

# Sintered glass–ceramic from municipal solid waste incinerator ashes

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## Abstract

In the present study, the sinter-crystallization behavior of a glass from municipal solid waste incineration ashes was investigated. The crystallization kinetics were estimated by DTA at different heating rates and the formed crystalline phases were evaluated by XRD. The sintering was studied at different heating rates and at different holding temperatures by dilatometry, measuring the % of linear shrinkage, while the structure of the sintered samples was observed by SEM. The bending strength and the Young modulus were evaluated after heating at 5 and 20 K/min and 1 h holding at 1123 K. The DTA show two overlapped crystallization peaks, corresponding to 440 and 430 kJ/mol activation energies of crystallization. The XRD highlight that the crystallization starts by pyroxene formation, followed by anorthite and gehlenite. The sintering of the glass particles is inhibited by the crystalline phase formation and stops after the formation of 10% of crystal phase. Higher densification may be obtained by applying fast heating rate (20 K/min), which also improves the mechanical properties.

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## 1. Introduction

The sinter-crystallization technique is considered as an alternative for the production of glass–ceramics [1–3] and generally is applied when more complicated shapes or dimensions are requested. It is well known that during the sinter-crystallization process, the nucleation is surface induced so that no nucleating agents or isothermal step are applied; the heat-treatment is designed for producing the sintering of the glass particles and the crystallization.

In the sintered glass–ceramics belonging to the cordierite, anorthite, apatite and wollastonite systems, the densification is accomplished before the beginning of the respective phase formation [2–5]. No residual poros-

ity is attained in the final materials and they are characterized by excellent mechanical and chemical properties. In other crystalline systems the crystallization takes place during the sintering and the densification might be inhibited; a residual porosity persists in the final material inducing scarce mechanical and chemical properties. This behavior was found in several glass compositions obtained by melting and sintering industrial wastes such as the sintered glass–ceramics from MSW ashes [6–12].

The present work is related to a typical glass from municipal solid waste incineration (MSWI) bottom ash. In a previous study with the same glass [9], the sintering activation energy was obtained by non-isothermal heat-treatment at different heating rates using dilatometer. By XRD, TEM and SEM it was also show that the phases formation starts by surface pyroxene formation and that the densification is fully inhibited after the formation of a very small amount of crystal phase, below 10%.

In the present work, the crystallization kinetics was studied by DTA and the phase formation- by XRD.

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The sintering is evaluated in iso-thermal conditions by dilatometry at different temperatures; the results are compared with these, obtained at non-isothermal conditions [9]. The mechanical properties of the sintered materials are also reported.

## 2. Experimental

A glass with composition: SiO<sub>2</sub> – 46.1, TiO<sub>2</sub> – 1.1, Al<sub>2</sub>O<sub>3</sub> – 14.1, Cr<sub>2</sub>O<sub>3</sub> – 0.1, FeO + Fe<sub>2</sub>O<sub>3</sub> – 6.4, CaO – 14.7, MgO – 3.5, BaO – 0.2, ZnO – 0.3, PbO – 0.1, CuO – 0.2, MnO – 0.2, Na<sub>2</sub>O – 10.3, K<sub>2</sub>O – 1.2 was obtained by melting municipal solid waste bottom ashes for 2 h at 1673 K in a corundum crucible. The melt was quenched in steel mould and the obtained glass was broken, milled and sieved.

The crystallization was evaluated by Differential Thermal Analysis (DTA) at different heating rates, using about 50 mg of powder samples (45–75 μm) by Netzsch STA 409 apparatus. The crystalline phases formed were determined by X-ray diffraction (XRD) technique (Philips PW1830 apparatus and CuK<sub>α</sub> radiation). The percentage of crystal phase formed was measured by comparing the intensity of the amorphous halo in the parent glass and the heat-treated samples respectively [1].

The parent samples with initial 10/4/4 and 50/4/3 mm<sup>3</sup> sizes were prepared by the 45–75 μm powder fraction with addition of 7% PVA solution and by pressing at 100 MPa.

After drying and a 30 min holding at 553 K (to eliminate the PVA) the 10/4/4 mm<sup>3</sup> samples were treated in 'Netzsch 402 ED' differential dilatometer at 5 and 20 K/min heating rates in the temperature interval of 553–1273 K. Other samples, after heating at 5 and 20 K/min were hold for 10 h at 1023, 1053 and 1273 K. The morphology of fractured samples sintered at different temperatures in the range 1023–1273 K was examined by Scanning Electron Microscopy (Philips XL30CP).

