Development of Glass-Ceramics from Soda Lime Silica Glass Waste by Direct Sintering Method for Opal Imitation

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Abstract. Natural opal, an amorphous, hydrous form of silica (SiO_2-n-H_2O), has been one of the favored precious gemstones for many centuries. Though beautiful, opal is very fragile and is damaged quite easily. Thus, opals of all varieties have been synthesized experimentally and commercially. The objective of this project was to synthesize and to compare crystalline opals. In this work, the development of powder sintered glass ceramics process based on soda lime silica glass waste with metal oxide powder enable jewelry applications. The substantial viscous flow of the glass led to dense products for rapid treatments at relatively low temperatures (900–1,000°C), whereas glass/metal powder interactions resulted in the formation of color agent crystals, provide enhancing optical properties. Several techniques were applied for characterization of the ingots. The chemical analysis was performed by Energy Dispersive X-ray Fluorescence (ED-XRF). The mineralogical compositions of the samples were determined by X-ray diffraction analysis. Raman spectroscopy was applied for optical characterization. The results were compared with a natural common opal. The present investigation demonstrated that the common opal with both color and colorless appearance can be synthesized by the technique, as the crystalline phase of opal structure was identified by XRD measurement. There is a great potential for such materials with novel functionalities for artificial gemstone application, i.e. opal forming.

Introduction

Recycling has become a very important for modern society due to the immense increasing of wastes and their impact on the environment, human health and safety. In particular, soda lime silica scrap glass, SLS glass, is a non-hazardous waste that mainly derives from packaging applications and is produced in increasing quantities in the world. In Thailand, during 2001 - 2010, the production of scrap glass has increased more than 9% and its use has risen for more than 14% [1]. However, the corresponding percentage of glass recycling in Thailand is rather low, ranging in the order of 27% [2]. Therefore, utilization of such waste is extremely importance.

Silica-based ceramics have dominated a newer generation of the most significant physical and optical properties. Considering sintering of glass powders, leading to "sinter-crystallized" glass-ceramics, has attracted much attention [3]. Direct sintering of mixtures of inorganic waste including recycled glasses act as fluxes is an important alternative. The products are not strictly considered as glass ceramics, since no vitrification, a stage in which the starting raw materials are mixed and converted into a glass, is involved [4]. However, there are evidences in the literatures supporting the classification of such products as "sintered glass-ceramics", owing to their observed phase evolution [4]. The recycled glass component, besides promoting an increase in density as a result of viscous flow sintering, reacts with the waste, leading to the formation of silicate and aluminosilicate crystals similar to those produced by devitrification of waste glasses [5]. The process offers remarkable energy savings, due to the absence of a high-temperature (1350 – 1400°C) melting stage [5].

Natural opal, an amorphous, hydrous form of silica (SiO_2-n-H_2O), has been one of the favored precious gemstones for many centuries [6]. Because of its amorphous character, it is classed as a mineraloid, unlike the other crystalline forms of silica, which are classed as minerals [6]. It is deposited at a relatively low temperature and may occur in the fissures of almost any kind of rock, being most commonly found with limonite, sandstone, rhyolite, marl, and basalt [6]. Though beautiful, opal is very fragile and is damaged quite easily. Thus, opals of all varieties have been synthesized experimentally and commercially. The discovery of the ordered sphere structure of precious opal led to its synthesis by Pierre Gilson in 1974 [7]. The resulting material was distinguishable from natural opal by its regularity; under magnification, the patches of color were seen to be arranged in a lizard skin or chicken wire pattern. Synthetics were also generally lower in density and were often highly porous. Two notable producers of synthetic opal are Kyocera and Inamori of Japan. Most so-called synthetics, however, are more correctly termed imitation opal, as they contain substances not found in natural opal (e.g., plastic stabilizers). The imitation opals seen in vintage jewelry are often foiled glass, glass-based, or later plastic materials.

The incorporation of wastes into a production process always involves at least two environmental advantages: diminishing of disposal problems and preservation of natural raw materials. The present study aims to investigate an alternative method for forming glass ceramic from waste as gems materials by using direct sintering method. The obtained materials, aimed for opal imitation, were characterized and compared with the natural ones. Optical purity, composition and adaptability are important prerequisites for perfectly matching the appearance of natural opal.

