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THERMAL AND SINTERING BEHAVIOUR OF BASALT GLASSES AND NATURAL BASALT POWDERS

J. Ma. Rincon[1], *J. Cáceres*[1], *C. J. González-Oliver*[2], *D. O. Russo*[2], *A. Petkova*[3] *and H. Hristov*[4]

[1]The Glass-ceramics Laboratory, Institute E. Torroja de CC. Construcción, CSIC, Madrid Spain
[2]División de Física, Centro Atómico de Bariloche, S. C. de Bariloche, Argentina
[3]Izida, Elin Pelin
[4]Applied Mineralogy Institute, The Bulgarian Academy of Sciences, Sofia, Bulgaria

Abstract

A study of three Spanish and one Bulgarian basaltic rock demonstrated that, after thermal treatment at temperatures higher than 800°C, crystallization of pyroxenes, anorthite and magnetic occurred. Following sintering of the original basalts and powdered original glasses, the same crystalline phases were nucleated and grown in the resulting glass-ceramics. Chemical and DTA/TG analyses suggested similar behaviour for the synthesized Canarian basalt glasses, which are located in the tephrite-basanite field, and different behaviour for the trachy-andesite Canarian and the basaltic-andesite Bulgarian basalt glass. In consequence of the high sensitivity of the specific heat to phase transformations, $C_p(T)$ and TMA experiments allowed a distinction between the tephrite-basanite and trachy-andesite Canarian glasses on the basis of their different thermal behaviour.

Keywords: Bulgarian basalt, glass-ceramics, glasses, heat capacity, Spanish basalts, thermal methods

Introduction

Basalt glasses and glass-ceramics obtained from the melting of basalt rocks have been investigated in the past and continue to be studied with regard to the production not only of erosion or wear-resistant materials, but also of fibered glasses and glass-ceramics, and as matrices for nuclear waste inertization. Different types of basalt rocks are being used for the production of such materials in Germany, the Czech Republic, Bulgaria, Russia, etc. [1]. More recently, in order to implement the industrial production of these materials, investigations are being carried out as concerns the use of Spanish basalts, mainly from the Canary Islands [2–4]. Basalt petrurgical materials are produced in Bulgaria and investigations of these materials are also of great interest. The kinetics of nucleation and crystallization of synthetic basalt glasses, the microstructural characteristics of heat-treated glasses and properties characteristic of a wide range of such glass-ceramics have been determined [5, 6]. However, the thermal and sintering properties of original basalts have not yet been considered in detail [7].

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The aim of this paper is to present and discuss results obtained by using several thermal methods for characterization of the high-temperature behaviour of some Canarian Islands basalts and starting glasses, and the sintering capabilities of these glasses for the production of 'sintered basalt glass-ceramics'. Likewise, for a comparison with Canarian basalts, the thermal behaviour of Bulgarian basalt and basalt glass used in the manufacture of petrurgical products was investigated.

Experimental

Materials

Three original basalt rocks from Tenerife, the Canary Islands, were selected (named B1, B2 and B5), together with a basalt rock from Bulgaria (named BB), which had previously been characterized as concerns the formation of fibres and petrurgical glass-ceramics [3]. They are located in the TAS diagram as indicated in Fig. 1.

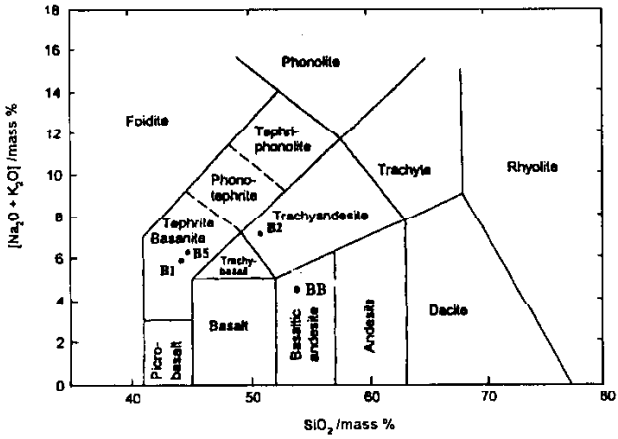

Fig. 1 TAS (total alkali silica) classification [7] of the basaltic rocks considered in this investigation by thermal methods

It can be seen that samples B1 and B5 are situated in the tephrite/basanite area, while B2 is in the trachyandesite area, with a higher silica content than those of the former samples. Basalt BB is located in the basanite/andesite area in the well-known TAS diagram for basaltic rocks [7]. These basalts were melted in an electric furnace at 1450°C and poured into brass moulds, and the glasses obtained were characterized by XRD, which confirmed their 'amorphous' character. Previous viscosity/temperature variation and DTA experiments demonstrated similar thermal behaviour for B1 and B5, with only one exothermic peak of crystallization, at 846 and 829°C, respectively, while glasses B2 and BB exhibited several exothermic peaks, which correspond to the formation of three crystalline phases, as will be discussed later [3].

