Synthesis of Foam Glass-Ceramic from CRT Panel Glass using One-step Powder Sintering

Hao Yuan*, Hongcheng Wu, Jie Guan
Shanghai Polytechnic University, 2360 JinhaiRd, Pudong, Shanghai, China
E-mail: yuanhao@sspu.edu.cn

Abstract. Foam glass-ceramic with high mechanical strength property was synthesized from waste CRT panel glass by using one-step sintering technology. This product contains columnar crystals in their microstructure and the crystal phases consist of Sr₅(PO₄)₃F and Pb₃(PO₄)₂. The content of additive agents and heating program on the bulk density and the compressive strength were evaluated. Physical properties of sintered material was measured, including the compressive strength 3.42 MPa, the density 0.78 g/cm³, the water absorption 0.41 wt.% and the thermal conductivity 0.052 W/m²·k. The results show that the CRT glass is susceptible to be used for high-performance foam glass-ceramic as building materials.

1. Introduction
In recent years, with the advances of display technology, a large number of conventional Cathode Ray Tube (CRT) televisions TVs have been replaced by new products such as Liquid Crystal Displays (LCDs) and Plasma Display Panels (PDPs). As a great power with an extensive manufacturing and consuming amount of domestic appliances, China has stepped into a peak period of replacing CRT TV sets and computers [1, 2]. Predictably, if no effective measures are taken, the amount of discarded CRT TV sets will come up to 270 million until 2020 in China [3]. If CRT glass discard casually and landfill without treatment, the ecological environment and human health will be seriously threatened [4, 5]. Therefore, CRT waste is thus becoming an urgent environmental issue.

Lots of work have been conducted to handle the discarded CRT waste problem [6]. Among them, the common method is to reuse CRT glass in construction products [7]. Lazău et al. [10] prepared ceramic glazes by melting CRT panel glass and raw materials at 1250 °C with a soaking time of 30 min. It is applied to architectural decoration because of its aesthetic appearance. Ling and Poon [11] indicated that the inclusion of glass cullet improved the fluidity impermeable surfaces of the CRT funnel glass used. However, due to the weak physical property of the CRT glass, they are not suitable to be used as load-bearing wall materials. Apart from them, foam glass has attracted growing attentions because of its unique structure—such as high physical strength, good thermal and sound insulation properties, favorable water absorbent and fire retardant properties [7]. Bernardo [8] and Petersen et al. [9] prepared foam glass by using CRT panel glass and different foaming agents (calcium carbonate and Sodium Carbonate). In addition, as a kind of new material which has uniformly distributed nanoscale pores and acicular crystals in glass phase matrix [12], foam glass-ceramic is prepared on the basis of foam glass by further crystallization process. However, the two-step synthetic method requires double heat treatments [9], resulting in greater energy consumption.

This paper provides a novel process for recovering wasted CRT glass. By using one-step powder sintering technology, foam glass-ceramic with good physical performance is synthesized. We have carried out a systematic study regarding the impact of additives’ concentration and heating treatment...
program on the foam density and compressive strength. XRD and SEM analysis were conducted to characterize its microstructure.

2. Materials and methods

The panel and funnel cullet glass used in this work are representative of end-of-life CRT from colored TVs and provided by Shanghai Xin Jinqiao Environment Protection CO, Ltd. (Shanghai, China). Powder mixtures were prepared using CRT panel glass powder (pulverized by planetary ball mill and sized under 75 μm, through 200 sieve mesh), carbon (≥ 99.85%, Sinopharm) as foaming agent, Na$_2$SiF$_6$ (≥ 99.0%, Sinopharm) as fluxing agent, Na$_3$PO$_4$ (≥ 98.0%, Sinopharm) as stabilizing agent and Cr$_2$O$_3$ (≥ 99.0%, Sinopharm) as nucleating agent. The mixture was uniaxially pressed at 40 MPa to obtain 31 mm diameter green bodies. Then it was placed in the electric furnace, sintered under different heating program. After the process of foaming, crystal, and anneal, the foam glass-ceramic was synthesized. In order to qualify the testing size, the samples are cut and polished in the mechanical property test.

The compressive strength was measured by universal test machine (Instron 3369). The crystalline phase was examined by the X-ray diffraction (XRD, D8-Advance), the crystal morphology and microstructure were investigated by Scanning Electron Microscope (SEM, S-4800). The Thermal Conductivity Measuring Instrument (FL-4010) was used to analysis the thermal conductivity.

