

Influence of cerium oxide (CeO₂) addition on the mechanical properties of glass ceramics precursor prepared from fly ash

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Influence of Cerium oxide (CeO₂) addition in crystallization behavior and mechanical properties of glass ceramics in the Na₂O-CaO-Al₂O₃-SiO₂ system have been studied. Thermal behavior and hardness were studied by DTA-TG and indentation techniques respectively. Glass ceramic precursors were prepared by fusing fly ash, window glass and fluorite either with (0.5 wt.%) or without cerium oxide at 1500 °C for 4 hrs followed by quenching in cold water. Crystallization of the amorphous precursor occurred after 30 min at 800 °C forming plagioclase-type minerals. Hardness of the glass ceramics sintered at 1000 °C was 5.66 GPa, while in the sample with cerium oxide was 7.45 GPa.

Key words: Fly ash, Glass waste, Rare earth oxide, Glass ceramics, Hardness.

Introduction

Sustainability is the most important tendency for the modern world's development [1]. Within the sustainable development concept, savings of resources, water and land are important factors. Sustainable development requires that waste should be minimized and an ecosystem's overall integrity should be kept. One of the largest volume wastes produced by human activity is fly ash, which is the waste from the production of electricity by burning coal. It is reported that worldwide over 750 million tonnes of fly ash are produced each year [2]. Coal combustion by-products such as fly ash and bottom slags are among the largest wastes disposing in the Ulaanbaatar city. For instance only in Ulaanbaatar city 3rd and 4th thermal power stations are producing over 400 thousand tonnes of the coal combustion by-products. Since the coal combustion by-products utilization rate is not high in Mongolia these wastes are kept in large ash ponds which require valuable land for the ash pond and water resources to maintain the water level. Therefore coal combustion by-products utilization in Mongolia is a potentially important resource for sustainable development. In our previous research, it was shown that fresh fly ash and pond ashes can be used to produce geopolymer type pastes and concretes [3], [4]. Another large volume waste in Ulaanbaatar are various glass wastes, including window glass and glass bottles, which is estimated to

be 9% (≈100 thousand tonne) of the total solid waste produced in Ulaanbaatar [5].

Therefore, utilization of these two types of wastes is an important step in the introduction of sustainable development in Ulaanbaatar city. Fly ash and glass can be utilized for building materials, concrete production and as well as for high tech materials such as glass ceramics [6-10]. Glass ceramics developed since 1950's represent improved mechanical properties such as better hardness and fracture toughness than the original glasses. There are reports on the positive influence of various nucleation agents and additives on the crystallization behavior of glasses [11-13]. Rare earth elements added into glass improve their mechanical and heat resistance and chemical stability [14]. Bonding of the glass is influenced by the rare earth ions that allows the tailoring of properties of the glass ceramics [15]. In this paper, the latest results on the influence of cerium oxide (CeO₂) on crystallization behavior and hardness of fly ash, window glass and fluorite based glass ceramics are reported.

Experimental Procedures

The primary raw materials were chosen Baganuur coal fly ash from 4th Thermal power station of Ulaanbaatar city, window glass and natural fluorite (CaF₂). Fluorite was used to improve crystallization of the glass precursor [12]. The composition selected was similar to the "slagsitall" described by Barbieri et al. [16]. Cerium oxide (99.99% purity (Baotou, China)) was added into raw mixture at 0.5% of weight. Chemical composition of the raw materials and prepared mixture is shown in Table 1.

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Table 1. Chemical composition of raw materials and prepared mixture.

Raw material	Content (wt.%)							
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	TiO ₂
Baganuur fly ash	55.75	13.82	14.25	1.675	0.22	1.325	10.43	0.41
Window glass	67.54	1.04	10.04	3.68	12.1	0.54	1.13	0.09
Fluorite (CaF ₂)	20.57	0.53	53.42	0.67	0.03	0.16	0.6	0.06
Slagsital (Na ₂ O-CaO-MgO-Al ₂ O ₃ -SiO ₂)	56-61	8-14	9-25	2-6	3-5	0.5-2	0-2.5	
Baganuur fly ash-55%								
Window glass-40%	58.71	7.50	14.52	2.43	4.96	0.95	6.22	0.26
Fluorite-5%								

On the basis of this composition the CIPW Norm indicates the formation of plagioclase, wollastonite and diopside have a high probability [17].

Mixtures with and without addition of cerium oxide were melted in a corundum crucible at 1500 °C temperatures with dwelling time of 4 hrs. Then crucibles were removed from the oven and quenched by pouring into cold water in order to have an amorphous microstructure.