Experimental

The soda lime glass containers, obtained from community discarded bottles, were selected for the present study. The metal powders were purchased from the Union Science Co., Ltd. Fig. 1. displays the overall processing of material preparation and samples sinter production. The glass powder was prepared by ball milling and sieving process to 100-200 μm size particles (step 5). Glass-ceramic samples comprised of fine powders of soda lime waste, silica powder, and other additive oxides. The preparing formula for colorless sample was 60% SLS, 36% SiO_2, 2% ZnO and 2% TiO_2. The pre-mixed powder was poured into the die and manually pressed layer by layer. In an attempt to synthesize color opal, the preparation of the sample has been slightly modified. Within each layer, metal oxides were added to the powder with different concentration as colored pigments to obtain different shades and optical effects. After manually compression, the die was brought to the cold isostatic pressing (CIP) machine. The sample in cylindrical shape or pellets form with a diameter of about 35 mm obtained from this process (step 8). A high temperature furnace was utilized for heating the samples. The heating rate, from room temperature to 600°C, was 60°C/min and holding at 600°C for 30 minutes; then from 600°C to the maximum firing temperature at 1000°C, with the heating rate of 20°C/min and soaking for 4 hours. The samples were left to cool inside the furnace.

Refractive index (R.I.) of all samples was measured by the refractometer, Duplex II. Chemical analysis was performed by Energy Dispersive X-ray Fluorescence (ED-XRF) using the EDAX Eagle III microprobe spectrometer. Crystalline phase and structure of all samples was determined by X-ray diffraction analysis (XRD) using the Advance x-ray diffractometer (Bruker D8). A Jobin Yvon spectrometer HORIBA (T64000), equipped with triple monochromator, 532 nm solid state excitation laser, and a focused spot size of about 0.8 μm by a 100X objective (NA = 0.9), was used for the Raman measurements. The analyses were carried out with two main purposes: (i) Identification of the crystallinity degree of products, i.e., the degree of structural order/disorder of the minerals. (ii) Identification of the eventual presence of accessory minerals in the samples. For comparison, natural opal, a semiprecious stone, was also characterized under the same conditions. Opal used, a non-transparent opal, typical and abundant in Madagascar, Africa, is commercially known as common opal [8].

1	2	3	4	5
Glass containers	Broken glass	Ball milling process	Sieving process	100-200 μm SLG powder

(a)

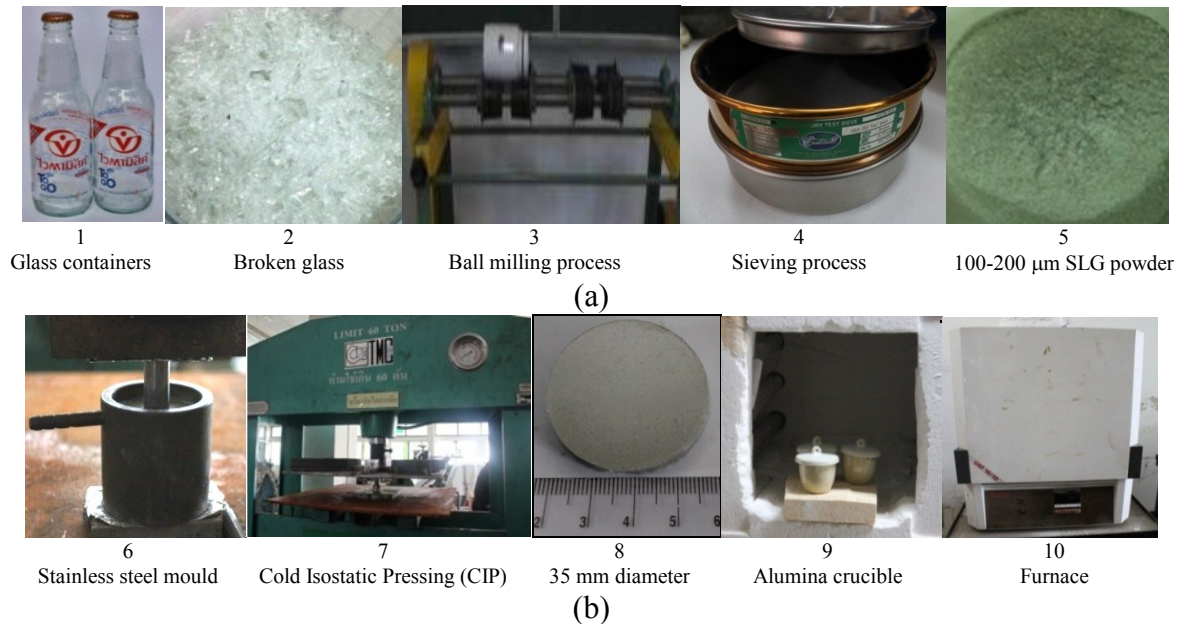| 6	7	8	9	10
Stainless steel mould	Cold Isostatic Pressing (CIP)	35 mm diameter	Alumina crucible	Furnace

(b)

Fig. 1. Overall samples preparation processing; (a) glass powder prepared by milling broken glass containers to 100-200 μm size particles; (b) the resulting ingot after the Cold Isostatic Pressing (CIP) process was sent to the furnace.