Two series of five samples (50/4/3 mm<sup>3</sup>) were sintered for 1 h at 1123 K at 5 and 20 K/min heating rates, respectively. The Young modulus was determined by means of the non-destructive resonance frequency technique (Grindosonic) and than the bending strength was evaluated by a three point bending test with 40 mm outer span and a speed of 0.1 mm/min (SINTEC D/10).

## 3. Results and discussion

The DTA traces of powder and bulk samples, obtained at 10 K/min, are plotted in Fig. 1. The glass transition temperature,  $T_g$ , and the liquid temperature,  $T_l$ , in the both samples are practically the same, while the crys-

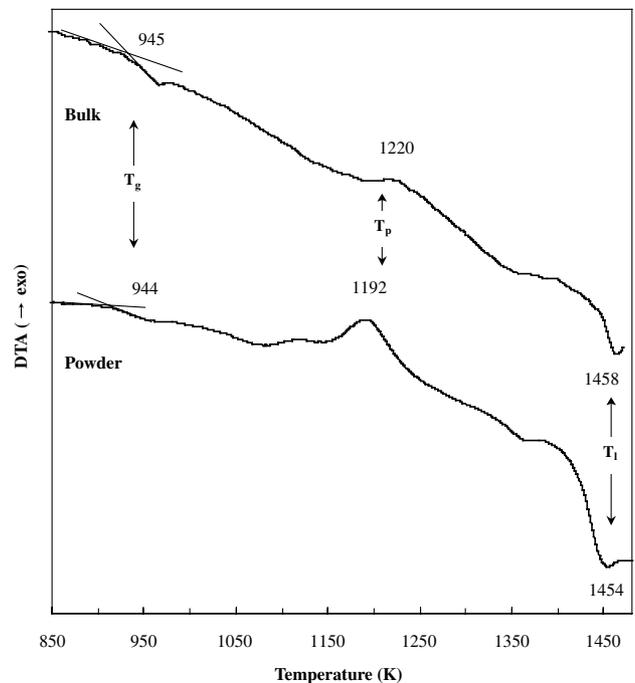


Fig. 1. DTA traces of powder, P, and bulk, B, samples.

tallization peak temperature,  $T_p$ , in the powder sample occurs at lower temperature and the peak has a higher intensity. This indicates that the crystalline phase formation starts predominately on the surface of the glass particles.

The temperature difference between  $T_g$  (945 K) and  $T_p$  (1192 K) is similar to the difference between  $T_p$  and  $T_l$  (1454 K), which according to the Hrubby coefficient ( $K_H = (T_p - T_g)/(T_l - T_p)$ ) [13–15] indicates a relatively high crystallization trend.

The traces at 5, 10, 15 and 20 K/min are shown in Fig. 2 and highlighted the overlapping of two exo-effects. The energy of crystallization,  $E_c$  for the first and for the second peak was estimated by the Kissinger equation [13,16]:

$$\ln(\phi/T_p^2) = -E_c/RT + \text{const} \quad (1)$$

where  $\phi$  is the heating rate and  $R$  is the gas constant. A plot of  $\ln(\phi/T_p^2)$  vs.  $1/T_p$  is a line, whose slope corresponds to  $E_c$ . The values of 440 kJ/mol and 430 kJ/mol were obtained for the first and for the second peak, respectively. The comparison with the energy of viscous flow, measured in the glass transition region (610 kJ/mol) [9], confirms the high crystallization tendency of the investigated compositions.

Fig. 3 shows the XRD spectra of samples, heated at 2 and 20 K/min, respectively, up to 1273 K and than immediately cooled at 10 K/min. The spectra highlighted the formation of pyroxene – CaO·MgO·SiO<sub>2</sub>, anorthite – CaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and gehlenite – 2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>, with a ratio between the different phases depending on the heating rate. At high heating rate the amounts of

