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An alternative method to study the cooling of glasses from melt to solid phase

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ABSTRACT

The aim of this preliminary work was to present a novel method, suitable to investigate the glass cooling, from melt to solid state, based on a fast, non-usual and easy microwave method. The following glass system $x\text{BaO} \cdot (100-x)\text{B}_2\text{O}_3$ ($x = 0\%$ and 40%) was selected as an example for this study. The melt was poured inside a piece of waveguide and then, its cooling was monitored by the microwave signal as a function of time. The variations in the signal can provide valuable informations about some structural changes that take place during the cooling stages, such as relaxation processes. This method can be useful to investigate the cooling and heating of other materials, opening new possibilities for investigation of dielectric behavior of materials under high temperatures.

1. Introduction

When the glass is subjected to a sudden variation of temperature (step temperature), in the neighborhood of the glass transition temperature (T_g), the physical properties such as specific heat, specific volume, viscosity, refractive index and enthalpy displays some lag towards the new equilibrium values [1]. The metastable equilibrium is then recovered after a certain relaxation time, required for the average molecular configuration to be consistent with the new state of the super cooled liquid. The evolution of a single step of cooling and heating can be described as a sum of infinite number of small temperature steps [2]. Such changes can be accompanied by effects of ion migrations in the glass structure, or fast relaxation processes that occur in the glass network [3–10].

These processes can be studied by means of dielectric properties. A simple technique used to perform dielectric measurements of phosphate glasses, at temperatures ranging between 25 and 300 °C (glass in the solid state), at microwave and radio frequency (impedancimetry) have been reported in some previous works [11,12]. The cooling of other glasses has been described elsewhere by means of mathematical simulation and heat transfer phenomenon [13,14]. However, the evaluation of dielectric properties of melted glasses by conventional impedancimetric techniques are not so easy to perform, in such a way that the aim of this short work was to present a novel, fast, non-destructive and easy method, using microwave circuitry, suitable to study the cooling of glasses and other materials from melt to solid state. Similar studies have not been found in literature at the present moment, in such a way that these measurements were performed by the first time. The advantageous of this method is that there is no contact between the sensor (crystal detector) and the melt, or any element, such as metallic plates and the sample, as found in impedancimetric methods [11,12,15,16]. The measurements were performed by means of the reflected component of the microwave signal, by the sample.

2. Experimental

The glasses were obtained from the fusion of the mixture of analytical reagent grade materials H_3BO_3, and $BaCO_3$. The batch was melted in an alumina crucible, inside an electric furnace at the temperature of 1000 °C for 1 h, in ordinary atmosphere (air). After the fusion, the melt was immediately poured through a hole (diameter 7 mm) made in the upper side of a waveguide. The microwave energy was supplied by a reflex klystron, protected by an isolator at the microwave power input. Initially, the waveguide was held at room temperature. The frequency of the klystron was 9.00 GHz and the power level was around 5 mW, and the propagation mode was TE_{10}. Fig. 1 shows the setup used for the experiments, consisting of a waveguide of dimensions $30.0 \times 10.0 \times 22.8\ \text{mm}^3$ tied to the klystron at one end, and at the other, terminated with a matched impedance load.

The reflected microwave signal was collected from the backward port of a directional coupler and a crystal detector, and measured using an acquisition data system (mod. IMPAC AD DA converter) acting as a voltmeter. A matched termination was necessary to obtain a null signal in the absence of any sample inside

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the waveguide. The signal was processed by a computer, as a function of cooling time of the melt. Data acquisition began at the same instant of the melt deposition inside the waveguide. The amplitude of the microwave reflected signal was, therefore, recorded as a function of time during the cooling from the melt to solid state. Each curve was obtained relative to different amounts of the glass poured inside the waveguide. The average diameter of each droplet was between 10 mm and 15 mm. The glass droplets were weighed after attaining the room temperature. Due to specific reasons, in this stage of work, measurements were performed as a function of time, assuming the initial temperature being that of the melt in the electric furnace.

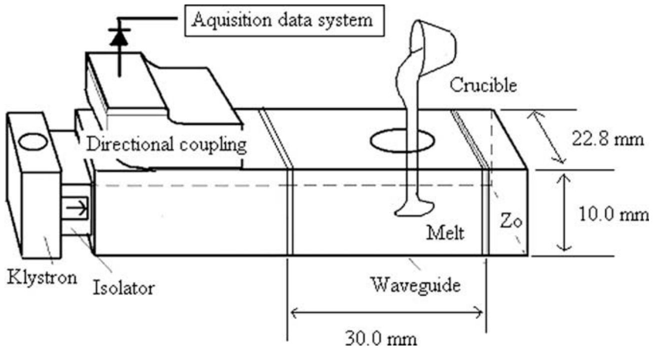

Fig. 1. Microwave setup for the experiments.

