


Original Research

Reproducibility of some solid-state phase transition temperatures as obtained from DTA/DSC

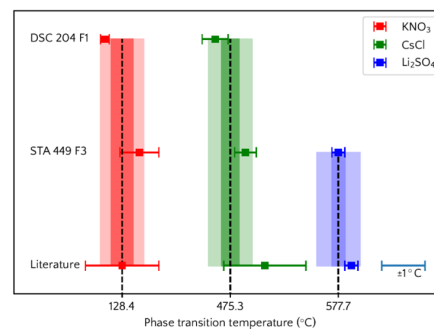
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Received: March 13, 2023
Accepted: May 9, 2023
Published: May 18, 2023:



Abstract: The reproducibility of some solid-state phase transition temperatures, as determined by differential scanning calorimetry, is assessed by a literature search and analysis of results obtained in the limit of zero heating rate for KNO₃, CsCl, and anhydrous Li₂SO₄, using different instruments. The study is complemented by an overview of previously published results for the phase transition temperatures of several inorganic materials commonly used for temperature calibration of thermal analysis instruments. Reproducibility among the onset temperature of solid-state phase transitions of inorganic salts, as determined by differential scanning calorimetry, can be conservatively estimated to be within ± 1 °C under favorable circumstances and around ± 2 °C in general.

Keywords: Differential scanning calorimetry, temperature calibration, phase transition.

Introduction

The solid-state phase transition temperatures of several inorganic compounds, while not fixed points in the International Temperature Scale of 1990 (ITS-90), are commonly used for temperature calibration of heat-flux differential scanning calorimeters (DSC) and differential thermal analysis (DTA) instruments, particularly when platinum crucible pans are employed [1-3]. Indeed, platinum crucible pans are helpful in DSC experiments, not only above 600 °C (when Al pans become unsuitable) but also due to chemical inertness and easiness of cleaning [1,4]. However, platinum is prone to make alloys with molten metals [1,5], which makes most of the fixed points defined by ITS-90 of little use for temperature calibration of DSC equipment operating with Pt pans. If not a fixed point of ITS-90, reference materials for DSC temperature calibration should at least have a phase transition temperature unequivocally defined from the viewpoint of thermodynamics and should not react with the crucible material or purge gas [1,5-9]. These conditions are fulfilled by some inorganic compounds exhibiting solid-state phase transitions within the temperature range usually probed by DSC experiments. However, the extent by which these inorganic compounds can be used as reference materials for DSC temperature calibration (apart from considerations regarding, for instance, chemical purity) is limited by the accuracy of the corresponding phase transition temperatures.

Hereafter, by reproducibility it is understood precision under reproducibility conditions, i.e., “observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in different test or measurement facilities with different operators using different equipment” [10]. In comparing our results to those of the literature, which were obtained using different samples of inorganic salts, the dispersion of the results is expected to be greater than that obtained, for instance, by using standard reference materials. In any way, comparing results from different sources gives a more robust estimation of the expected uncertainty for solid-state phase transition temperatures as obtained under typical laboratory conditions.

This work critically assesses the reproducibility of solid-state phase transition temperatures for some inorganic compounds commonly used for temperature calibration of heat-flux differential scanning calorimeters and differential thermal analysis instruments. With this aim, the onset temperatures for the solid-solid phase transitions of KNO₃, CsCl, and Li₂SO₄ were obtained systematically and following rigorously the same procedure by extrapolating the onset temperature of phase transition to zero heating rate and using two different thermal analysis instruments calibrated against a set of ITS-90 reference temperatures. Furthermore, the dispersion of the results obtained from samples of the same batch of these three inorganic salts using two different instruments and the compilation of the same results as reported in the literature allows for inferring the reproducibility of the estimated phase transition temperatures under typical operating conditions.

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Experimental Section

Materials

The metals used in this work for temperature calibration, silver (Ag), gold (Au), bismuth (Bi), indium (In), and aluminum (Al), were all supplied by Netzsch-Gerätebau GmbH. Reference melting temperatures were obtained from Della Gatta et al. [2]. The inorganic salts consisted of potassium nitrate (KNO₃, Química Moderna, 99% purity), cesium chloride (CsCl, Merck, 99.5+% purity), and monohydrated lithium sulfate (Li₂SO₄·H₂O, Merck, 99% purity). The sample of Li₂SO₄·H₂O was previously dehydrated by heating to 200 °C immediately before use.