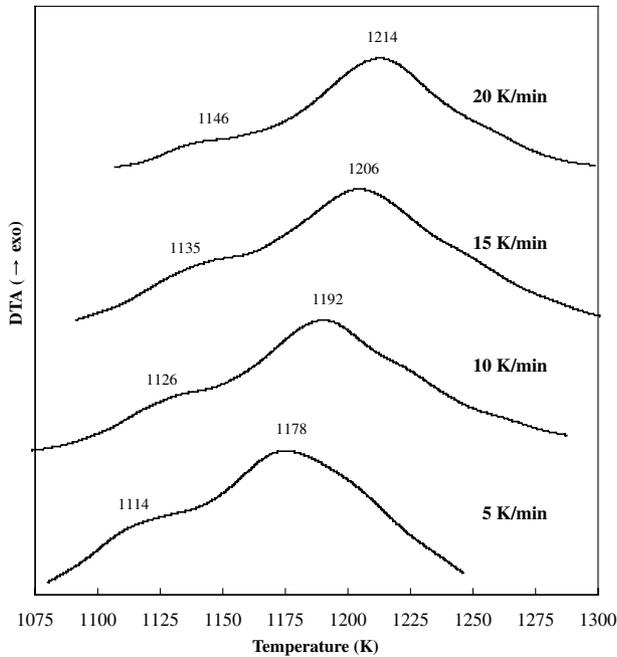


Fig. 2. DTA traces of powder samples at different heating rates.

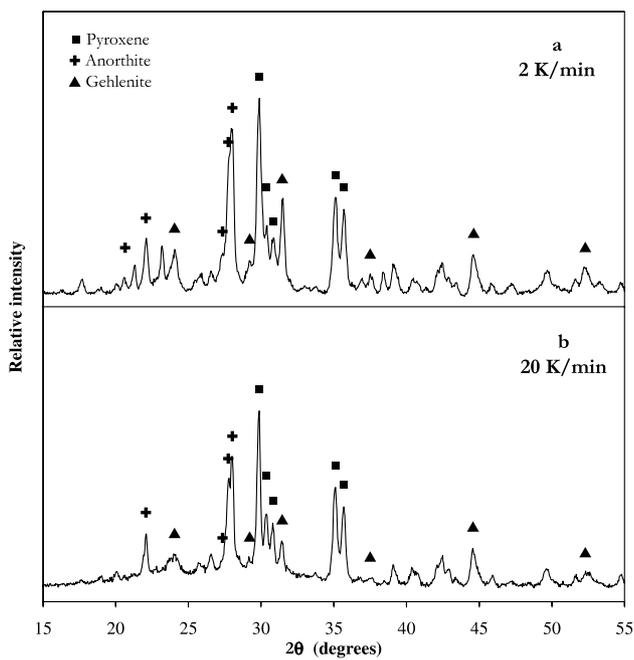


Fig. 3. XRD spectra of samples heat-treated up to 1273 K by 2 K/min (a) and 20 K/min (b), respectively.

gehlenite and anorthite is reduced while the variation of the intensity of pyroxene phase is negligible. The ratio pyroxene/(anorthite and gehlenite) also depends on the holding temperature. At low temperatures (10 h at 1023 K) the intensity of pyroxene increases, while at high temperatures (1–2 h at 1173–1223 K) the amount of anorthite and gehlenite increases and the total crystallinity reaches a 70–75 wt%.

In previous work [9], the sinter-crystallization was investigated, by dilatometry at different heating rates. It was demonstrated that the beginning of the crystallization inhibits the sintering and that higher densification may be obtained applying high heating rates. In the present study, the sintering was investigated in isothermal conditions. The samples were heated at 5 and 20 K/min and hold for 10 h at 1023, 1053 and 1273 K. The results are compared with the ones obtained at constant heating rates up to 1273 K [9]. Fig. 4(a) shows the non-isothermal dilatometric trace at 5 K/min (solid line) together with the sintering curve, obtained after holding at 1023 K (dashed line); Fig. 4(b) shows the non-isotherm at 20 K/min with the corresponding isotherm at 1053 K.

The results show that during isothermal heat-treatment at 1023 and 1053 K the densification stops after about 50 and 220 min holding times, respectively. Nevertheless of the prolonged sintering times, the shrinkage values, obtained in isothermal conditions are lower than these, measured during the non-isothermal treatment.

This demonstrated that the densification might be improved only by non-isothermal sintering at high heating rate. At non-isothermal sintering the densification at 5 K/min stops at 1082 K reaching shrinkage of 11.5%, while at 20 K/min a 14% shrinkage is obtained. This behavior is explained by the simultaneous occurrence of sintering and crystallization, i.e. the intensive phase formation increases the apparent viscosity of the system thus inhibiting the densification.

