

DETERMINATION OF THE FICTITIOUS FRIT TEMPERATURE BY RAMAN SPECTROSCOPY

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ABSTRACT

The fictitious temperature of a frit and its relationship to surface microhardness was determined. It was observed that both the Si-O-Si bond angle and microhardness decreased with the fictitious temperature, a result attributed to silica phase separation from the rest of the frit components when the frit was heat treated.

1. INTRODUCTION

The fictitious temperature, T_f , of a glassy material can be defined as “the temperature at which glass reaches equilibrium when quickly cooled at that temperature from a specific state”. It is well known that many glass properties depend on T_f , such as, for example, density, viscosity, mechanical strength, microhardness, the thermal expansion coefficient, refractive index, etc. Since some of these properties increase while others decrease with T_f , it is extremely important to be able to predict at what temperature the glaze composition developed with the frit should be treated in order to provide it with a certain property or set of properties in the fired glaze coating. Based on this fact, the T_f of a ceramic frit commonly used in the ceramic floor tile industry was determined in this work. T_f can be determined using infrared (IR) or Raman spectra; however, given that frits have IR spectra very wide wave bands, the use of Raman spectroscopy is preferred. The results obtained in this work show how T_f is directly related to the microhardness of the frit used in the glaze.

2. EXPERIMENTAL

In this study, a transparent glaze used commonly in the ceramic floor and wall tile industry was used. The frit was processed in an electric kiln at temperatures of 380, 400, 420, 430, 440, 460, 480, 500 and 520 °C for 4 hours for the first three temperatures, 3 hours for the following two, and 2 hours for the final two temperatures. The frits treated were subsequently analysed by Raman spectroscopy and Vickers indentation. The Raman spectra were obtained with a Renishaw in Via Raman spectrophotometer using a 514 nm laser. Each final spectrum is an average of 10 performed analyses. The microhardness measurements were made with a Leco microdurometer using a 500 g load for 15 s. At least 10 measurements were made to obtain an average value. The standard deviation was below 3% in all cases.

3. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the pieces of frit treated at different temperatures. Very wide spectra with largely undifferentiated bands were observed, as would be expected with multi-component glassy materials. Two basic bands can be seen in these spectra, situated at about 1030 cm^{-1} and 480 cm^{-1} , corresponding to the ω_4 (TO) and ω_1 vibrations of the Si-O-Si frit bonds, respectively. The position of these bands is related to T_f , as already shown in different studies [1, 2, 3].

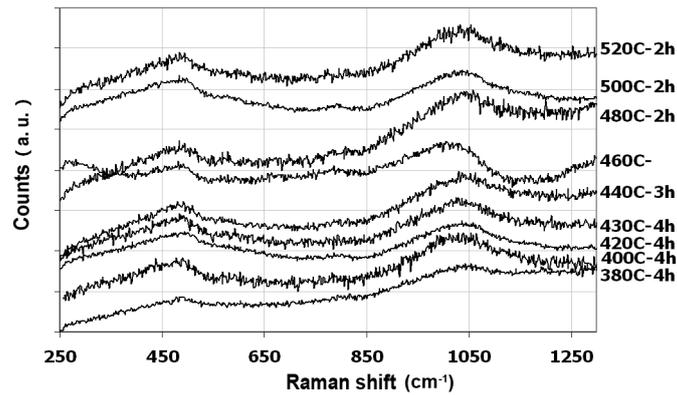


Figure 1. Raman spectra of heat-treated frits.

Figure 2 shows the relative variation of these bands with respect to the initial position, i.e. the position at which the first analysis temperature appears (so that the first value is 0). This figure shows how the ω_4 (TO) band position decreases with temperature, while the ω_1 band increases. These changes are similar to those observed in glassy silica, which were attributed to a decreased average value of the Si-O-Si bond angle of the glassy network and the number of 3 and 5-membered silica rings (2).

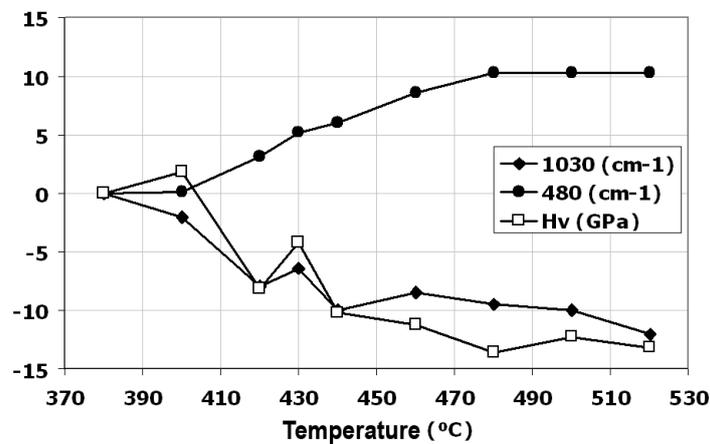


Figure 2. Variation of Raman positions and microhardness of frits with T_f .

Figure 2 also shows the percentage variation in the microhardness value of the frits treated at different temperatures. It may be observed that microhardness decreases with temperature in the same way as with conventional sodium-calcium glasses [3]. This decreased microhardness should be accompanied by an increased Si-O-Si bond angle. However, the opposite occurs, so that it can be concluded that in the case of multi-component frits, when the temperature of the silica increases, it has a tendency to separate from the other oxide components and form a silica-rich phase of the glassy silica type. This separation of silica from the rest of the components leads to a loss of cohesion in the glassy network of the frit, which in turn leads to loss of microhardness of the material.

4. CONCLUSIONS

This work shows the relationship between the fictitious temperature of a frit and its surface microhardness. It was observed that both the Si-O-Si bond angle and microhardness decreased with temperature, owing to silica phase separation from the rest of the frit components.

REFERENCES

- [1] A. E. Geissberger, F. L. Galeener. Phys. Rev. B. 28 (1983) 2366-3271.
- [2] T.M. Gross, M. Tomozawa. J. Non-Cryst. Solids 354 (2008) 4056-4062.
- [3] S. Fujita, A. Sakamoto, M. Tomozawa. J. Non-Cryst. Solids 330 (2003) 252-258.