Methods

Differential scanning calorimetry analyses were carried out in a simultaneous thermal analyzer STA 449 F3 Jupiter (Netzsch, Germany). Samples were heated in Pt and Al₂O₃ crucibles (the latter for calibration purposes), at different heating rates (10, 5, 3, 2, and 1 °C/min), under a flow of 40 mL/min purge gas (N₂, Air Products, 99.999% purity). The temperature readout of the STA 449 F3 was calibrated against the melting temperature of indium, bismuth, aluminum, silver, and gold, for heating rates of 10, 5, 3, 2, and 1 °C/min, using alumina crucibles with lids. Oxygen partial pressure in the nitrogen purge gas was reduced by using an oxygen trapping system (OTS, Netzsch). The extrapolated onset temperature for zero heating rate, which is not dependent on crucible material, was obtained from a linear fitting of the onset temperatures for melting of these metals at different heating rates.

In fact, the extrapolation to zero heating rate allow using the temperature calibration curve obtained for the same instrument using high-purity metals (fixed points in the ITS-90) and Al₂O₃ crucibles to correct the temperature (also extrapolated to zero heating rate) obtained from experiments with the inorganic salts and Pt crucibles, which are incompatible with metals, particularly at high temperatures.

For comparison, complimentary DSC measurements for KNO₃ and CsCl were performed in a Netzsch 204 F1 Phoenix heat-flux scanning calorimeter. This instrument was calibrated against the melting temperature of indium, bismuth, and aluminum using alumina crucibles with lids. All onset temperatures were extrapolated to zero heating rate, as before. Data analysis was implemented in Python using Jupyter Notebooks. Uncertainty estimation was performed using the UNCERTAINTIES package [11].

Results and Discussion

Some inorganic substances recommended for temperature calibration of DSC instruments with platinum crucibles are listed in Table 1, reproduced from Ref. [12]. For the materials in Table 1 referred to in more than one reference, the average transition temperatures have uncertainties over a range of ±1.5 °C up to ±2.3 °C. Furthermore, results reported in the literature for the same inorganic substance vary over ±1 °C up to ±7 °C (for SrCO₃). Accordingly, judging by the phase transition temperatures reported in the literature and summarized in Table 1, typical reproducibility in phase transition temperatures of inorganic substances used for DSC temperature calibration lies at best in the ±2 °C range. In fact, experienced operators may well achieve reproducibility in temperature measurement of ±0.1 °C

using DSC instruments under favorable conditions. However, we are not evaluating the reproducibility of temperature measurement of DSC instruments. Here we are reporting on the variability of solid-state phase transition temperatures for a set of inorganic salts, reported in the literature and obtained using different instruments. The dispersion of these results has contributions from sample purity and particle size, instrument calibration, and, naturally, operator skills.

Table 1. Materials (and their solid-solid phase transition temperatures) compatible with platinum crucibles and customarily used for temperature calibration of differential scanning calorimeters. Uncertainties are given as stated in the original references (in brackets). Average's uncertainties (quoted in bold) correspond to an estimated 1σ interval. Reproduced in part from Ref. [12].

Substance	Phase transition temperature/ °C
KNO ₃	128±5 [13, 14]
	128.1 [15]
	129.22±0.02 [16]
Average	128.4±1.7
KClO ₄	299±6 [13, 14]
	299.7 [15]
	300.41±0.06 [16]
	300.8±0.3 [17]
Average	300.0±1.5
Ag ₂ SO ₄ ^a	424±7 [13, 14]
	426.20±0.11 [16]
	426.9 [15]
Average	425.5±2.3
CsCl	476.9±1.9 [18]
SiO ₂ ^b	571±7 [16]
	571±5 [13, 14]
	573.3±0.4 [17]
	573.9 [15]
Average	572.3±2.2
Li ₂ SO ₄	578.28±0.25 [8, 5]
K ₂ SO ₄	582±5 [16]
	582±7 [13, 14]
	583.7±0.4 [18]
	583.9 [15]
	585.3±0.1 [17]
Average	583.4±1.7
K ₂ CrO ₄	665±7 [13, 14, 16]
	665.9 [15]
	669.0±0.1 [17]
	669.1±0.2 [19]
	669.9±3.0 [18]
Average	667.8±1.5
BaCO ₃ ^c	805.9 [15]
	807.4±0.4 [17]
	808±8 [13, 14]
	808.8±1.4 [20]
Average	807.5±2.0
SrCO ₃ ^{e,d}	923.9 [15]
	928±7 [13, 14]
	931.4±0.8 [20]
Average	927.8±2.3

^a Not stable [14].