In order to evaluate the amounts of crystalline phases formed during the thermal treatments, samples were heat-treated in an electric furnace, at 5 and 20 K/min, up to the sintering onset temperatures (1082 and 1122 K respectively), hold 1 min and quenched in water. The relative XRD spectra are shown in Fig. 5: At 5 K/min the spectrum appears amorphous by X-ray with some initial traces of pyroxene formation; at 20 K/min the percentage of crystal phase was evaluated around 10%.

The isothermal step did not improve the sintering even at 1273 K; after 10 h holding the shrinkage remains practically constant (i.e. about 11.5% at 5 K/min and 14% at 20 K/min). SEM observations of the glass-ceramic structures provided a further confirmation of this dilatometric result. Figs. 6 and 7 show the structures after 1 min and 10 h steps at 1273 K, respectively. The images highlight similar structures with a residual porosity of about 15%; just some pore coalescence is evident after 10 h.

High heating rates positively influence the mechanical properties. The evaluation of the bending strength  $e$  and the Young modulus of the glass-ceramics heated at 20 K/min showed values of  $59 \pm 5$  MPa and  $45 \pm 4$  GPa while for the samples heated at 5 K/min the obtained values are  $49 \pm 4$  MPa and  $42 \pm 5$  GPa, respectively.

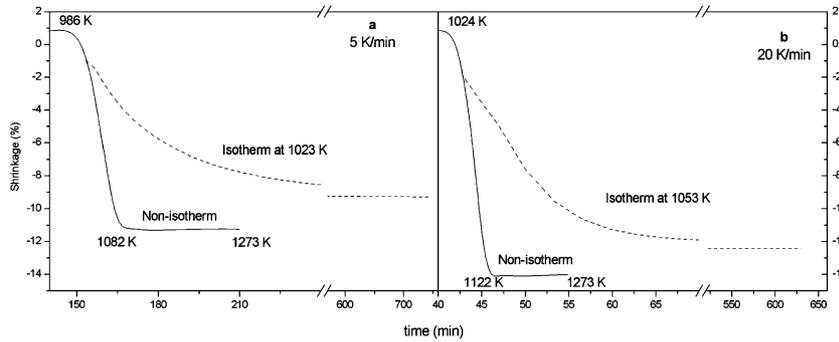


Fig. 4. Dashed line: isothermal sintering curves at 1023 and 1053 K; solid line: non-isothermal curves at 5 and 20 K/min up to 1273 K.

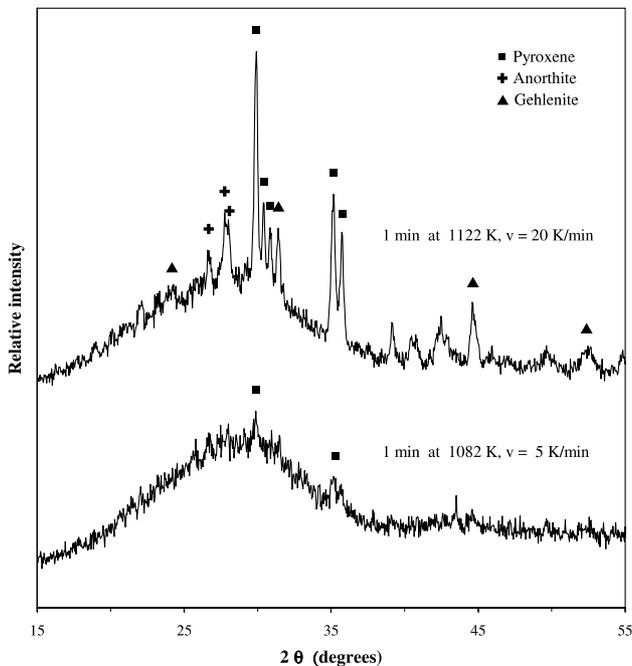


Fig. 5. XRD spectra of samples, heat-treated to the sintering onsets at 5 and 20 K/min.

