium carbonate from 24 wt% to 40 wt% and theses values are slightly lower than those of the lead glass at the same composition. These confirmed that the refractive index largely depended on the density of the materials. Results of the 32 wt% barium and lead contained glasses prepared from various places of local sand found that the average refractive index of the barium glass and the lead glass were 1.63 and 1.67 respectively. The dwell time of the barium glass was found longer than that in the lead glass.

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