Results and discussion

Fig. 2 displays the appearance of natural opal selected for study in this work and the macro-images of typical samples before and after firing process. It can be appreciated how plastic-like surface before firing (step S1) transformed to gems materials after firing (step S2); the body color changes to yellowish white after firing. It is interesting to note that the appearance of the sintering materials is very similar to the natural common opal. The product is non-transparent. Table 1 lists the chemical composition and some properties of all samples based on X-ray fluorescence analysis. For the natural sample, the major component is silica as expected. Its refractive index (n=1.49) falls into the common opal group but its specific gravity (S.G.=1.78) is less than the average value of the common opal (S.G.=2.15) [9]. This deviation might be due to the hydrated amorphous nature of opal. For glass-ceramic samples (OP1), the major component is also silica. The specific gravity (S.G.=2.07) is in the average value of the common opal and below the value of quartz (S.G.=2.65) [9]. Its refractive index (n=1.53) is close to the natural one.

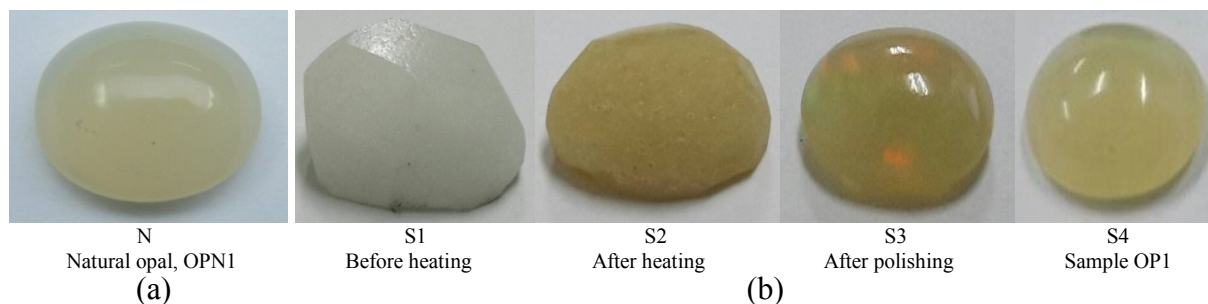| N	S1	S2	S3	S4
Natural opal, OPN1	Before heating	After heating	After polishing	Sample OP1

(a)   (b)

Fig. 2. (a) Appearance of natural common opal; (b) alteration of ingot from pressing to heating and finally cutting and polishing for gemstones imitation.

Table 1. Oxide compounds and some specific properties of natural opal, glass-ceramic opal and SLS glass. Note that S.G. = specific gravity; R.I. = refractive index; M.H. = Mohs hardness.

Sample	Oxide compounds (%wt)											S.G.	R.I.	M.H.
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	Cu_2O	ZnO	ZrO_2			
OPN1	0	0	4.82	93.28	0.58	0.70	0	0	0	0	0	1.78	1.49	5.5-6.5
OP1	0	0	0	89.87	0	5.33	0.99	0.38	0.10	2.14	0.11	2.07	1.53	7.0-7.5
OP7	0	0	0	83.06	0	7.79	2.27	0.47	0.47	4.38	0.66	2.44	1.55	7.0-7.5
OP9-3	0	0	0.82	85.55	0	6.11	2.11	0.51	0.10	3.88	0.22	2.49	1.55	7.0-7.5
SLS glass	13.88	3.53	1.42	69.55	0.47	10.57	0.13	0.21	0.02	0.02	0.02	2.53	1.52	5.5

