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Glass-ceramics from a zinc-electroplating solid waste: Devitrification promoted further crystallization of parent glass upon heat treatment

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ABSTRACT

A solid waste from a zinc electroplating production line was successfully used as a main raw material for synthesizing glass-ceramics with a fine microstructure. X-ray fluorescence spectroscopy analysis on dried solid waste shows that the waste mainly contains iron and zinc oxides. X-ray diffraction (XRD) analysis identifies Fe_3O_4 and ZnO phases in calcined waste samples. Based on the above results, silica sand, lime stone and potassium feldspar were proportionally added to make parent glasses by melting the batches at 1450 °C for 2 h. The as-synthesized products show typical DSC and thermal expansion curves with obvious glass transition phenomenon. However, XRD patterns reveal that they had devitrified to form $ZnFe_2O_4$ phase during the shaping and cooling of the melts. The devitrification became weaker when more potassium feldspar was added. It is interesting to find that the pre-crystallization of $ZnFe_2O_4$ in the devitrified sample was beneficial to its further crystallization during the following heat-treatment. The result implies that the devitrification of parent glasses is not necessarily a detriment to the preparation of glass-ceramics via controlled crystallization process.

1. Introduction

With the expansion of industries and economic development, the world is increasingly facing the challenges of resource shortage and environmental pollution from industrial wastes. Electroplating industry is one of the major pollutant origins. It produces large quantities of wastewaters containing heavy metal ions such as Cr^{6+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and other pollutants [1,2]. The metal ions in electroplating wastewaters could be extracted [3] or treated by chemical precipitation method, which leaves behind waste residues as sludges [4,5]. These sludges could be naturally dried or subjected to dehydration treatment, turning into harmful solid wastes. Attempts have been tried to use the sludge wastes as a raw material for fired clay bricks [6], adsorbents [7] and catalysts [8], etc.

Heavy metal ions are valuable resources in glass production. For example, zinc is a valid component to increase glass chemical stability and refractive index [9]. Therefore, it is possible to use the solid waste generated in electroplating industry as raw materials in making glass articles [10]. However, the solid wastes from electroplating industry generally contain large amounts of iron species, which are from acid washing of iron or steel objects. It is well known that the content of iron in any transparent glass is strictly limited, as iron ions can afford glasses yellow- or blue-greenish color [11]. A glass contains a high amount of iron can loss transparency and even be totally black. Therefore, solid wastes with high concentration of iron cannot be used in normal glass production as a main raw material. An alternative possibility is to reuse such type of iron-rich solid waste to prepare glass-ceramics [12]. Especially for functional glass-ceramics [13], the crystalline phases and the resultant functionalities rather than the transparency and color are mostly concerned. For example, a glass-ceramic with franklinite ($ZnFe_2O_4$) phase may find application in the hyperthermia treatment of cancers [14] and glazes [15]. And a glass-ceramic containing petedunnite ($CaZnSi_2O_6$) may have bioactive performance [16]. Therefore, based on the composition of a solid waste from a zinc-electroplating factory, herein we tried to use it as a main raw material for making $ZnFe_2O_4$ or/and $CaZnSi_2O_6$ containing glass-ceramics [15].

Glass-ceramics are generally formed by controlled crystallization of parent glasses upon heat treatment. The crystallization typically involves nucleation and crystal growth steps. Glass composition, nucleating agent, thermal treatment procedures are among the factors influencing the controlled crystallization of parent glasses [17]. In normal flat and bottle glass production, devitrification which occurs in the forming and cooling process is regarded a serious detriment to production as it can make glass articles loss transparency and strength [11]. In the synthesis of glass-ceramics, devitrified parent glasses are also often discarded or not studied further due to the worry about the negative effect of pre-crystallization of the parent glass on latter controlled crystallization process. In this work, our results indicate that the

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Table 1
Compositions of the glass batches (wt%).

	K10	K20	K30
Solid waste	48.00	42.67	37.33
Potassium feldspar	**10.00**	**20.00**	**30.00**
Sand	32.00	28.44	24.89
Limestone	10.00	8.89	7.18

devitrification of parent glass may not do harm to the controlled crystallization of glass. Instead, it is evidenced the pre-crystallization of $ZnFe_2O_4$ phase greatly benefited the further crystallization of the same phase during the heat treatment process of making glass-ceramics.

2. Materials and methods

A solid waste was taken from a zinc-electroplating factory in Shandong province, China. Before the preparation of glass batches, the solid was first dried at 120 °C for 12 h, followed by being ground to pass a sieve of 100 meshes. It was further calcined at 600, 800 and 1200 °C for 2 h with a ramp rate of 10 °C/min. Both the dried and calcined samples were analyzed by X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). Other raw materials including silica sand, lime stone, potassium feldspar ($KAlSi_3O_8$) and fluorite (as a reflux) were given by local factories producing window glasses.

The batch compositions are listed in Table 1. Extra 1% of fluorite was added in each batch, respectively. The ratios of the solid waste: sand: limestone were fixed at 24:16:5 by weight. The main difference in the batch composition is the content of potassium feldspar, which varies from 10% to 30%. As a result, the percentage of the solid waste accordingly decreases from 48% to 37.33%.

