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Original Article

Lead-free high refractive index glass using local Thai sands

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Abstract

Due to harmful effects of lead in the high refractive index glass processing, the production of lead-free high refractive index glass by using other materials to replace lead has been studied. In this work, local sand from various sites in Thailand was used to fabricate the lead-free high refractive index glass. Barium carbonate was used to replace lead oxide in order to reduce the amount of lead in glass. Results from the experiments found that the local sands and the processes for making glass were satisfactory. The refractive index of greater than 1.60 was found in the glass specimen prepared from a concentration of barium carbonate of more than 30 weight-%.

Keywords: lead-free, high refractive index, glass, local sand

1. Introduction

Glass has been made into practical and decorative objects since ancient times. The variations of glass differ widely in chemical compositions and physical qualities. High refractive index glass is a lead containing glass, which shows the refractive index of greater than 1.52 and contains a lead oxide concentration of greater than 12 weight-%. Lead is used because it plays an extremely important role in lowering the melting point and creating the ferroelectric characteristics of glass that uses as electronic devices. It also acts as a fluxing agent and gives lead glass a lower softening point than soda-lime glass (Rosenhain, 1912; Malony, 1968; Holloway, 1973; Paul, 1982; Pfaenfer, 1983; Ichninose, 1987; Doremus, 1994). However, both lead oxide and lead vapor from melting process can cause dangerous air pollution harmful to the environment and to human beings. Therefore, it will not be easy to replace it with a more harmless element. However, the lead glass is currently threatened by regulatory pressure both with in the Europe and the U.S.A., to exclude lead from consumer products due to safety reasons. Several leadless glasses have been developed using other heavy elements replacing leads, finally, barium compounds seem to be the best material for lead-free glass production (Rada *et al.*, 1995).

Glass consists predominantly of silica (silicon dioxide, SiO_2). The source of silica is sand. Sand consists of small grains or particles of minerals and rock fragments. Although these grains may be of any mineral composition, the dominant component of sand is the mineral quartz, which is composed of silica. Glass sand is a special type of sand that is suitable for glass making because of its high silica content, and its low conduct of iron oxide and other compounds. It may be produced from both unconsolidated sands and crushed sandstones (Baumgart *et al.*, 1984). Following the U.S. Bureau of Standards sand for glass making should contain 95 weight-% SiO_2 (min.), 4 weight-% Al_2O_3 (max.), 1 weight-% Fe_2O_3 (max.), and 0.5 weight-% CaO+MgO (max.) (Murphy, 1960), and after the British Standard for sampling and analyze of glassmaking sand the

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sand should contain 98.5 weight-% SiO_2 (min.) and 0.30 weight-% Fe_2O_3 (max.) (BS 2975, 1988). In Thailand, deposits of glass sand are found at the surface or near to the surface, mainly in Trat, Chanthaburi, Rayong, Chumphon, Songkhla, Nakhon Si Thammarat, Phuket, and Pattani. All are beach sand deposits, and most of them are present beach sands, except those from Chanthaburi, Rayong, and Pattani that are older beach sands (Jarooglas, 1982).

The previous works indicated that local raw materials included zircon sand and basalt rocks were close to the requirements for the glass industrial process (Pimkhaokham *et al.*, 1990). The local sands were satisfactory for lead crystal glasses (Visetchat *et al.*, 2003). It was also found that the glass produced from local raw materials can be used for art and craft productions, and that the local and the foreign sands were similar; except a high iron oxide impurity (Iamjitkusol *et al.*, 2004).

In this work, colorless lead-free high refractive index glasses were prepared from sands from various localities in the southern area of Thailand with the addition of barium compounds. Their physical and optical properties were studied.

2. Materials and Methods

2.1 Sand composition and structural analysis

The chemical composition of four sand samples from various sites in southern Thailand, such as Chumphon, Songkhla, Phuket, and Pattani, were determined by an wavelength dispersive X-ray fluorescence spectrometer (Phillips, Model MagixPro PW 2400) operated with a LiF 200 crystal, scintillation and flow proportional detectors, and a Rh-tube at 60 kV and 125 mA. The physical structure investigations of the local sand samples were carried out using a scanning electron microscope (Jeol, Model JSM-5910 LV) operated at 20 kV. The samples were prepared using standard metallographic techniques followed by etching in a 0.5 vol.-% hydrofluoric acid at room temperature for 30 sec and then coated with a thin layer of gold prior to observation. The grain distributions of the local sand samples were analyzed by using a particle size analyzer (Malvern Instrument, Model Mastersizer) using polydisperse analysis, and operating with a beam length at 2.40 mm and a range lens at 300 RF mm.