Fig. 3 displays XRD and Raman measurement of all samples. Basically, the XRD pattern of precious opals (amorphous opals) have a broad and diffuse reflection at about 22° and it was named a "glass-peak" because of its resemblance with the signature diffuse peak of glass at this particular position [10]. As for the natural one, the major features of the patterns, e.g., the shapes, positions, and widths of the 22° band and the 36° peak are clearly observed differ significantly from [10]. The diffraction pattern contains peaks that coincide closely with the positions of the most intense α-cristobalite diffraction maxima [11]. These observing features rather support our sample to be in the opal-CT group which is known as disordered α-cristobalite with α-tridymite stacking [12]. For sintering products, the 22° and 36° XRD peaks are significantly shaper than the natural one. The extent of well-ordered is further elaborated because three XRD-peaks at 21°, 23° and 27°, respectively, are very well separated and in contrast to the board band of the natural opal. We believe that our sintered samples belong to the opal-C group which is higher well-ordered α-cristobalite than the opal-CT [12]. Note that the width of the most intense Bragg reflection of opal-CT, which is less ordered, exhibits broader Bragg reflections (FWHM > 5.6°) [13].
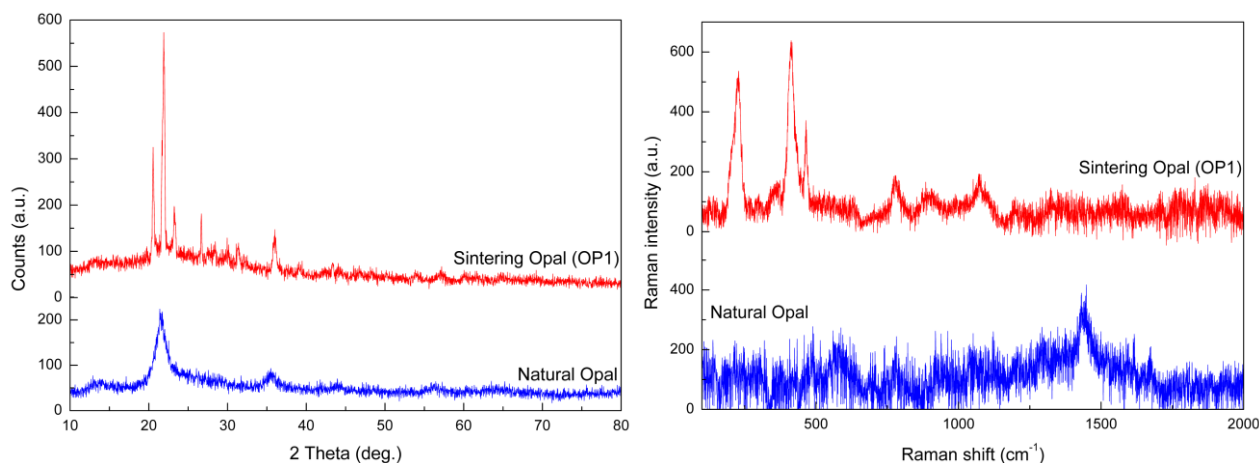

Fig. 3. (a) X-ray diffraction spectra and (b) Raman spectra of natural opal and sintering opal.

Raman is sensitive to the spatial arrangement of atoms to about several bond lengths, which inform us about local structure if not bulk-wise [14]. Different non-crystalline silica materials have displayed different spectral shape below 650 cm^{-1} with one intense Raman scattering at ~495 cm^{-1} and the strongest peak in the Raman spectrum of α-cristobalite was positioned at ~420 cm^{-1} [15]. As for our measurement, the Raman spectra of all samples revealed several peaks between 100 and 2000 cm^{-1}, due to different stretching and bending vibration modes of the Si-O system [16]. In the spectra of natural opal, we observed a broad band centered at ~350 cm^{-1} and a weaker band at ~300 cm^{-1}, which are typical of opal-CT [17]. These bands were not well resolved, as opal is a poor Raman scatterer. Small features at 1086, 955, and 780 cm^{-1} were also presented, together with a weak but clear water signal at about 1450 cm^{-1} [18]. For imitated opal, it exhibits Raman scattering

at 412 and 226 cm^{-1}. These peaks are attributed to planar of three and four-member ring Si-O, called D1 and D2 respectively, and also the two absorption bands are assigned to normal modes of vibration of the transverse optical network (TO) and longitudinal (LO) Raman active, revealing α-cristobalite as their dominating structural component [13], in good agreement with the X-ray diffraction data. These peaks are broader than those of α-cristobalite, in accordance with the greater structural disorder of materials. The Si-OH characteristic band is reported at ~800 cm^{-1} [19]. The peak at 462 cm^{-1} is characteristic of quartz [20] and it indicates the presence of quartz in the sample, which is in accordance with the XRD data. Two CO_2 modes at 1100 and 1300 cm^{-1} are observed, which indicated bending mode and symmetrical stretch, respectively.