Sintering experiments were carried out on the powdered rocks and original powdered glasses at an initial heating rate of 10°C min^{-1}, with stabilization for 60 min at maximum temperature, and a cooling rate of 10°C min^{-1}. B2 was heat-treated at 820°C for 5 h, and B2 at 1100°C for 10 h.

Methods

Several classical thermal methods were applied: DTA/TG (Mettler TA2), TE (thermal expansion) (Adamel Lhomargy DI-24), TMA (thermomechanical analysis), determination of molar heat capacity (C_p) *vs.* sample temperature, and in some cases HSM (heating stage microscopy) (II A-P Leitz) at 10°C min^{-1} in an ambient atmosphere. Dynamic measurements with increasing heating of glass samples were carried out under the following conditions: a heating rate of 10°C min^{-1} in air atmosphere, with a sample mass of 16 mg. TMA was followed by using an STA 1500 Stanton Redcroft IA instrument, which also allows the determination of heat capacity with a calorimeter attached to the same computer station. Crystalline phases were identified by X-ray diffraction of powdered samples and SEM/EDX on gold-sputtered specimens. Chemical etching was performed with HNO_3 because of the high iron oxide content.

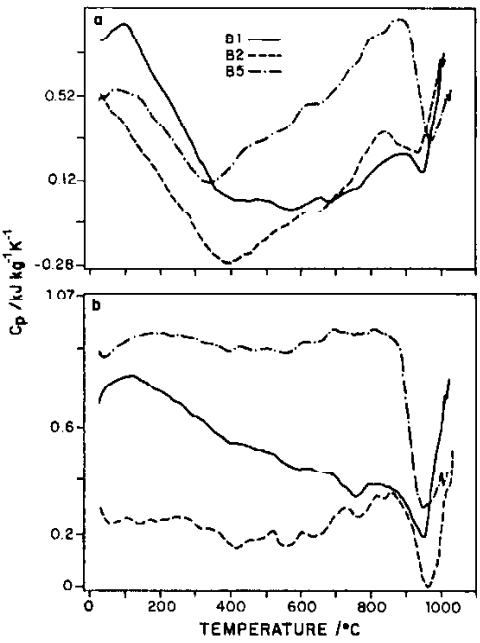

Fig. 2 a) – Variation in $C_p(T)$ with temperature for the Canarian basalts B1, B2 and B5; b) – The same experiment repeated with the final sample maintained in the specimen holder of the calorimeter

Results and discussion

Thermal characterization of original basalts and original glasses

Figures 2a, b and 3a, b depict the specific heat variation (C_p) and TMA results for samples B1, B2 and B5 (curves a) and for the same samples after heating and repetition of the experiment without removal of the sample. The specific heat attained minimum values near 350–400°C for these basalts, due to the loss of volatile components and the starting of agglomeration between particles. Some phase transformations of original minerals such as pyroxenes correspond to the maxima observed in the interval 850–900°C for the curves obtained from the original basalt powders (Fig. 2a). The minima observed at 940–980°C in the same curves correspond to the start of glassy phase formation from feldspar components. Repetition of the experiment with the product formed in the previous test gave $C_p(T)$ with less variation on heating. This is evident for basalt B5 and less evident for basalt B2, while for sample B1 the specific heat decreases with heating until the 950°C minimum is reached, which is common for all the basalts here considered and must be related to the softening of the material.

The repeated TMA experiment confirmed the glassy character of the basalts after heating to 1000°C: the curve displayed a variation similar to that of the dilatometric behaviour of conventional glasses [8] (Figs 3a and b). In this sense, during the initial heating basalt B5 exhibited a more linear behaviour, close to that of a glass, which indicates its more vitreous character. This fits in well with the above-mentioned al-

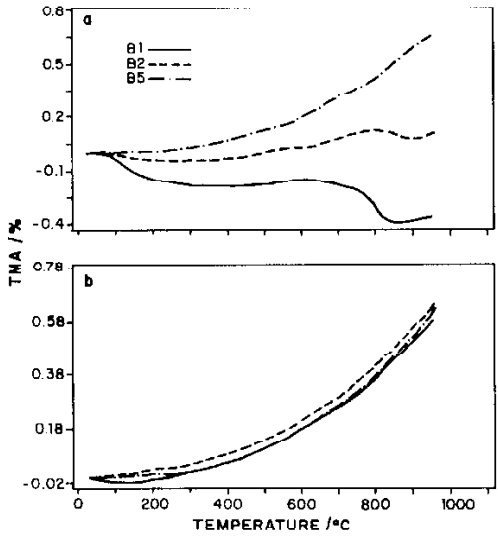

Fig. 3 a) – Variation in length (TMA) (expressed in %) with temperature for the Canarian basalts B1, B2 and B5; b) – The same experiment repeated with the final sample maintained in the specimen holder of the calorimeter

most stable behaviour of C_p for basalt B5. Original basalts B1 and B2 revealed different TMA variations on heating, due to the transformations of the minerals which constitute these rocks (Fig. 3a). In this respect, it is very interesting to see how basalts B1 and B5, considered similar materials in the TAS compositional representation, in fact differ in TMA behaviour because of the mineralogical composition. This is in good agreement with the behaviour exhibited by both basalts after being vitrified (Fig. 3b), because B1 and B5 give identical TMA curves.