2.2 Glass sample preparation at laboratory scale

The colorless lead-free high refractive index glasses were prepared into 16 glass samples at the laboratory scale. The glass samples with 150 g weight of each sample were made with primary mixture contained 40 weight-% sand, appropriate amounts of reagent-grade carbonates of sodium and potassium (Na_2CO_3 and K_2CO_3) and boric acid (B_2O_3), and then the samples were divided into three sets. The first set, the nine glass samples that based on sand from a Chumphon site and added with various concentration of reagent-grade barium carbonate ($BaCO_3$) ranging as 24, 26, 28, 30, 32, 34, 36, 38, and 40 weight-%, has been produced by the standard methods. The second set, the four samples contained reagent-grade $BaCO_3$ that was fixed at 32 weight-%, was prepared with 40 weight-% local sand taken from different sites in Chumphon, Phuket, Songkhla, and Pattani. All mixtures were melted in a ceramic crucible in an electric furnace at normal atmosphere at a maximum temperature of 1,250°C with 4 hrs dwelling time. The melted glasses were removed from the furnace and cooled down to room temperature by pouring into a cylindrical steel mould. The transparent and bubble-free glass samples were obtained for property measurements. The last set comprises three samples that were prepared with local sand from a Chumphon site with different kinds of barium compounds such as reagent-grade $BaCO_3$, reagent-grade barium sulfate ($BaSO_4$), and local barite from a Chiang Mai site were added. The glass mixtures were melted in a ceramic crucible in an electric furnace at normal atmosphere at a minimum temperature of 1,250°C with a minimum dwelling time of 4 hrs.

2.3 Refractive index measurements

Prior to the measurement of the refractive index of the glass samples, pieces of samples were prepared using conventional metallographic technique. They were mounted in epoxy resin, their surfaces were ground smooth, and then polished with alumina paste down to 0.3 µm. The refractive indices were determined using a refractometer (Rayner Model Duplex II) with a refractometer fluid $n_D \leq 1.79$, operated at room temperature by using sodium light.

3. Results

3.1 Composition and structure analysis

The determination of the local sand composition showed that most samples contained more than 95 weight-% silica and low contents of iron and other materials, as shown in Table 1. The sand from a Chumphon site has the highest silica content (99.14 weight-%) and the lowest content of other compounds, while, the sand from a Pattani site has been the lowest silica content (95.98 weight-%). The concentration of Al_2O_3, Fe_2O_3, CaO+MgO, and Na_2O+K_2O were between 0.57 to 2.60 weight-%, 0.03 to 0.37 weight-%, less than 0.01 to 0.06 weight-%, and less than 0.01 to 0.57 weight-%, respectively.

The SEM micrographs revealed that the grain shape of the local sands from Chumphon, Pattani and Phuket, and Songkhla were angular, angular-to-rounded, and rounded, respectively. Most of them showed a fine grain size, except from the Phuket site that showed a fine-to-coarse grain size, as shown in Figure 1.

The particle analysis found that the average mineral density of all local sands was 2.60 g/cm^3. The values of the grain size, the grain concentration, and the specific area were

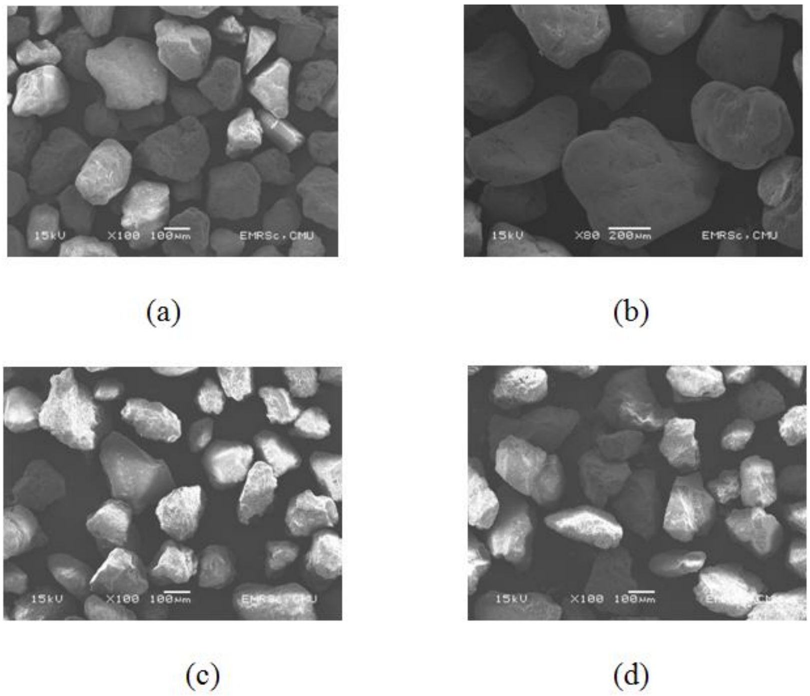

Figure 1. Morphology of local sands: (a) Chumphon, (b) Phuket, (c) Songkhla, and (d) Pattani.

Table 1. Composition of local sands analyzed by XRF technique.