^b Complex transition [14, 21].

^c Results from the first and second heating runs differ due to marked sintering of the sample [20, 14].

^d Decomposes under an inert atmosphere [20, 14].

From the materials listed in Table 1, some exhibit complex phase transition, decompose under an inert atmosphere, or exhibit onset temperature varying from first to second heating run (see table footnotes).

Of those materials in Table 1 which are free from these complications, by way of illustration, KNO_3 , CsCl , and Li_2SO_4

were selected for a preliminary analysis, owing to estimate the reproducibility of phase transition temperature under more controlled conditions. In particular, data for Li_2SO_4 is scarce in the literature, and this compound was included in this work aiming to provide further checking on the available data. In fact, anhydrous Li_2SO_4 has a solid-state phase transition near

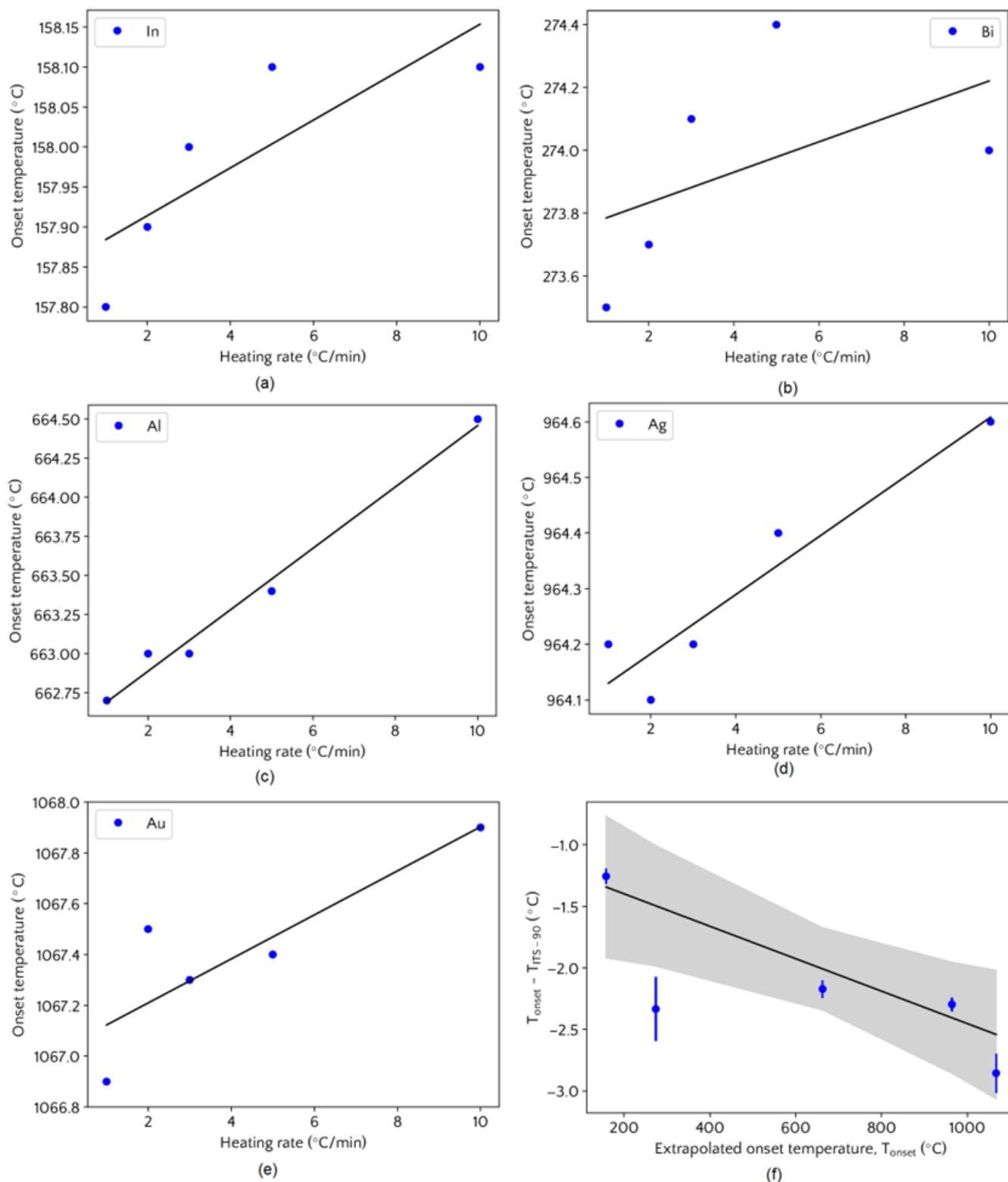


Figure 1. Dependence of peak onset temperature on heating rate, as obtained with the STA 449 F3, for the melting of (a) In, (b) Bi, (c) Al, (d) Ag, and (e) Au. (f) Temperature calibration curve calculated from the onset melting temperature of high-purity metals extrapolated to zero heating rate. T_{exp} (experimental) and T_{nom} (nominal) represent the experimentally determined extrapolated melting onset temperature and the nominal solidification temperature according to ITS-90, respectively. The gray band represents the 2σ prediction interval.

the upper-temperature limit for Al crucible pans, which makes this inorganic salt an interesting choice for DSC temperature calibration.

Temperature calibration of the two instruments used in this work was performed based on the extrapolated onset temperature for zero heating rate, which is independent of the choice of crucible material, and was obtained from a linear fitting to the onset temperatures for the melting of high-purity metals at different heating rates. These curves, along with the STA 449 F3 temperature calibration curve for zero heating rate, are represented in Fig. 1. Some of the metals used for temperature calibration (for instance, In and Bi) deviate somewhat from linear behavior and contribute to increasing the width of the prediction band around the calibration curve. As expected, temperature fluctuations are way less in Netzsch 204 F1 Phoenix heat-flux scanning calorimeter results (see below).