3. Results and Discussion

3.1. Effect of additive on glass foam-ceramic

3.1.1. Foaming agent. Foaming agent plays a crucial role on properties of foam glass-ceramic. It is generally recognized that foaming agents can be grouped into redox and neutralization agents. As a redox agent with good performance in foaming, carbon was chosen as foaming agent in our study. The content of foaming agent also have an effect on the foam products’ performance [9]. Figure 1 plots the density and compressive strength of foam glasses as a function of carbon concentration. The compressive strength decreased with increasing carbon concentration, and the density attains a minimum value when carbon is 0.5 wt.%. The present study confirmed that with increasing foaming agent exhibited a dense sintered glass shell around a foamed core, indicating that it was reacted before the glass particles sintered and closed the porous structure. However, the collapse of the foam at relatively high concentration occurs as a result of interconnected structure and gas releasing, which cause the bad physical properties [13].
3.1.2. **Fluxing agent.** Addition of fluxing agent can reduce the melting temperature of raw material and increase the viscosity of the system simultaneously [14]. It can also prevent the generation of small bubbles which interconnect to form large bubbles. Thus, fluxing agent contributes to the stable bubble structure. Sodium fluorosilicate (Na$_2$SiF$_6$) are used as fluxing agent in this work. The results show that the density has little distinction with increasing concentration of Na$_2$SiF$_6$, while the compressive strength decreases a lot when the content is over 4 wt.% (Figure 2). The main reason of this circumstance was the presence of Na$_2$O in the silicate network, which provided nonbridging oxygens and decrease viscosity [9].

3.1.3. **Stabilizing agent.** In the sintering–foaming process, the phosphate can lower the surface tension and increase the foam life time, so that sodium phosphates are added as “foam stabilizers” [15]. Na$_3$PO$_4$ was chosen as stabilizing agent in this study. Figure 4 gives clearly results that 4 wt.% of Na$_3$PO$_4$ doping amount bring out favourable physical properties both in density and mechanical strength.

3.1.4. **Nucleating agent.** The dopant of nucleating agent in the mixture can reduce the interfacial energy, which induce the formation of nucleus in the supercooled state of the batch material. Nucleating agent is a key factor to improve the mechanical properties of the microcrystalline foam glass. We use metallic nucleating agent Cr$_2$O$_3$ and explore the influence of its different concentrations (Figure 5). It can be certainly found that the addition of nucleating agent significantly improved the compressive strength, but it changes little when the content exceeds 1 wt.%.

To sum up, we mixed CRT panel glass powder with additive agent content of 0.5 wt.% carbon, 4 wt.% Na$_2$SiF$_6$, 4 wt.% Na$_3$PO$_4$ and 1 wt.% Cr$_2$O$_3$.

3.2. **Effect of heating treatment program**

Foaming temperature and residence time had a substantial correlation. If the foaming temperature is high, the melt viscosity will be low, and controlling the structure will become difficult because bubbles rise to the top of a mold. Conversely, if the temperature is low and possess a higher glass viscosity, then the gas expansion becomes difficult and little increase in volume occurs [16]. The influence of foaming temperature, residence time and heating rate were examined in figure 5. The results show that the foaming glass had low density and high compressive strength when the final temperature around 875 °C, which demonstrated the findings about the appropriate temperature for foaming process with carbon-containing materials as redox foaming agents. The extension of residence time made both density and compressive strength decrease, but the density had a sharp increase when it extended over 40 min. This could be explained that the bubble rose to the surface in
the melt under the effect of gravity, which increase the size of pores and the heterogeneity of their distributions in the foam glass [17].

Fig. 5. The foam density and compressive strength of the samples with different foaming temperature (a) and residence time (b).

Overall, our method provided an appropriate heating treatment program described as following steps: First, the sample was heated at 10K/min to 875 °C. Subsequently, the sample was retained 875 °C for 40 min. Then, it was cooled to 600 °C at 10 K/min for annealing, and sustain 20 min for better stabilizing. After that, the synthesis was air-cooled to room temperature.

3.3. Performance analysis

3.3.1. Phase composition analysis. XRD analysis conducted on the specimen and raw material shows that crystallization is occurred in the glass phase during the heat treatments to some extent. Figure 6 indicates the raw material transfer into foam glass-ceramic after heat treatment at 875 °C. Cr2O3 is added into the raw materials as nucleating agent, contributed to decrease interface energy of the glass system for crystallization. P2O5 is an oxide which can form glass network introduced by Na3PO4 as foam stabilizer. It can easily form unsymmetrical phosphoric acid polyhedron within Si-O network [9]. Moreover, field intensity of P+ is larger than Si+. Therefore, Sr2+ and Pb2+ contained in the batch tend to separate P5+ from Si-O network to form crystal phase. The main crystalline phases found after the foaming process were Sr5(PO4)3F and Pb3(PO4)2.