The amorphous glass was dried and ball milled down to particle size of less than 76 µm. The powders were then heated at 10 °C/min in a DTA-TG (Hitachi, TG/DTA 7300) instrument to find out the crystallisation temperature through the appearance of an exothermic reaction.

Milled powders were pressed into a tablet form by uniaxial pressing with a 20 MPa force. Tablets were calcined close to exothermic effects seen during the DTA i.e. 700, 800, 900 and 1000 °C temperatures for 30 min.

Crystallization of the new compounds was investigated by XRD (Shimadzu, MAXima_X XRD-700) and microstructure with a light microscope (Nikon). For the light microscope observation the selected samples were polished and observed via transmitted light.

Samples crystallized at 700, 800, 900 and 1000 °C with and without Cerium oxide additive were hardness tested by indentation (Equotip proceq D). Samples were polished and 210000 N/mm² force used with the data presented being the average value of 15 indents. Density of the sintered samples was determined by weight and volume ratio of cylindrical sample and linear shrinkage by change of the diameter after sintering.

Surface observation of the crystallized samples was undertaken using electron microscopy (Hitachi, TM 1000) after etching using 5% HF solution for 15 sec.

Results and Discussion

Fig. 1 shows DTA traces of the fused powders prepared with and without cerium oxide addition.

The DTA traces are very similar with the main difference being the temperature of the exothermic peak. Both samples show two exothermic effects at

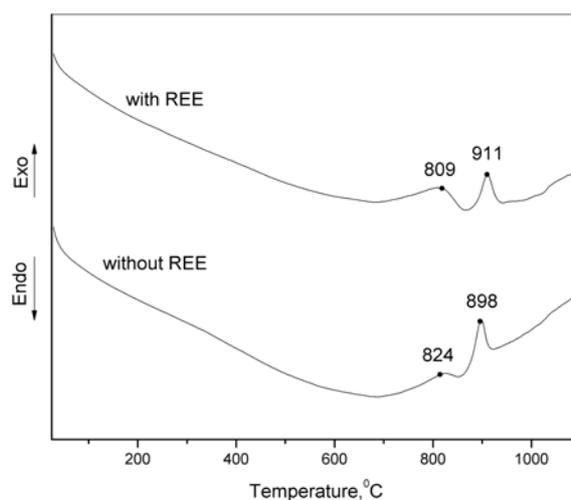


Fig. 1. DTA traces of the fused powders prepared with and without cerium oxide addition.

around 800 and 900 °C, respectively. Addition of the cerium oxide decreases the temperature of the first exothermic effect from 824 to 809 °C, while the second exothermic temperature increases from 898 to 911 °C. The first exothermic peak in the cerium oxide containing sample became broader.

The first exothermic effect likely to be caused by nucleation of a new crystalline phase, the second one is by its crystallization [13]. The integrated area of the first exothermic effect in cerium oxide containing sample is 5 fold higher than that in non-cerium oxide containing sample. It can be suggested that nucleation of a crystalline phase occurs much beneficially in the cerium oxide containing sample, though, the energy evolved in crystallization was almost similar for both samples.

XRD patterns indicate that the main crystalline component in the both samples is a member of the plagioclase group ($NaAlSi_3O_8$ - $CaAl_2Si_2O_8$) which consists of albite, oligoclase, anorthite etc. with many overlapping peaks.

The cerium oxide-containing sample after calcination at 1000 °C showed the probable presence of diopside (PDF 087-0698), although this is hard to confirm as the XRD patterns are very similar and there is considerable