Dried and ground solid waste and other mineral raw materials were weighed respectively and directly mixed thoroughly in a mortar. They were melted in alumina crucibles at 1450 °C for 2 h in an electric furnace. The melts were shaped in a preheated steel mold, followed by annealing at 500 °C for 2 h. For the heat-treatment, the parent samples were kept in an electric furnace for 2 h at temperatures determined by differential scanning calorimetry (DSC) (see the discussion section). The ramp rate used in the crystallization process was 5 °C/min. The samples were encoded respectively as K10, K20 and K30 according to the contents of potassium feldspar added in the batches.

The chemical compositions of the dried and calcined waste samples were analyzed using XRF technique on an S8 TIGER spectrometer (Bruker AXS, Germany). Differential scanning calorimeter and thermal gravity analysis (DSC-TG) on the dried solid waste was performed on a Mettler DSC/DTA 1600HT thermal analyzer. The test was under N_2 atmosphere. The heating rate applied was 10 °C/min. The density of the as-synthesized samples was measured on a FA1004J density balance (Xuhui, China) using the Archimedes method. Distilled water was applied as immersion liquid for the density tests. Three parallel samples were measured and the data were averaged. The thermal expansion coefficients (TEC) of the as-synthesized samples were measured on a dilatometer (Xuhui, DIL2014, China) with a ramp rate of 5 °C/min. The samples are 30–50 mm in length, 5–10 mm in the cross-section. Expansion data from 50 to 300 °C were adopted to calculate the TEC of the samples. DSC curves of the glass samples were recorded on a Mettler, DSC/TGA 1 (Switzerland) type thermal analyzer. The particle size of the sample used in this DSC test was 105–125 μm. The samples were heated in an inert Ar atmosphere (gas flow rate was 20 ml/min) from 50 °C to 1200 °C with a heating rate of 10 °C/min. The crystalline phases of the samples were identified using D8 ADVANCE X-ray diffraction (XRD) (Bruker, Germany) with Cu Kα radiation. The grain sizes of crystallites were calculated based on the Scherrer equation. The relative contents of the crystalline phases in the heat-treated samples were estimated using the Matrix-flushing method. The microstructure

Table 2
Chemical compositions of the solid waste (wt%).

Component	Dry sample	Calcined sample	
		600 °C	1200 °C
Fe_2O_3	28.52	36.53	39.79
ZnO	26.46	37.29	33.15
Cl	5.62	6.66	0.17
Na_2O	5.41	8.66	11.87
SiO_2	1.46	1.63	4.8
Cr_2O_3	1.38	1.64	1.89
SO_3	1.36	2.01	3.36
Al_2O_3	1.19	1.95	1.8
MgO	0.81	1.09	1.14
MnO	0.71	0.86	0.97
Trace	1.08	1.68	1.06
Undetected	26.00	–	–

of a controlled crystallization sample was observed on QUANTA-250-FEG scanning electron microscope (FEI, US). EDS analysis was performed to acquire composition information of observed crystallites. Newly fractured cross section of the sample was sputtered with a thin film of gold or carbon before the SEM or EDS measurements.

3. Results and discussion

3.1. Characterization of the solid waste

The chemical compositions of dried and calcined waste samples are shown in Table 2. It can be seen that the dried waste mainly contains Fe_2O_3 and ZnO, whose total amount is about 55%. The data also show that XRF undetected elements (mostly light elements such as H, C, N) account for about 26%. The XRD analysis result (Fig. 1) identifies the existence of FeO(OH), $Zn(ClO_4)_2$, $NaSi_2O_6$ and NaCl phases in the dried waste. These crystalline phases were the products of complex reactions occurred in electroplating solution and wastewater treatment process. In addition, the high background and diffused diffraction peaks suggest the possible existence of amorphous phases in the dewatered sludge.

Fig. 2 presents the DSC-TG-DTG curves of the dried solid waste. The TG curve displays a total weight loss of 35.5% from room temperature to 1300 °C. The DTG curve indicates that the total weight loss consists of several stages, suggesting complex thermal reactions occurred during the heating process. The temperatures correspondent to the maximal weight loss rate at each stage are labeled beside the DTG curve. The endothermic effects depicted by the DSC curve suggest the weight losses were mainly due to the evaporation, sublimation and decomposition of components in the solid waste upon heating. Due to the difficulty in

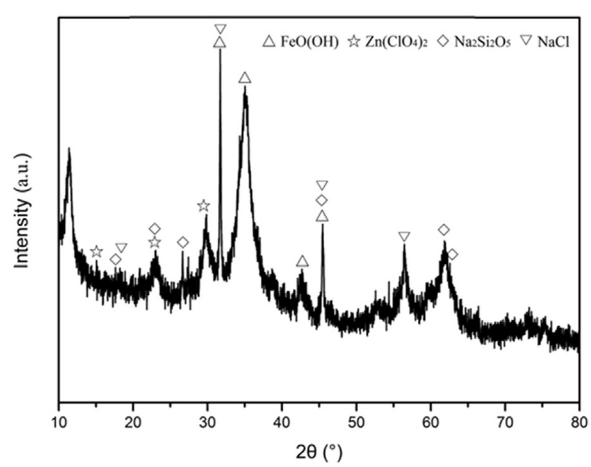

Fig. 1. X-ray diffraction pattern of the dried solid waste.