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THE INFLUENCE RARE EARTH OXIDE ON CRYSTALLIZATION BEHAVIOR OF GLASS-CERAMICS FROM WASTE GLASS AND FLY ASH

Fused glasses were prepared from waste window glass and fly ash of the IV thermal power station of Ulaanbaatar city (Mongolia). Raw mixtures for the glass consist of waste glass (30-40 wt.%), fly ash (55-65 wt.%), fluorite (5 wt.%). Cerium (IV) oxide was used (0.5 wt.%) as rare earth oxide additive. Mixtures with and without rare earth oxide addition were melted at 1500^0C temperature. The influence of cerium (IV) oxide on the crystallization behavior of glass ceramics were investigated by differential thermal analysis-thermogravimetry and x-ray diffraction (XRD) analyses.

The differential thermal analysis scan results indicated that the temperature of sharp exothermic peak appearing at 898^0C is increasing to 911^0C in rare earth oxide containing mixture. XRD analysis showed that the crystalline phases in the glass-ceramic was albite [$NaAlSi_3O_8$].

Keywords: *waste glass, fly ash, glass-ceramics, rare earth oxide, differential thermal analysis, x-ray diffraction analyses, albite*

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ВЛИЯНИЕ РЕДКОЗЕМЕЛЬНЫХ ОКСИДОВ НА КРИСТАЛЛИЗАЦИЮ СТЕКЛЯННЫХ КЕРАМИКОВ, ПОЛУЧЕННЫХ ИЗ ОКОННЫХ СТЕКОЛ И ЛЕТУЧИХ ЗОЛЬ

Плавленные стекла была получены из отходных оконных стекол и летучих золь, полученных от IV тепловой электростанции города Улаанбаатара (Монголия). Исходное сырье для стекло-керамики состоит из оконного стекла (30-40 вес.%), летучих золь (55-65 вес.%), флюорита (5 вес.%). В качестве редкоземельных оксидов использованы оксид церия (IV) (0.5 вес.%). Смесь без примеси и с примесью редкоземельных оксидов были прокалены при температуре 1500^0C. Влияние оксида церия (IV) на ход кристаллизаци стеклянных керамиков изучены методом дифференциальной термальной анализ и рентгеноструктурной дифракции (XRD).

Результаты диффренциального термического анализа показывают, что температура острого экзотермического пика появляется при 898^0C и увеличивается до 911^0C в массе содержащей редкоземельные оксиды. Рентгеноструктурный дифракционный анализ показал, что кристаллические фаза альбит ($Na(AlSi_3O_8)$) образуется в стекло-керамике.

Ключевые слова: *летучий золь, стекло окна, стекло-керамики, кристаллизация, редкоземельный оксид, дифференциальный термический анализ, рентгеноструктурный дифракционный анализ, альбит*

Introduction

Recently, the industrial and domestic wastes and their potential impacts on humans and the environment during management and disposal continue to pose one of the most challenging problems facing society. Coal fly ash produced in thermal power plants poses serious environmental problems [1]. Approximately, over 6 million tons of pulverized coal used in the thermal power stations produced more than 600,000 tons of coal combustion by-products per year in Ulaanbaatar, Mongolia. Coal fly ash containing a large amount of CaO, SiO_2, and AI_2O_3 can be good raw materials in the CaO-AI_2O_3-SiO_2 system for glass-ceramics production [2-4]. Preliminary heat treatment of the coal fly ash and waste glass and fluorite can acquire glass-ceramics production of the various new crystalline phases and properties [1].

Rare earth containing glasses have attracted a great deal of interest due to their macroscopically properties such as high mechanical resistance, chemical stability and heat-resistance [5]. The rare earth ions can participate in the overall bonding of the glass to tailor the desired properties since their structural roles in the glass structure are related to their size and coordination number [6]. Kansal et al. has investigated the influence of different rare earth oxides (La, Nd, Gd and Yb) on the structure and crystallization behavior of diopside based glasses [7]. Wang et al. has studied the effects of La_2O_3 and CeO_2 addition on the crystallization and transparency of glass-ceramics prepared via heat treatment of glass from the MgO–Al_2O_3–SiO_2 system [8].

Glass-ceramics have been generally applied as biomaterials for dental restoration and orthopedics for bone replacement, coating materials for industrial dies, chemical processing equipments, and metallurgical industry, and optical industries [9].

The main aim of this study, is preparation of glass-ceramic from fly ash and waste glasses during post heat treatment and, effects of adding rare earth oxide on the crystallization behavior of the fused glasses.