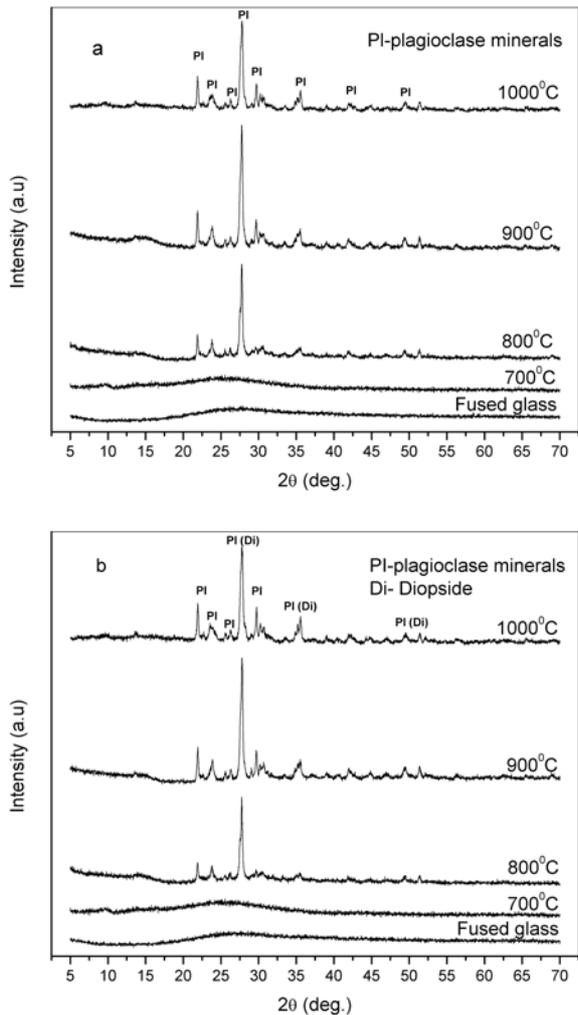


Fig. 2. XRD patterns of the glass ceramics without (a) and with (b) cerium oxide added glass ceramics.

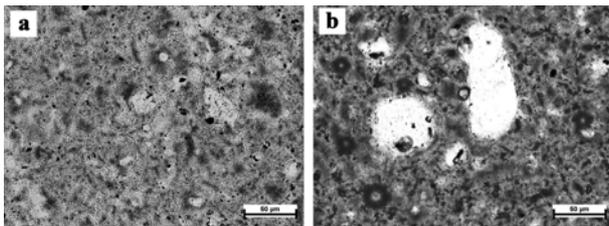


Fig. 3. Optical micrographs of the polished samples calcined at 900 °C temperature; (a) without and (b) with cerium oxide addition.

overlap. Based on the chemical composition it can be shown that calcium-containing feldspar would form the majority of crystallized plagioclase.

Fig. 3 shows optical micrographs of the samples calcined at 900 °C.

Optical micrographs showed that the size of crystallites was smaller in the absence of cerium oxide indicating the cerium was enhancing growth over nucleation. Table 2 shows volume weight, linear shrinkage and hardness of the samples calcined at various temperatures.

Table 2. Mechanical properties of the glass ceramics crystallized at various temperatures.

Temperature °C	Samples name	Volume weight /g/cm ³ /	Linear shrinkage %	Hardness* /GPA/
700	without REE	1.5	1.94	–
	with REE	1.43	1.67	0.80(0.19)
800 °C	without REE	2.10	13.0	2.62(0.18)
	with REE	2.06	13.7	3.31(0.37)
900 °C	without REE	2.10	13.4	6.34(0.36)
	with REE	2.16	15.3	6.34(0.45)
1000 °C	without REE	2.42	15.7	5.66(0.33)
	with REE	2.40	15.8	7.45(0.40)

*-values in brackets are the standard deviation of the measured values.

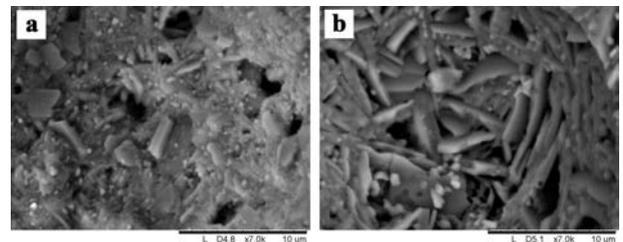


Fig. 4. SEM micrographs of the samples calcined at 900 °C (a) without and (b) with cerium oxide addition.

Hardness test indicates that cerium oxide added samples are 15-20% harder than non cerium oxide added samples. The increase in hardness is an indication of high rate of crystallization or formation of harder phases. XRD shows (Fig. 2) that there is very little difference between the samples in terms of crystalline compound. Moreover, even assume that in the cerium oxide containing sample was crystallized diopside at 1000 °C, the hardness should not be increased, because the plagioclase class minerals are showing higher hardness than diopside mineral. Changes in linear shrinkage and density were almost the same between the samples calcined at the same temperature. It suggests that the increased hardness more likely related to the increased crystallization rate of the cerium oxide-containing samples. Fig. 4 shows SEM micrographs of the samples calcined at 900 °C.

SEM micrographs show that crystallite became more elongated in cerium oxide added sample. In other words, cerium oxide addition caused increase in crystals size. The reason for the improved hardness thought to be related with the composition of glass phase. Both samples contain similar amount of fluorite as the flux. Cerium oxide addition leads viscosity decrease of the glass phase that enhances easier nucleation and growth of crystals.

Conclusions

Glass ceramics can be prepared from waste materials

such as fly ash and window glass by a two-stage process, amorphisation and thermal crystallization into plagioclase-group phases. Cerium oxide added to glass ceramics precursor by 0.5 wt.% showed enhanced hardness which thought to be due to a decrease in liquid phase viscosity leading to an increased crystal size.

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