Following the same experimental procedure, this time using Pt crucibles, the onset temperature for the solid-state phase transitions of KNO_3 , CsCl , and anhydrous Li_2SO_4 was determined from the corresponding endothermic peak in the DSC signal obtained for different heating rates. This set of results was thus used to obtain the onset temperature of transition extrapolated to zero heating rate, as represented in Fig. 2. The corresponding phase transition temperatures for KNO_3 , CsCl , and Li_2SO_4 are given in Table 2.

Table 2. Literature's average values for solid-solid phase transition temperatures of KNO_3 , CsCl , and Li_2SO_4 (see Table 1 for details) and results obtained in this work in the limit of zero heating rate. STA and DSC refer to results obtained from measurements with Netzsch STA 449 F3 and DSC 204 F1, respectively. Uncertainties in this work's results refer to the 2σ interval (see text for a critical appraisal of this uncertainty, which is possibly under-estimated).

Substance	Phase transition temperature/ $^{\circ}\text{C}$
KNO_3	
Literature	128.4 ± 1.7
This work (STA)	129.2 ± 0.9 (2σ)
This work (DSC)	127.6 ± 0.2 (2σ)
This work's average	128.4 ± 0.5
CsCl	
Literature	476.9 ± 1.9
This work (STA)	476.0 ± 0.5 (2σ)
This work (DSC)	474.6 ± 0.6 (2σ)
This work's average	475.3 ± 0.4
Li_2SO_4	
Literature	578.28 ± 0.25
This work (STA)	577.7 ± 0.3 (2σ)

The same procedure was repeated using a Netzsch 204 F1 DSC to assess the reproducibility of the phase transition temperatures for KNO_3 and CsCl . Data used for temperature calibration, as the calibration curve itself, and the onset temperatures for the solid-state phase transitions in KNO_3 and CsCl for different heating rates are represented in Fig. 3. The corresponding phase transition temperatures are summarized in Table 2.