Experimental

2.1. Materials

Baganuur fly ash from the IV thermal power station of Ulaanbaatar city in Mongolia, window waste glass, fluorite of Dundgovi province were used to prepare glass-ceramics. As a rare earth source was added cerium (IV) oxide (0.5 wt.%) Chemical composition of the raw materials used in this study is shown in Table 1.

Table 1

Chemical composition of raw materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Ti_2O	MgO	Na_2O	P_2O_5	others
Baganuur fly ash	55.75	13.82	10.43	14.25	1.325	0.41	1.675	0.22	0.06	2.06
Window glass	67.54	1.04	1.13	10.04	0.54	0.09	3.68	12.1	0.04	3.8
Fluorite (CaF_2)	20.57	0.53	0.6	53.42	0.16	0.06	0.67	0.03	0.04	23.92

2.2. Preparation of milled mixture

The two mixtures (Table 2) of raw materials (moisture content 40-50 wt%) were milled by using ball mill in water medium for 24 h, in order to homogenize the powders and dried in a dry oven at 70^0C for 24 h. The average particle size of the mixture was about 75 μm.

Table 2

Composition of the used mixtures

Components (mass %)	Sample 1	Sample 2
Baganuur fly ash	55	55
Waste window glass	40	40
Fluorite	5	5
Cerium (IV) oxide	-	0.5 (by mass)

2.3. Preparation of glass-ceramics

The samples were melted at 1500^0C (Xinyoo, XY-1700) for 4 h at heating rate of 10^0C/min and then poured into cold water. Then were collected, dried in oven at 70^0C for 24 h, and then ball milled and sieved to obtain particles with size below 75 μm.

After milling, the 1 g powder sample was pressed into cylindrical shape having a diameter 10 mm without using any binder (moisture 10 wt.%) under a 20 MPa pressure (Jinan, WDW-50). The samples were crystallized at 800 and 900^0C for 30 min.

Differential thermal analysis (DTA) (Hitachi, TG/DTA 7300), were carried out in order to determine the crystallization temperature.

The XRD (Shimadzu MAXima_X XRD-700) measurements of the melted and crystallized samples were carried out at the 2θ-range from 5 to 70° with Cu-Kα radiation.

Results and discussions

3.1. Thermal analysis and heat treatment

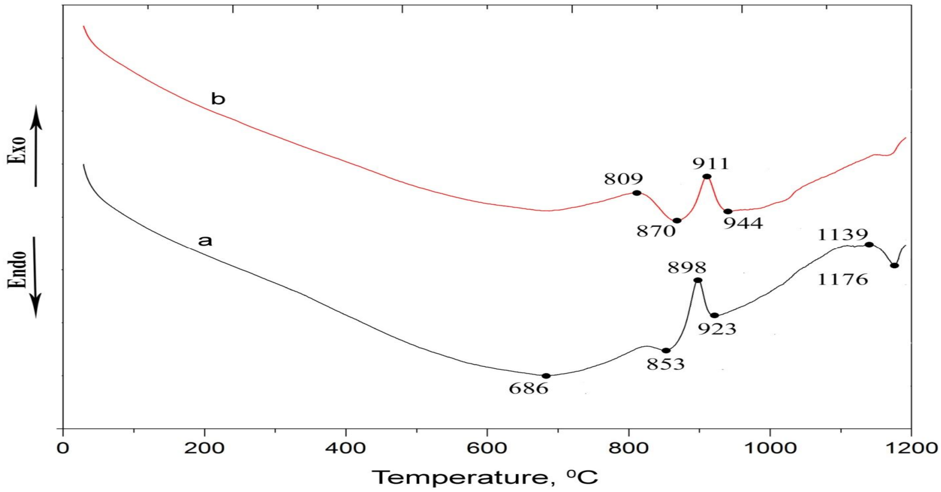

Fig. 1. DTA (a) sample 1 and (b) sample 2.

Fig. 1 shows the differential thermal analyses traces of the prepared glasses with and without rare earth additive (Ce IV). A sharp exothermic peak due to crystallization appears in 898^{0}C is increases to 911^{0}C in the rare earth containing sample.

