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Opponent's assessment of the dissertation by **Ing. Diego Alejandro Valdés Mitchell**

“Kinetics of processes in the volume and the surface of amorphous materials“

Doctoral thesis - the dissertation contains 72 pages of text and 6 pages with 162 citations and a subset of 6th published articles, which has another references for individual publications. The dissertation is written in English and is compiled clearly and shows a very good overview of the dissertation on the study of glass-crystalline materials of chalcogenides, i.e. a field that has acquired in recent (and not least) years of data in both theoretical and experimental and dissertation is part of the long-term excellent contribution of the University of Pardubice in this internationally recognized field.

The dissertation is properly arranged and reads well. However, the introductory part of glass thermal properties could have been more comprehensive, as it reflects a number of questions (and even some yet unanswered) relevant to the issue of glassy state (glassformation stability vs. glassformation ability). In the dissertation I miss a targeted discussion, where some questions of possible applicability of the above considerations could be discussed, including experimentality of obtained data of chalcogenide materials. I would also appreciate if the dissertant defined his personal opinion on process optimization, including estimates of future prospects.

Studies in the field of thermoanalytical kinetics have a long tradition dating back to the 1960s [1,2]. As with any research approach, there were applied some simplifications legitimate from the outset that have stayed preferred over the years. Determining the reaction temperature of the sample based on the resilience subtraction of the controlled reference temperature can be considered as a basic simplification. Another is the fundamental assumption that heat propagates and dissipates immediately, which in the end led to the establishment of the thermoanalytical school, in which the degree of conversion is deducted by simply portioning the peak area in relation to the temperature read on the inert reference. Having no objection against such a widely used kinetic (mainstream) approach in which the dissertation work is presented it, however, would be good if the dissertant is aware about such introduced simplifications being capable mention them in his dissertation.

Comments:

Eq.1., so called Hruby glassforming coefficient, is just one of many descriptions in the practical use. It would be recommendable to extent this introduction to a more detail using both glassforming stability and glassforming ability, see e.g. [3,4].

In Fig.5. it would need to introduce identification of individual (colored) atoms for a better distinction, similarly in next Fig. 7.

Eq. 19 is valid for power-compensating DSC not for heat-flux DSC (\approx calibrated DTA), see e.g. [1,5-7].

Used *SensysEva* DSC apparatus is according to the Seteram internet promotion just a calibrated type of DTA (i.e. heat-flux DSC) and not a true power-compensating DSC. Therefore it is necessary to use the balance of heat fluxes including the effect of heat inertia, see e.g. early reference [5]. Not to properly indicate the instrument of application is an essential oversight.

Crystal grow models are OK even if they can be alternatively seen more branched as in [2]; particularly worth of attention could be the effect of dimensionality while considered interface and/or diffusion controlled, see Table 13.4, page 265 in [8].

Eq.33. brings with it the quandary of so-called kinetic compensation effect (KCE) of the mutual interaction of E_g and u_0 see e.g. [1,2]. It also brings question what is a proper meaning of the term 'activation energy' to be enough functional in solid state [9,10].

Viscosity matter should also be cited via [11-13] and VTA model has more alternatives [12].

In Fig. 26. discriminate, please, between deconvolution as applied by yours and a potential refining due to the effect of heat inertia as functional otherwise [6,7].

Added literature:

1. P. D. Garn. Thermal Analysis of Investigation, Academic. New York 1965.
2. Koga, J. Šesták, P. Šimon, Some fundamental and historical aspects of phenomenological kinetics in solid-state studied by thermal analysis, in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and NonCrystalline Materials), Springer, Berlin, 2013, pp. 1–45 (Chapter 1).
3. Kozmidis-Petrovic AF Sensitivity of the Hrubý, Lu–Liu, Fan, Yuan, and Long glass stability parameters to the change of the ratios of characteristic temperatures T_x/T_g and T_m/T_g . *Thermochim Acta* (2010) 510: 137-143.
4. A. Kosmidich-Petrovič, J. Šesták, Forty years of Turnbull reduced glass transition temperature and Hrubý glass-forming coefficient in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and Non-crystalline Materials, Springer, Berlin, 2013, pp. 75–99 (Chapter 4)
5. M. J. Vold. Differential Thermal Analysis. *Anal. Chem.* **21** (1949) 683-8.
6. P. Holba, J. Šesták, D. Sedmidubský, Heat transfer and phase transition in DTA experiments in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and Non-crystalline Materials, Springer, Berlin, 2013, pp. 99–135 (Chapter 5).
7. J. Šesták, P. Holba. Heat inertia and temperature gradients in the treatment of DTA peaks. *J Thermal Anal Calorim.* 2013; 113:1633– 1643.
8. E. Illeková, J. Šesták, Crystallization of metallic micro-, nano- and noncrystalline alloys, in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and Non-crystalline Materials, Springer, Berlin, 2013, pp. 257–290 (Chapter 13).
9. A.K. Galwey. What theoretical and/or chemical significance is to be attached to the magnitude of an activation energy determined for solid-state reactions? *J Therm Anal Calorim* (2006) 86 (267-286)
10. Šimon P, Dubaj T, Cibulková Z. Equivalence of the Arrhenius and non-Arrhenian temperature functions in the temperature range of measurements. *J Therm Anal Calorim*, 2015; 120: 231-238;
11. J. Málek, J. Šánělová, Crystallization kinetics in amorphous materials studied by means of calorimetry, microscopy and dilatometry, in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and Non-crystalline Materials, Springer, Berlin, 2013, pp. 291–324 (Chapter 14).
12. M. Ikeda, M. Aniya: Bond Strength—Coordination Number Fluctuation Model of Viscosity: An Alternative Model for the Vogel-Fulcher-Tammann Equation and an Application to Bulk Metallic Glass Forming Liquids. *Materials* **3** (2010) 5246-5262.
13. J. Málek, R. Svoboda, Structural relaxation and viscosity behavior in supercooled liquids and the glass transition in: J. Šesták, P. Šimon (Eds.), Thermal Analysis of Micro-, Nano- and Non-crystalline Materials, Springer, Berlin, 2013, pp. 147 –175 (Chapter 7).

Overall, I am very satisfied with the work, particularly its published part in the respected journal of non-crystalline solids presented as key part the dissertation.

I evaluate both its processing and content very well and I rank it among the above-average dissertations submitted in related fields of physical chemistry and targeted materials research within the domain of physics, chemistry and technology of condensed systems.

The dissertation meets the requirements for dissertations of both the Ministry of Education and the University of Pardubice and therefore

I recommend

thesis for defense and dissertation for granting PhD.

Sincerely

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