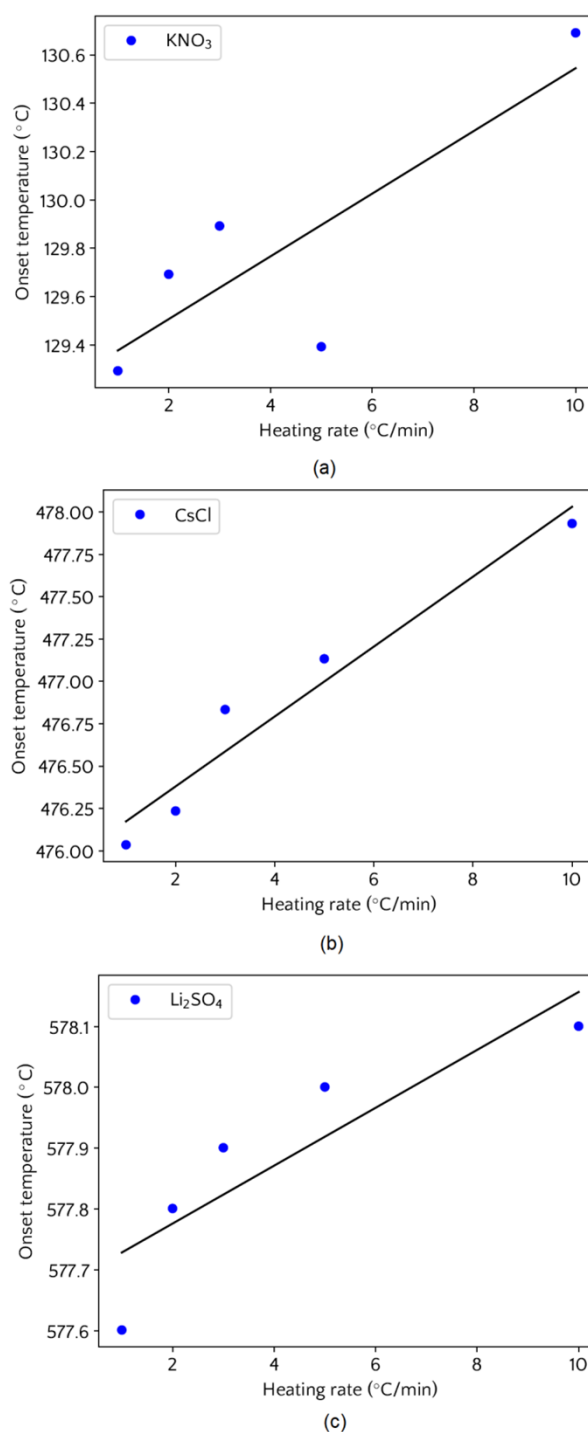


Figure 2. Dependence of peak onset temperature on heating rate, as obtained with the STA 449 F3, for the solid-state phase transitions of (a) KNO_3 , (b) CsCl , and (c) anhydrous Li_2SO_4 .