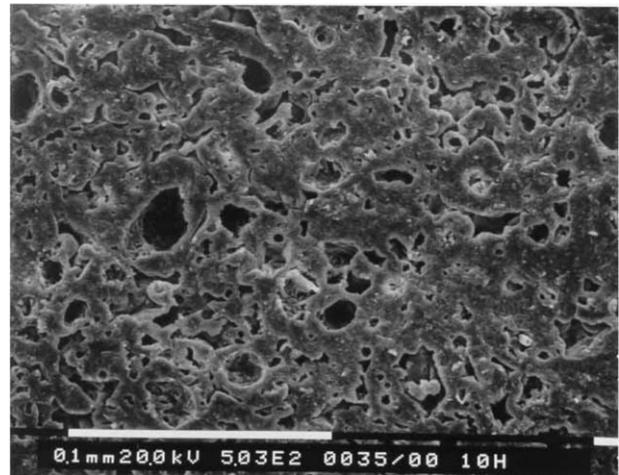


Fig. 7. SEM image of fractured sample after 10h holding at 1273 (20 K/min).

#### 4. Conclusion

In the investigated glass from municipal solid waste incineration ash, the crystallization starts by surface pyroxene formation, followed by anorthite and gehlenite phases. The ratio between the crystal phases depends on the heating rate and on the holding temperature.

The crystallization and the sintering processes take place simultaneously; as a result the densification is inhibited and a residual porosity remains in the glass-ceramic. The densification doesn't improve by isothermal holding; better sintering may be obtained by applying high heating rate, which also increases the mechanical properties of the glass-ceramic.

#### References

- [1] Z. Strnad, Glass-Ceramic Materials, Elsevier, Amsterdam, 1986.
- [2] W. Höland, G. Beall, Glass-Ceramic Technol., The American Ceramics Society, Westerville, 2002.
- [3] E.M. Rabinovich, J. Mater. Science 20 (1985) 4259.
- [4] W. Winter, J. Mater. Science 32 (1997) 1649.
- [5] K. Sujirote, R.D. Rawlings, P.S. Rogers, J. European Ceram. Soc. 18 (1998) 1325.

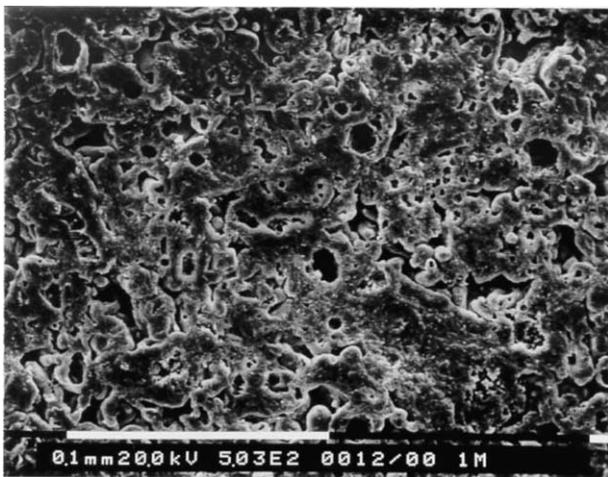


Fig. 6. SEM image of fractured sample after 1 min holding at 1273 (20 K/min).

- [6] A. Boccaccini, M. Petitmeret, E. Wintermantel, *The American Ceramic Society Bulletin* 11 (1997) 75.
- [7] L. Barbieri, A. Corradi, I. Lancellotti, *J. Eur. Ceram. Soc.* 20 (2000) 1637.
- [8] A. Boccacini, G. Schawohl, H. Kern, B. Schunck, J. Rincon, M. Romero, *Glass Technol.* 41 (2000) 99.
- [9] A. Karamanov, M. Aloisi, M. Pelino, *J. Eur. Ceram. Soc.* (in press).
- [10] M. Ferraris, M. Salvo, F. Smeacetto, L. Augier, L. Barbieri, A. Corradi, I. Lancellotti, *J. Eur. Ceram. Soc.* 21 (2001) 453.
- [11] T.W. Cheng, T.H. Ueng, Y.S. Chen, J.P. Chiu, *Ceramics Int.* 28 (2002) 779.
- [12] A. Karamanov, M. Pelino, A. Hreglich, *J. Eur. Ceram. Soc.* 23 (2003) 827.
- [13] J. Sestak, *Thermophysical Properties of Solids – Their Measurements and Theoretic* Academia Prague, Academia Prague, 1984.
- [14] A.A. Cabra, A.A.D. Cardoso, E.D. Zannoto, *J. Non-Cryst. Solids* 320 (2003) 1.
- [15] I. Avramov, E.D. Zannoto, M.O. Prado, *J. Non-Cryst. Solids* 320 (2003) 9.
- [16] H.E. Kissinger, *Anal. Chem.* 29 (1957) 1702.