Site	Composition (weight-%)				
	SiO_2	Al_2O_3	Fe_2O_3	CaO+MgO	Na_2O+K_2O
Chumphon	99.14	0.57	0.03	<0.01	0.02
Phuke	97.04	0.85	0.37	0.01	0.03
Songkhla	96.92	1.85	0.12	0.01	0.57
Pattani	95.98	2.60	0.10	0.06	<0.01

Table 2. Distribution of local sand particles.

Number	Grain size	Site			
		Chumphon	Phuket	Songkhla	Pattani
1	Mean diameter D(V.0.5), µm	219	331	222	241
2	Concentration, vol.-%	0.15	0.21	0.12	0.14
3	Specific area, m^2/g	0.04	0.04	0.16	0.05

between 219 to 331 µm, 0.12 to 0.21 vol.-%, and 0.04 to 0.16 m^2/g, respectively, as shown in Table 2.

3.2 Glass preparation

Once the melted glasses were poured and cooled, they led to homogeneous and bright glasses. The results from the glass making with the different kinds of barium compounds showed that both the soaking temperature and the time of the samples with local barite were higher than those samples with $BaSO_4$ and $BaCO_3$, respectively, as shown in Table 5. The melting temperature was lower than 1,250 °C, higher than 1,250°C, and higher than 1,350 °C, and the dwelling time was 4, 6, and more than 6 hrs for the samples with $BaCO_3$, $BaSO_4$, and the local barite, respectively.

Table 3. Refractive index of glasses prepared from various sites local sand based on 32 weight-% $BaCO_3$ measured by refractometer.

Site	Refractive index at 589 nm
Chumphon	1.610
Phuket	1.612
Songkhla	1.615
Pattani	1.618
Average	1.614

Table 4. Properties of glasses prepared with various concentration of barium carbonate based on sand from Chumphon site.

Concentration of Barium carbonateweight-%	Refractive index at 589 nm
24	1.548
26	1.558
28	1.580
30	1.602
32	1.610
34	1.624
36	1.632
38	1.642
40	1.654

3.3 Glass properties

From the study, it was found that the refractive indices of glasses prepared from various sites of sand measured between 1.610-1.618, as indicated in Table 3. In the glass samples, the refractive indices increased from 1.548 to 1.654, with details indicated in Table 4. These values increased linearly with the increase of the barium content, as shown in Figure 2.

4. Discussion

The compositions of the local sands from southern Thailand are in accordance with internationally acceptable standards for glass production. The colorless lead-free high refractive index glasses were successfully prepared by adding barium compounds to replace lead oxide and their properties were investigated. Barium carbonate was the best of the barium compounds used to produce lead-free high refractive index glass. Results of the 32% barium containing glass samples prepared from local sand from various sites showed that the average value of the refractive index was around 1.614. The index of refraction of the glass with barium carbonate content was found to increase linearly with increasing additional amount of barium carbonate. This relationship confirmed that the values of the refractive index were mainly depended on the mass of the materials.

5. Conclusions

In conclusion, the chemical analysis of the sands from the various sites from southern Thailand showed that the sands have met the international standards stipulated for glass production. Only the sand from Chumphon site met both the US and the British standards. Compilation and distribution information of location and abundance showed that the sand from a Chumphon site was the best with high silica content, low alumina, and iron oxide impurities. The local sands were qualified for the glass making and the lead-free high refractive index glasses were fabricated by using barium carbonate replacing lead oxide. The prepared glasses represent environmental friendly materials.

The further work found that the lead-free high refractive index glass can be used as materials for restoration or as decorative glass to restore and conserve antiques and heritage places or as material to decorate onto the surface of new wood carving products, or as colored glass for handmade art and craft products and as well as glass jewelry, which support SME products (Dararutana and Sirikulrat, 2006

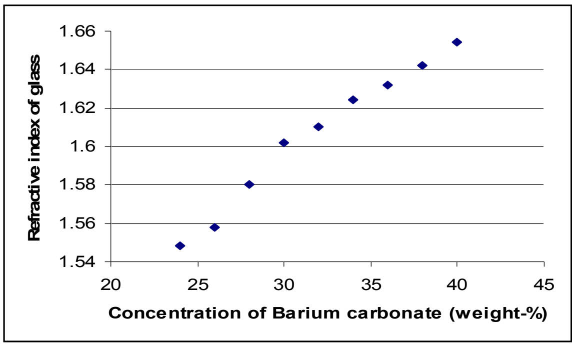

Figure 2. Relationship between concentration of $BaCO_3$ and index of glass

Table 5. Comparison of different melting processes.

Properties	Barium compound		
	Barium carbonate	Barium sulfate	Barite
Melting temperature, °C	≤ 1250	≥ 1250	≥1350
Dwelling time, hr	4	6	8

a,b,c,d; Dararutana *et al.*, 2006). Until now some of the research knowledge has been transferred to communities by short-course trainings.

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