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Dependence of a glass transition temperature on a heating rate in DTA experiments for glasses containing transition metal oxides

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ABSTRACT

It has been known for >60 years that thermal events taking place during DTA measurements (e.g. glass transition or crystallization) depend on heating rate. In this paper, we collected numerous data of DTA measurements of various glasses containing transition metal oxides (V_2O_5, FeO, Ti_2O_3) carried out at different heating rates (1 to 25 °C/min). We showed that glass transition temperature vs. heating rate can be well described by both Kissinger's and Lasocka's formulas. Additionally, we discuss an accuracy of extrapolation based on data taken at high heating rates to low heating rates. Our result show that glass transition temperatures at low heating rates can be satisfactorily extrapolated from higher ones, with a relative error <3.5% in every case (and mostly <1%), due to linear change with heating rate both in Kissinger's and Lasocka's plots.

1. Introduction

Thermal analysis (TA) is an advantageous method to observe thermal events taking place in samples upon heating/cooling. It is, however, important to remember that samples are not in equilibrium state and temperatures observed at TA measurements depend on a heating/cooling rate. In most cases, the heating rate of 10–20 °C/min is chosen for experiments. This results in high signal and reasonably short time of the experiment. As a consequence, observed temperatures may differ significantly from values observed in quasi-equilibrium measurements. Therefore, it is important to be very cautious trying to correlate results obtained at one heating rate with other measurements (e.g. electrical [1,2]) carried out at different heating rate.

In 1950s H. E. Kissinger studied properties of materials by differential thermal analysis (DTA) performed at various heating rates and proposed a suitable expression [3], which may be rewritten as follows:

$$\ln\left(\frac{\theta}{T_m^2}\right) = -\frac{Q}{k_B T_m} + C, \tag{1}$$

where: θ — heating rate in °C/min, T_m — characteristic temperature of a thermal event, k_B — Boltzmann constant, Q — activation energy of the event and C — a constant. Originally, his work had been devoted to thermal decomposition of kaolinites, but as it was shown later (e.g. by [4]), Kissinger's formula may also be used to describe dependence of a glass transition temperature (T_g) on the heating rate.

Two decades later, M. Lasocka studied T_g in splat-cooled $Te_{85}Ge_{15}$ glasses and proposed a much simpler formula [5]:

$$T_g = A + B\ln\theta, \tag{2}$$

where: A, B — empirical constants, θ — heating rate in °C/min. A practical advantage of this expression, except for its simplicity, is that the fitted parameter A is equal to the glass transition temperature upon heating with θ = 1 °C/min. The B parameter is said to be related to the sample preparation method — it is supposed to reflect configurational changes of the atomic structure "frozen" during rapid quenching in the glass transformation temperature region [5]. Despite its simplicity and reasonable accordance with experiments, Lasocka's formula met modest recognition and her paper has been cited more than 240 times since its publication in 1976 (13 times in 2014, 12 in 2015, e.g. by [6–9]).

It is known that Lasocka's formula is applicable to determine the glass transition temperature in metallic glasses [10]. In this paper, we wanted to take a closer look at both Kissinger's and Lasocka's formulas and check: i) their applicability in case of various glasses containing transition metal oxides which are described by other structural models than metallic glasses; ii) how well T_g(θ = 1 °C/min) can be extrapolated from higher heating rate measurements.

Our group is mostly concerned with a phenomenon of thermal nanocrystallization in various oxide glasses containing transition metal oxides, such as V_2O_5 [11,12] and FeO [13]. In our previous papers, we showed that heating these glasses to temperature close to crystallization temperature led to a significant increase in their electrical conductivity: ca. 1000 times for $90V_2O_5 \cdot 10P_2O_5$ composition [14] and up to 10^9 times for Li_2O–FeO–V_2O_5–P_2O_5 system [15]. Therefore, it

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Table 1
Details on the composition and synthesis conditions of the samples.

Glass type	Sample ID	Nominal composition	Melting temperature/°C	Melting time/min
VP	P_4	$90V_2O_5 \cdot 10P_2O_5$	1100	60
	P_5	$90V_2O_5 \cdot 10P_2O_5$	1200	60
	P_6	$90V_2O_5 \cdot 10P_2O_5$	1280	60
LFVP	F_{08}	$27.2Li_2O \cdot 43.5FeO \cdot 2.1V_2O_5 \cdot 27.2P_2O_5$	1280	15
	F_{15}	$29.4Li_2O \cdot 36.8FeO \cdot 4.4V_2O_5 \cdot 29.4P_2O_5$	1280	15
	F_{20}	$31.25Li_2O \cdot 31.25FeO \cdot 6.25V_2O_5 \cdot 31.25P_2O_5$	1280	15
LMPF	N_1	$60LiF \cdot 20V_2O_5 \cdot 20P_2O_5$	1280	30
	N_5	$60LiF \cdot 10V_2O_5 \cdot 10Ti_2O_3 \cdot 20P_2O_5$	1280	30
	N_6	$57.1LiF \cdot 14.3V_2O_5 \cdot 9.5FeO \cdot 19.1P_2O_5$	1280	15

was essential to collect DTA traces for studied materials at low heating rates (e.g. 1 °C/min) in order to compare them with conductivity changes observed at temperature-dependent impedance measurements. In these experiments, each impedance spectrum was collected in isothermal conditions and the heating rate between two measurements was close to 1 °C/min. In that way, conductivity changes can be correlated with temperatures of glass transition and crystallization determined at low heating rates. However, we usually perform DTA scans for several heating rates, starting from 1 °C/min up to 25 °C/min. Therefore, it is a good idea to analyze the collected data with reference to applicability of Kissinger's and Lasocka's formulas.