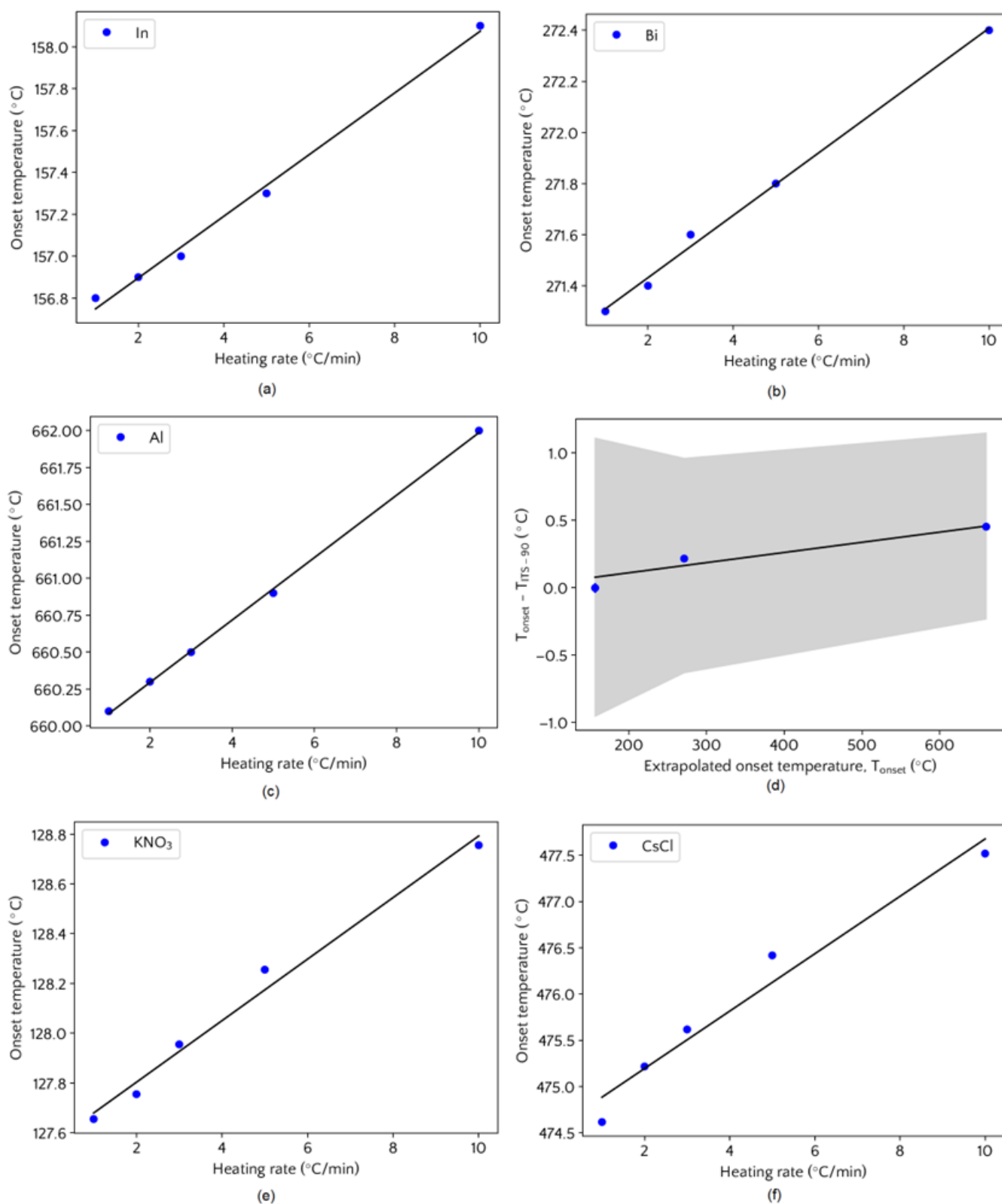


Figure 3. Dependence of peak onset temperature on heating rate, as obtained with the DSC Netzsch 204 F1, for the melting of (a) In, (b) Bi, and (c) Al. (d) Temperature calibration curve calculated from the onset melting temperature of high-purity metals extrapolated to zero heating rate. T_{exp} (experimental) and T_{nom} (nominal) represent the experimentally determined extrapolated melting onset temperature and the nominal solidification temperature according to ITS-90, respectively. The gray band represents the 2σ prediction interval. Dependence of peak onset temperature on heating rate for the solid-state phase transitions of (e) KNO₃, and (f) CsCl.

A comparison between average phase transition temperatures from literature and onset temperature extrapolated to the limit of zero heating rate for the solid-solid phase transitions in KNO₃,

CsCl, and Li₂SO₄ as obtained from measurements carried out using STA 449 F3 and DSC 204 F1 is presented in Fig. 4.

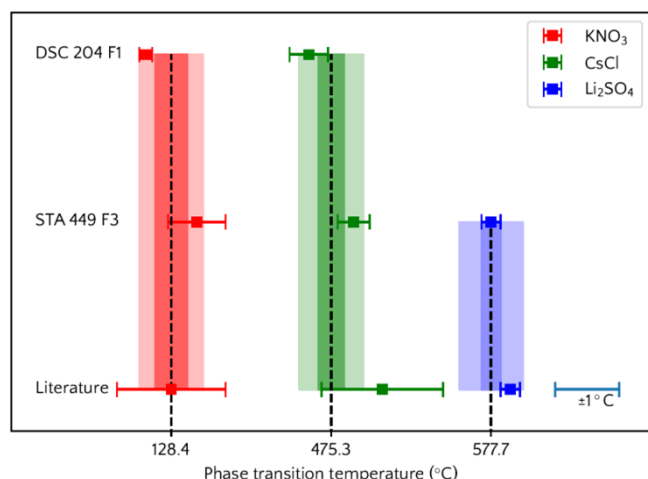


Figure 4. Comparison between average phase transition temperatures from literature and onset temperature extrapolated to the limit of zero heating rate for the solid-solid phase transitions in KNO_3 , CsCl , and Li_2SO_4 , as obtained from measurements carried out using STA 449 F3 and DSC 204 F1. The error bars in the literature's data and this work's results correspond to the 1σ and 2σ intervals, respectively. Light color bands represent a $\pm 1^\circ\text{C}$ interval around this work's average. Dark color bands represent the respective uncertainty around this work's average as given in Table 2.