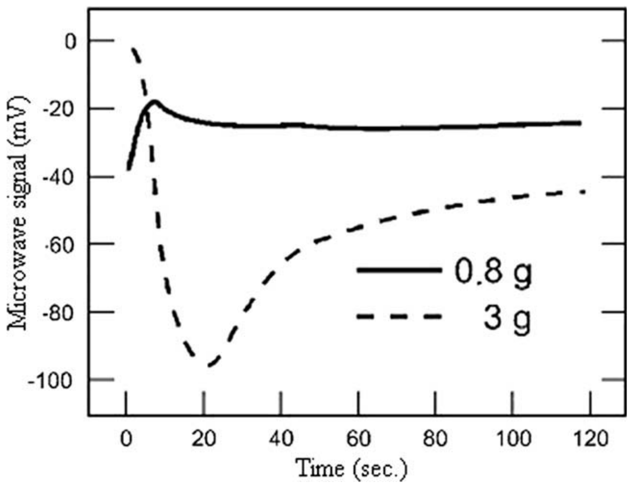

Fig. 2. Examples of microwave signal amplitude function of cooling time for the glass B_2O_3 glass droplets of 0.8 g and 3 g, respectively.

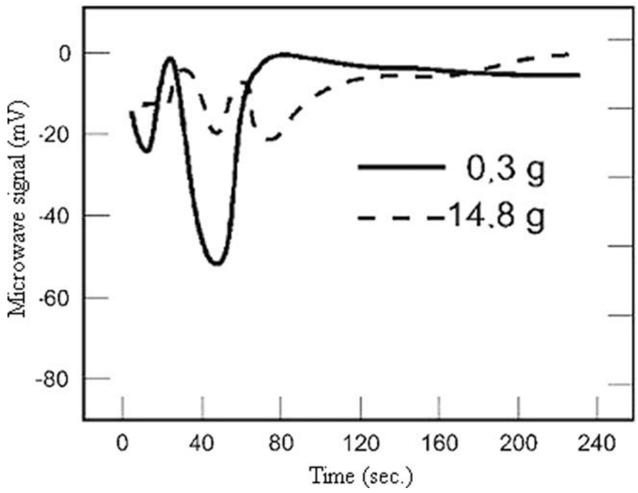

Fig. 3. Examples of microwave signal amplitude function of cooling time for $60B_2O_3 \cdot 40BaO$ glass droplets of 0.3 g and 14.8 g, respectively.

Table 1
Cooling times of some borate glasses.

Mass of glass droplet	Cooling time
0.8 g B_2O_3	>30 s
3 g B_2O_3	>100 s
0.3 g $60B_2O_3 \cdot 40BaO$	>120 s
14.8 g $60B_2O_3 \cdot 40BaO$	>200 s

3. Results

Fig. 2 shows examples of reflected microwave signal evaluated as a function of two different cooling times of B_2O_3 glass, for droplets of 0.8 g and 3 g, respectively.

For small amounts of melted glasses poured inside the waveguide, the cooling time becomes so shorter, so that no relaxation time becomes visible. On the other hand, for greatest amounts of melted glasses, the cooling time becomes larger, so that some signal variations can now be visible. Similar behavior can be found in other works [12], in which the dielectric constant begins to increase within the temperature interval 25–300 °C. Above this temperature range, one can expect a fall in the dielectric constant values, because the thermal vibrations of the glass structure increases above the glass transition temperature (T_g), overcoming the polarizability effect of the dipoles by the electric field [17]. As the temperature continues to increase, other more complex effects such as temperature dependence relaxation processes, ionic configurations, can take place, contributing or not to the polarizability of the material. The variations in the microwave signal can be attributed to the relaxation processes [18] that occur during the glass cooling. In the glassy state, the average molecular configuration is frozen into fixed positions, in such a way that the microwave reflected signal beyond 30 s and 100 s, respectively, becomes approximately constant. Fig. 3 shows examples of plots of microwave reflected signal as a function of cooling time for the glass $60B_2O_3 \cdot 40BaO$.

It can be observed that the addition of barium oxide in the B_2O_3 glass composition modifies the shape of the microwave signal, increasing the cooling time of the glass and further, contributing to the introduction of more relaxation processes, as compared to the Fig. 2. The extra relaxation processes can arise from BaO structures in the glass. Table 1 shows the approximate cooling times for these glasses formed inside the waveguide.

4. Conclusions

The method described in this work was found to be fast and sensitive to study the glasses during their cooling stages. The variations observed in the microwave reflected signal can be attributed to some complex temperature dependent relaxation processes that occur during the glass cooling, which affects the dielectric properties. This method seems to be a potential tool in order to investigate the physical properties of other materials during the heating and cooling, opening new possibilities for other dielectric investigations, at very high temperatures. However, further studies and experimental improvements are still needed in order to better elucidate these behaviors. Possibly, one of the variations observed can be the T_g of the glass.

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