2. Materials and methods

Glasses of several systems/compositions were investigated: a) $90V_2O_5 \cdot 10P_2O_5$ (VP); b) Li_2O–FeO–V_2O_5–P_2O_5 (LFVP); c) LiF–V_2O_5–M_xO_y–P_2O_5 (LMPF), where M = V, Fe, Ti. Details on procedures and compositions are presented in Table 1. In each case, the samples were melted in alumina crucibles. The molten mixtures were rapidly poured onto a stainless-steel plate held at the room temperature and immediately pressed with another identical plate.

2.1. VP glasses

Amorphous samples of VP were prepared from predried V_2O_5 (Aldrich, 99.5%) and $(NH_4)H_2PO_4$ (POCh — Polish Chemicals, 99.5%) [11], which were ground and mixed in an agate mortar and divided into several batches, labeled P_4, P_5, P_6. The numeration of batches and preparation procedure is the same as in [14]. Samples P_4, P_5 and P_6 were melted at 1100 °C, 1200 °C and 1280 °C, respectively.

2.2. LFVP glasses

Amorphous samples of LFVP compositions were prepared from predried Li_2CO_3 (Aldrich, 99.9%), $FeC_2O_4 \cdot 2H_2O$ (Aldrich, 99.9%), V_2O_5 (Aldrich, 99.5%) and $(NH_4)H_2PO_4$ (POCh, 99.5%). The synthesis process is described elsewhere [13]. The samples were labeled F_x, where x is a molar vanadium content in the nominal composition $LiFe_{1-5/2x}V_xPO_4$.

2.3. LMPF glasses

LMPF batches were prepared from predried LiF (Aldrich, 99.995%), $(NH_4)H_2PO_4$ (POCh, 99.5%) and V_2O_5 (Aldrich, 99.5%), $FeC_2O_4 \cdot 2H_2O$ (Aldrich, 99.9%) or Ti_2O_3 (Aldrich, 99.9%). In the first step, the stoichiometric mixture of V_2O_5, $FeC_2O_4 \cdot 2H_2O$ or Ti_2O_3 with $(NH_4)H_2PO_4$ was slowly (3 °C/min) heated to 200 °C in air and kept at this temperature for 2 h. In the second step, LiF was added to the batch (with 10% mol excess, due to its evaporation in high temperatures) and the crucible was placed in a furnace preheated to 1280 °C. The batch was melted for 15–30 min in air. The double crucible technique [16] was used to

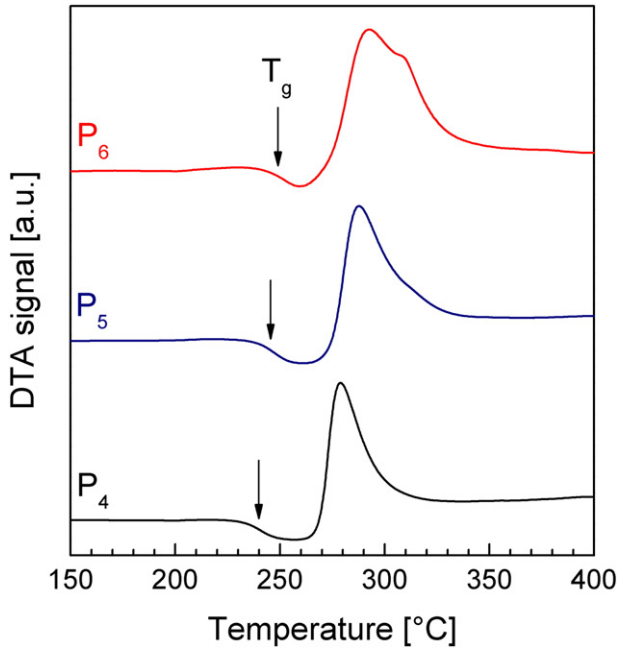

Fig. 1. DTA traces of VP glasses (θ = 10 °C/min).

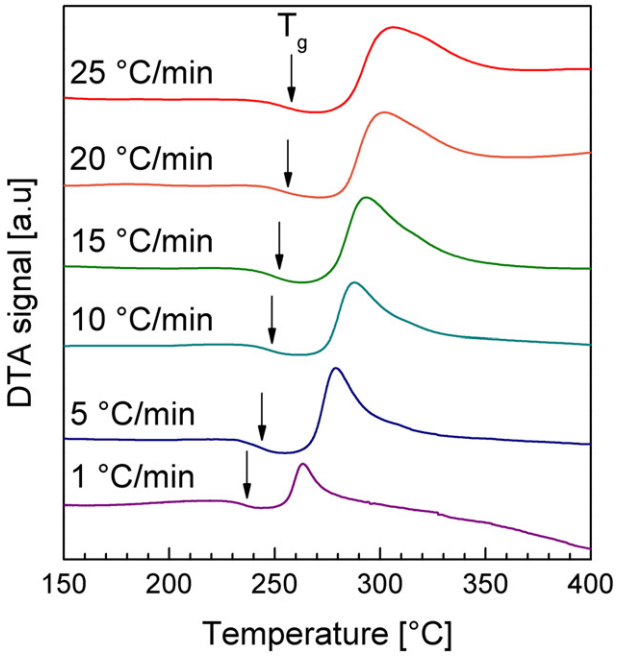

Fig. 2. DTA traces of sample P_5 taken at different heating rates (θ = 1, 5, 10, 15, 20, 25 °C/min).