Fig. 6. XRD patterns of raw material and foam glass-ceramic.
3.3.2. SEM analysis. The foam glass-ceramic sample has been cut and polished in 30s with 1% concentration of hydrofluoric acid corrosion. Details of the typical inner microstructure and morphology of the porous glass specimens are shown in figure 7 and figure 8, respectively. A large number of pores ranging from 1-2 mm are uniformly distributed in the sample as shown in figure 7. In figure 8, intertwined columnar crystals are observed on the surface of glass medium. This may contribute to a superior physical property of the product.

Fig. 7. SEM images of a fracture surface of foam glass-ceramic (200×).

![SEM images of a fracture surface of foam glass-ceramic (200×).](image)

Fig. 8. SEM micrograph of foam glass-ceramic(a:20,000×, b: 50,000×).

3.3.3. Performance indicators. As a suitable construction and building material, foam glass-ceramic has great superiority in physical properties. Besides density and compressive strength, water absorption and thermal conductivity is test in our work, compared with foam glass (table 1). It is clear that the performance indicators were higher than foam glass national standard (JCT647-2005) and met the requirements of lightweight load-bearing wall materials.

| Materials         | Density (g/cm³) | Compressive strength (MPa) | Water absorption (wt.%) | Thermal conductivity (w/m²·k) |
|-------------------|-----------------|-----------------------------|-------------------------|-------------------------------|
| Foam glass-ceramic| 0.78            | 3.42                        | 0.41                    | 0.052                         |
| Foam glass        | 0.14-0.20       | 0.40-0.80                   | 0.50                    | 0.037-0.070                   |
4. Conclusions
In this work, a foam glass-ceramic is prepared from waste CRT panel glass and its properties are studied by using different technology. Based on the experimental results, the following conclusions can be drawn:

1. A foam glass–ceramic is sintered from waste CRT glass by using one-step powder sintered method.
2. With the addition of 0.5 wt.% carbon as foaming agent, 4 wt.% Na2SiF6 as fluxing agent, 4 wt.% Na3PO4 as stabilizing agent and 1 wt.% Cr2O3 as nucleating agent, foam glass-ceramic can be obtained at 875 °C. The density is 0.78 g/cm³, compressive strength is 3.42 MPa, water absorption is 0.41 wt.%, thermal conductivity 0.052 w/m²-k.
3. The XRD pattern indicated that the crystals of the foam glass-ceramic are Sr5 (PO4)3F and Pb3(PO4)2, which contributes to the improvement of the foam glass-ceramic’s mechanical property.

Acknowledgments
The authors gratefully appreciate the financial support from National Natural Science Foundation of China (51678353), Shanghai Alliance Plan (LM201607), and Cultivate discipline fund of Shanghai Polytechnic University (XXKPY1601). The authors also acknowledge the Graduate Student Funding Program of Shanghai Polytechnic University (EGD17YJ0042), and project supported by Shanghai Cooperative Centre for WEEE Recycling (ZF1224).

References
[1] Wang Z, Zhang B and Guan D 2016 Nature 536 23
[2] Song Q, Wang Z, Li J and Zeng X 2012 Waste Manage. 32 1926
[3] Tian X, Wu Y, Zhang J, Yin X and Li M. 2014 Ecological Economy 30 101
[4] Pant D and Singh P 2013 Environ. Sci. Pollut. Res. 21 2414
[5] Nnorom I C, Osibanjo O and Ogwuegbu M O C 2011 Resour., Conserv. Recycl. 55 275
[6] Xu Q, Li G, He W, Huang J and Shi X 2012 Waste Manage. 32 1566
[7] Yao Z, Ling T C, Sarker P K, Su W, Liu J and Wu W 2018 Renewable Sustainable Energy Rev. 81 595
[8] Bernardo E and Albertini F 2006 Ceram. Int. 32 603
[9] Petersen R R, König J, Smedskjaer M M and Yue Y 2014 Glass Technol. 55 1
[10] Lazău I, Borcănescu S, Păcurariu C and Vancea C 2013 J. Therm. Anal. Calorim. 112 345
[11] Ling T C and Poon C S 2012 J. Cleaner Prod. 29–30 46
[12] Guo H W, Gong Y X and Gao S Y 2010 Mater. Lett. 64 997
[13] König J, Petersen R R and Yue Y 2014 J. Eur. Ceram. Soc. 34 1591
[14] Tian Y, Zou Y, Zhao F and Wu J 2001 J. B. Univ Technol. 27 247
[15] Østergaard M B, Petersen R R, König J and Yue Y 2018 J. Non-Cryst. Solids 482 217
[16] Mucsi G, B. Csóke, Kertész M and Hoffmann L 2013 J. Mater. 2013 1
[17] Méar F, Yot P and Ribes M 2006 Mater. Lett. 60 929