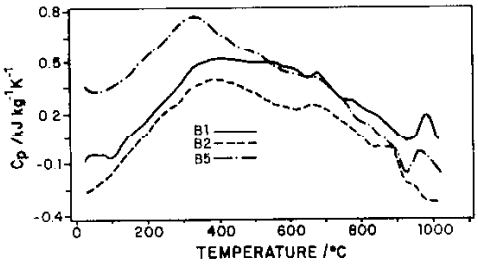

Fig. 4 Differential representation of specific heat for Canarian basalt samples B1, B2 and B5; $\Delta C_p = C_p$ (sample maintained in holder) $- C_p$ (original sample)

Differential curves of $C_p(T)$ between the repeated heating experiment with the sample maintained in the holder and the original heating experiment are drawn for B1, B2, and B5 in Fig. 4. From these curves, the similarities between B1 and B5 and the difference from B2 are evident. Thus, between 950 and 1000°C one common maximum is observed for B1 and B5, which is related to the softening of these basalts. The wide maximum between 300 and 400°C results from the volatilization of components from the original minerals which constitute these basalts.

As seen in previous work [3] the DTA/TG results for Canarian glasses B1 and B5 display only one exo-peak, near 850°C, while glasses B2 and BB give three exo-peaks (Fig. 5) as a consequence of their more complex mineral composition (trachy-andesite and basaltic-andesite character, respectively, for B2 and BB, as can be seen in Fig. 1. In the case of B2, these are at 858, 1054 and 1173°C, these temperatures corresponding to the formation of magnetite, pyroxene and anorthite feldspar. The Bulgarian basalt glass gives rise to exo-peaks at 657, 912 and 1223°C. When the basalt glass is heated at a lower rate, the 912°C peak becomes a doublet at 868 and 891°C, due to a phase transformation or the immiscibility of pyroxene phases.

Sintering behaviour of Canarian and Bulgarian basalts and the respective original glasses

Figures 6a–d show the linear contraction (%) determined by measurement of the geometry of samples by HSM after different thermal treatments of the original rocks and respective glasses (powdered samples). A more linear contraction can be seen on heating in the Bulgarian than in the Canarian rock, implying higher temperatures of sintering for the former industrial petrurgical raw material. Similarly, the sintering behaviour of the original glasses is related to the original rocks. Thus, in order to at-

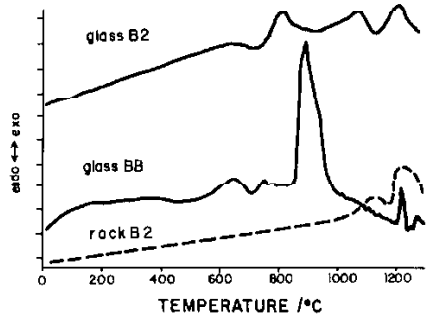

Fig. 5 DTA/TG traces of rock B2, glass B2 and original glass BB

tain maximum contraction, the Bulgarian glass needs a higher temperature of sintering (1200°C), while maximum sintering can be obtained at 900°C with the original Canarian glass B2.

Microstructure and microanalysis of sintered materials

Figure 7 depicts some of the microstructures observed and analysed by SEM/EDX for sintered glass B2 heat-treated at 820°C for 5 h and at 1100°C for 10 h. Both materials have a glass-ceramic character, but at lower temperature, when the contraction is only 50% (Fig. 6), crystals of ilmenite (iron and titanium-enriched phase) are formed in a glassy matrix where incipient diopside (pyroxene) crystals are nucleated. Such a pyroxene phase is not visible, but was clearly identified by XRD in this material. At a higher temperature of sintering (1100°C), the contraction is maximum and a similar microstructure is observed by SEM, but including the precipitation of feldspar anorthite crystals, which display an intermediate grey contrast.