Except for KNO_3 , whose phase transition temperature average value as determined in this work coincides with the literature average, the absolute difference for CsCl and Li_2SO_4 amounts to 1.6°C and 0.58°C , respectively. The discrepancies in phase transition temperature are well within the 1σ interval around the literature's average value, $\pm 1.7^\circ\text{C}$ and $\pm 1.9^\circ\text{C}$ for KNO_3 and CsCl , respectively. How much of this interval is due to differences in sample-related particularities, including, for instance, sample purity, can be estimated by comparing the onset temperatures of phase transition for KNO_3 and CsCl as obtained in this work using samples from the same batch but different instruments.

Although estimated uncertainties in onset temperatures obtained in this work are always less than 1°C (at a 95% confidence level), there are differences of 1.6°C and 1.4°C for the phase transition temperatures of KNO_3 and CsCl , respectively, as determined with the STA 449 F3 and DSC 204 F1. These results are within $\pm 1^\circ\text{C}$ of their average, as represented by light color bands in Figure 4. In fact, the difference between the STA 449 F3 and DSC 204 F1 is well accounted for by the uncertainty quoted in Table 2 for the average between these two experimental results (except for the DSC 204 F1 result for KNO_3 , which is slightly off). Differences observed for samples of the same batch are of the same order as that observed between this work's results and the literature's average. Accordingly, most of the result's variability seems to be due to inherent limitations of the technique in determining the phase transition temperature of inorganic salts, which is possibly influenced by the sample's thermal contact with the crucible pan, the sample's thermophysical properties, and particle size, whose effect on the onset temperature of phase transition seems to be more severe than when dealing with the fusion of metallic samples, the preferred method for DSC temperature calibration.

Reproducibility among the onset temperature of solid-state phase transitions of inorganic salts obtained with different

instruments seems limited to within $\pm 1^\circ\text{C}$ under the best circumstances and often to $\pm 2^\circ\text{C}$ and over more generally.

Skillful experimenters may well obtain more reproducible results (remembering that we are not referring here to the precision with which temperature can be measured by thermal analysis instruments). Furthermore, even considering the estimated uncertainties could probably be reduced by repeating measurements (for instance, by replicating the measurements reported in Fig. 1 used for temperature calibration) and using averages, the reproducibility of phase transition temperatures for inorganic salts as determined by DTA/DSC can hardly be expected to attain the same level as for high-purity metals used as ITS-90 fixed points (around $\pm 0.1^\circ\text{C}$).

Conclusion

A systematic evaluation of the onset temperature for solid-state phase transitions in KNO_3 , CsCl , and Li_2SO_4 allows estimating a conservative lower limit for the reproducibility of onset temperature (as determined by DTA/DSC) within $\pm 1^\circ\text{C}$. In fact, a literature survey reveals that phase transition temperatures as determined by thermal analysis typically vary over much larger intervals. This contrasts with much better reproducibility for the melting temperatures of metals and points to the need for inorganic salts reference materials with solid-state phase transition temperatures traceable to ITS-90, for temperature calibration of DTA/DSC instruments using Pt crucibles, particularly in the high-temperature regime.

Acknowledgments

The support from the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) - grants 305253/2018-2 (CAP), and 305528/2018-1 (JEZ), and Programa de Apoio a Núcleos de Excelência (PRONEX), Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), is gratefully acknowledged. Thanks are also due to D. Golle (Netzsch Gerätebau) for helping us with the many thermal analysis experiments.

Author Contribution

C. A. P. was responsible for the overall concept and design of the study, C. A. P. and J. E. Z. contributed to data survey and analysis, C. A. P. and J. E. Z. wrote the manuscript. All authors have approved the final version of the manuscript.

Conflicts of Interest

The authors have declare no conflicts of interest.

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