3.2. X-Ray powder diffraction

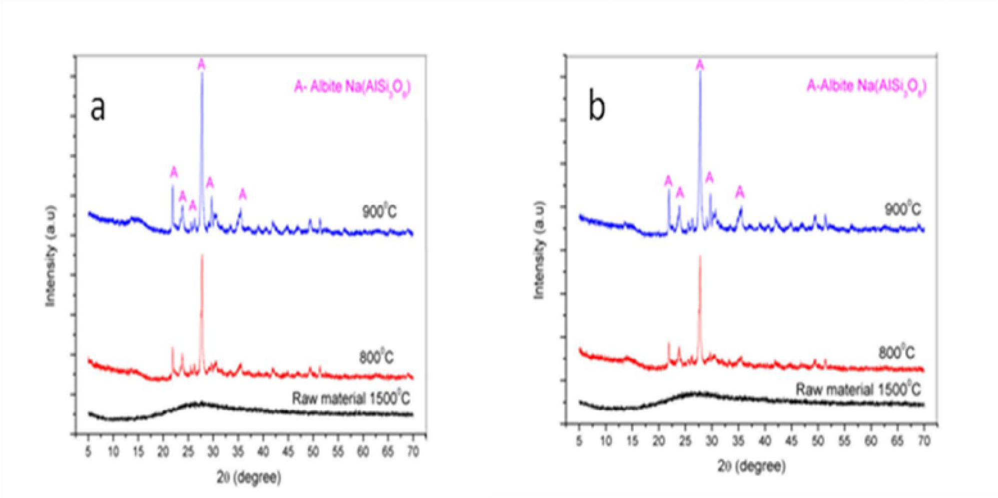

Fig. 2. X-ray diffraction patterns of the (a) sample 1 and (b) sample 2 melted at 1500^{o}C for 4 h and crystallized at 800^{o}C and 900^{o}C for 30 min

Fig. 2 shows that the major crystalline phases qualitatively identified in the both mixtures. Fig. 2 (a) shows crystalline diffraction peaks due to albite ($Na(AISi_3O_8)$) appeared for the both 800°C and 900°C temperatures. The intensity of albite peaks increases with increasing of the crystallization temperature. Albite high ($Na(AISi_3O_8)$) phase also appeared for the cerium (IV) oxide added sample crystallized at 800°C and 900°C for 30 min (fig. 2 (b)). XRD indicates that there is no difference in terms of mineralogical composition of glass ceramics prepared with and without cerium addition.

3.3. Micrographs

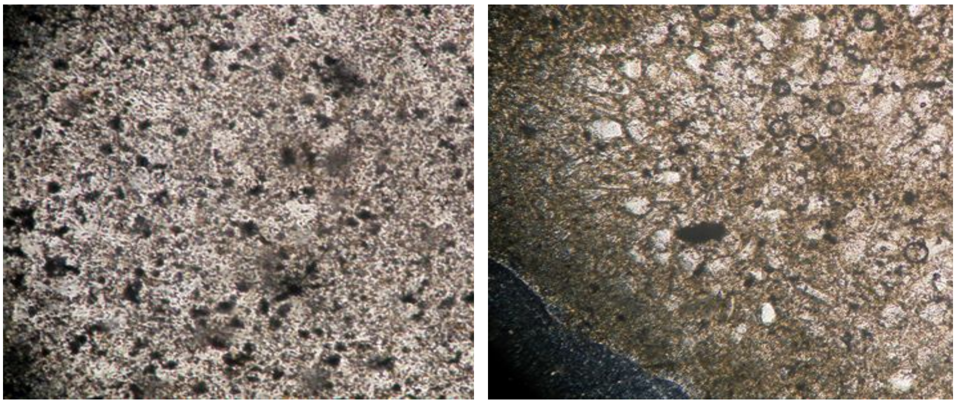

Fig. 3. Micrograph of the sample 1 and sample 2 (cerium (IV) oxide added) glass-ceramic crystallized at 800°C for 30 min

Fig. 3 (a) and (b) shows micrographs of polished surfaces of glass ceramics. The number of pores decreased and content of crystalline phase and its size increases for cerium (IV) oxide added sample 2 compared to that of sample 1. Thus, the rare earth oxide improves crystallization behavior of glasses but doesn't show influence in mineralogical composition of the crystallized glass-ceramics.

Table 3 shows density and linear shrinkage of the crystallized glass ceramics.

Table 3

Density and linear shrinkage of the prepared glass ceramics

	800°C		900°C	
	Density, g/cm^3	Linear shrinkage, %	Density, g/cm^3	Linear shrinkage, %
Sample 1	2.43	11.54	2.39	11.64
Sample 2	2.48	12.9	2.46	14.3

Table 3 indicates that the cerium oxide addition improves sintering of the glass ceramics. At both 800 and 900^{o}C temperatures, those samples with cerium oxide addition showed better consolidation and in agreement with their micrographs (fig. 3).

Conclusion

Albite containing glass-ceramics were prepared from the melted mixtures of fly ash, window waste glass and fluorite. The main crystallization of the mixtures with and without cerium oxide addition occurs at about 900^{o}C. The results indicated that the albite containing glass-ceramics could be produced from the various wastes such as fly ash, window waste. The rare earths oxide (CeO_2) improves crystallization rate of the albite ($Na(AISi_3O_8)$) and sintering of the sample.

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