As for coloring opal, after firing, several color blending were observed in these products. Most of them were high in porosity and were breakable. Two samples which were tough enough to be cut and decorated as jewelry, i.e. samples OP7 and OP9-3, as seen in Fig. 4, were selected for fully characterization. These samples are semi-transparent with slightly color shade, i.e. greenish shade (OP7) and bluish shade (OP9-3). Fig. 5 displays X-ray diffraction spectra and Raman spectra of natural opal and synthesis opal. According to XRD results, the product basically appears to be in non-crystalline form, confirming by no clear reflexes in the spectra and the occurrence of raised background. The XRD pattern shows wide width and asymmetric peak centered at 2θ ≈ 13 and 27°, respectively. This clearly shows that sintered material is amorphous regardless of the kind of additives and its content. Note that, generally natural precious opals do not show any crystalline X-ray diffraction pattern, signifying that they are structurally amorphous. Moreover, the Raman measurement was unable to indicate the formation of crystalline form of opal α-cristobalite in this sample as found for sample OP1. Indeed it is mostly in amorphous phase with other crystallized silicas confirming the XRD measurement.
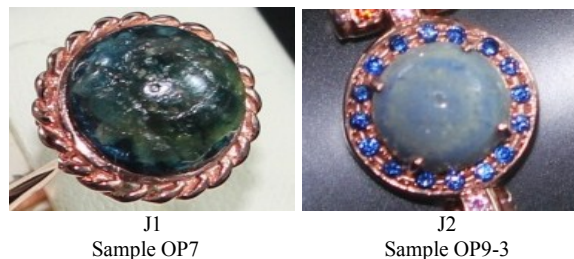

J1
Sample OP7

J2
Sample OP9-3

Fig. 4. (a) Appearance of sintering opal from the present work, i.e. OP7 (greenish shade) and OP9-3 (bluish shade).
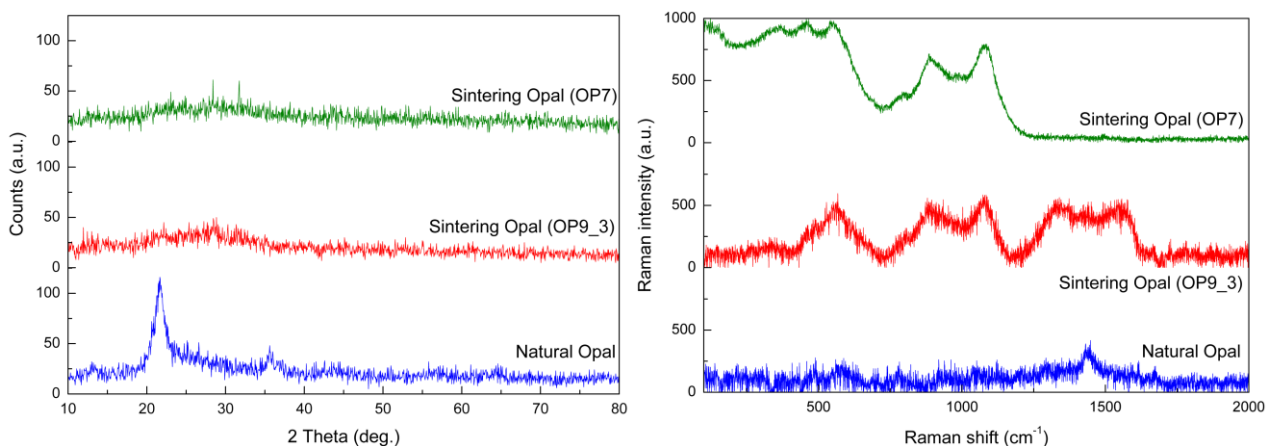

Fig. 5. (a) X-ray diffraction spectra and (b) Raman spectra of natural opal and sintering opal.

Summary

Alternative method of recycling soda lime silica waste glass were characterized and employed to obtain glass ceramic materials by combined sintering and crystallization process. In this work, the development of powder sintered glass ceramics process based on metal powder enable jewelry

applications. Several techniques were applied for characterizing the ingots. The chemical analysis was performed by Energy Dispersive X-ray Fluorescence (ED XRF). The mineralogical compositions of the samples were determined by X-ray diffraction (XRD) analysis. Raman spectroscopy was applied for optical characterization. The sinter materials were compared with a natural opal. It is demonstrated that the common opal of both colorless and coloring can be synthesized by the technique. It is a great potential for such materials with novel functionalities for artificial gemstone application.

Acknowledgements

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