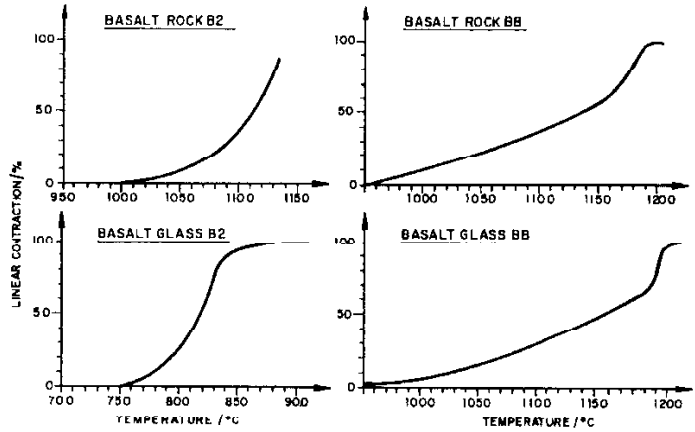

Fig. 6 Linear contraction (%) determined in pressed powders of a) – basalt rock B2; b) – basalt rock BB; c) – original glass B2 and d) – original glass BB

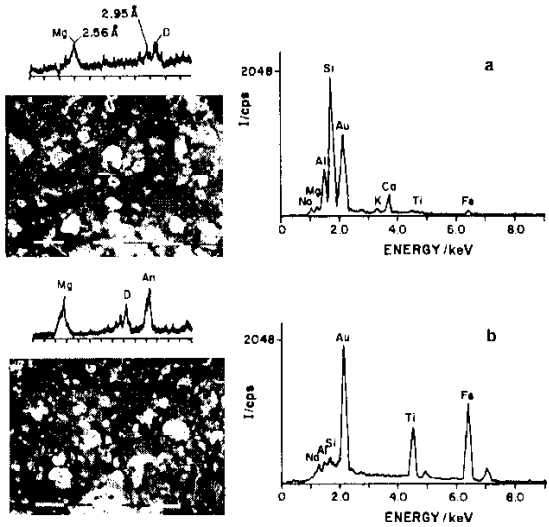

Fig. 7 SEM/EDX micrographs and spot analysis of phases from glass B2 heat-treated at a) – 820°C for 5 h and b) – at 1100°C for 10 h

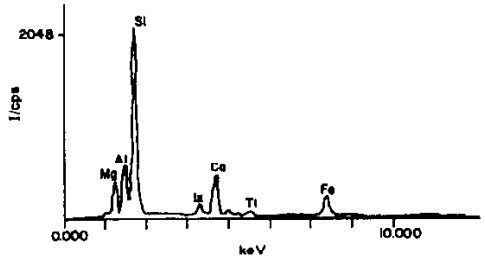

Fig. 8 SEM/EDX analysis of the sintered Bulgarian basalt glass

EDX microanalysis carried out on the phases from these materials revealed a matrix with low contents of Fe and Ti. In contrast, the white phase enriched in Fe and Ti probably involves ilmenite crystals which were not identified by XRD. In contrast with the nucleation and crystallization of bulk basalt glasses previously investigated [2, 5, 6], where the crystallization of magnetite crystals is usual, nucleating pyroxene crystallization, in the sintered basalt glasses the iron phase is a Ti–Fe ilmenite. It seems that the diffusion of iron throughout the small particles of glass could be responsible for the formation of ilmenite in this case and the exsolution of iron from the pyroxene areas. EDX analysis of the sintered Bulgarian basalt revealed (Fig. 8) its higher magnesium content, giving rise to the formation of enstatite crystals, which makes this glass sintered at higher temperatures than for Canarian basalt glass. In this case, the magnetite crystals and pyroxene are precipitated in the sin-

tered glass. Therefore, the magnesium content here is the determinant of the retention of iron in the magnetite (spinel) phase and could be related to two exo-peaks observed in the DTA experiments at lower heating rates.

More work now is in progress in order to elucidate the relations of the phase formation with the microstructure in the diopside-anorthite and iron-related systems [9]. This is a typical eutectic system, giving rise to eutectic microstructures, as demonstrated previously [6, 10]. However, when heat treatment is carried out on the powdered pressed original glass, the high surface area interface involved in the sintering process makes the surface predominant over the volume nucleation, which is more characteristic for eutectic growth. Finally, with the high diffusion of iron to the surface of the grains during the heating process, as is the case for the basalt melts investigated here, the surface growth is enhanced.

Conclusions

We have investigated the thermal behaviour of several basalts and basalt glasses from the Canary Islands and Bulgaria. After thermal treatment at temperatures higher than 800°C, the crystallization of pyroxenes, anorthite and magnetite was demonstrated. Similarly, on sintering of the original basalts and powdered glasses, the same crystalline phases were nucleated and grew in the resulting glass-ceramics. The chemical composition and DTA/TG behaviour suggest similar behaviour for glasses B1 and B5, which is different from that of glasses B5 and BB; nevertheless, the $C_p(T)$ and TMA experiments allow a distinction as concerns different thermal behaviour and structural character between glasses B1 and B2, which is due to the high sensitivity of the specific heat to phase transformations.

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