Precision measurements of the specific heat capacity with the temperature modulated DSC (TMDSC) at lower temperatures

The specific heat capacity $c_p$ is one of the most important quantities used to characterize the thermodynamic properties of materials in the condensed phase. This is especially true for the static and dynamic changes in properties in structural phase transitions and glass transitions. Prominent examples of such transition phenomena that are in the forefront of current research activities are ferroelectric and ferromagnetic phase transitions, transitions in liquid crystals and superconductors, glass transitions in structural and classical (canonical) glasses etc. The transition temperatures of interest lie typically between a few degrees Kelvin and many hundreds of degrees Kelvin. The $c_p$ investigations in the region of phase changes can be roughly divided into two classes: costly and time-consuming precision measurements using adiabatic or ‘alternating current’ (AC) calorimetry, and survey measurements using conventional DSC. The application possibilities of commercial DSC instruments for the investigation of phase transition phenomena are limited mainly by their thermostat systems. This is true for the temperature range, the measurement accuracy and the time during which uninterrupted measurements are possible (time domain [1]).

Fig. 1: Adiabatic calorimetry (b) and time domain TMDSC (a) of PDP. For further explanations see text.

The purpose of this work is to show that ‘temperature modulated’ DSC (TMDSC) provides an excellent alternative to the above mentioned precision methods. The measuring principle of TMDSC allows investigations at quasi constant temperature (temperature modulation at a heating rate of zero), i.e. quasi isothermally in the time domain [1] and with small measurement signals; on top of this it allows studies of latent heat or of entropy production. TMDSC has therefore, at least in principle, all the characteristics of a precision measurement method.

Most of the investigations described here were performed with a modified Mettler-Toledo DSC821® calorimeter with ADSC option and a new FRS5 ceramic sensor. The modifications (done in our institute) concern only the cooling system of the instrument. A pre-chamber vaporizer cryostat was developed that could be operated with both liquid nitrogen and liquid helium. The furnace with its heating system and the DSC sensor were retained and integrated in the new cooling system. The new heat exchanger allows the furnace to be cooled down to less than 30 K. At the same time, the temperature of the surroundings of the furnace can be kept constant to within several hundredths of a degree.

Nevertheless, even at 80 K, cooling rates of 10 K/min are still possible. Two substances, potassium dihydrogen phosphate (PDP) and strontium titanate (SrTiO$_3$), were chosen as models to test the quality of the new measurement system in a temperature range that is not normally
accessible to purely commercial DSC instruments. PDP shows a weak first order ferroelectric phase transition at $T_c = 122.7$ K. Precision $c_p(T)$ investigations performed using adiabatic calorimetry in the region of the transition temperature are reported in the literature for PDP [2]. Figure 1 shows a comparison of the literature data with our own data which was recorded with the time domain TMDSC. Curve (a) was measured with the following parameters: heating rate ($r$) = 0, amplitude ($a$) = 0.02 K, period ($p$) = 30 s. It is known from the literature that even at normal pressures $T_c$ lies very close to the tricritical point [3]. At the tricritical point the first order phase change changes into a second order phase change.

The marked rise of $c_p(T)$ in the low temperature phase approaching $T_c$ indicates the closeness to the tricritical point. The sharpness and height of the $c_p$ anomaly shown in figure 1 demonstrates both the high quality of the crystal and also the excellent quality of the measurement technique.

Figure 2 demonstrates the ‘mean field’ behavior of the phase transition observed as well as the closeness of $T_c$ to the tricritical point. In this figure, the square of the ratio of the temperature to the critical part of the specific heat capacity is shown as a function of temperature [1,4]: 
\[
\left(\frac{T}{T_c}\right)^2 \propto \frac{T}{T_o}.
\]
It turns out that $T_c$ and $T_o$ are the same ($T_c \approx T_o = 122.6$ K) within the limits of temperature accuracy. It follows that the ferroelectric phase transition of our PDP sample occurs in the immediate vicinity of the tricritical point.

The evaluation of a $c_p(T)$ curve in the region of a phase transition is made more difficult in that both the crystal quality and also a poorly chosen measurement scenario can have a similar effect on the measurement results. Figure 3 shows the comparison of two time domain TMDSC measurements of the same quality on a quasi defect free PDP sample (curve a) and on a PDP sample with enriched surface defects brought about by mechanical polishing (curve b). It is evident
that the enrichment of defects leads to a significant ‘smearing’ of the phase transition. On the other hand one recognizes the power of the TMDSC method for the detection of such defects.

In the case of phase transitions that demonstrate only weak $c_p$ anomalies, a slightly increased concentration of defects caused by polishing can make the detection and the evaluation of a phase transition appreciably more difficult. Figure 4 shows two TMDSC investigations in the region of the phase transition of SrTiO$_3$ at $T_c = 105$ K. Curve (b) was performed on a mechanically polished sample. At best, only indications of a phase transition in the region of $T_c$ can be made out. Curve (a) was measured on the same sample after removing the lattice defects by etching strongly. The well known weak second order phase transition can now be clearly identified.

The importance of the choice of a suitable scenario for the measurement of the behavior of the specific heat capacity at the phase transition and therefore for the phase transformation behavior is demonstrated again in figure 5 for the defect-rich PDP sample. As expected, both the position and the shape of the $c_p(T)$ curve depend on the heating rate, the modulation frequency and the amplitude of modulation. By all appearances, the time domain TMDSC technique supplies the most reliable $c_p$ data. It can be concluded from these results that the TMDSC technique is very suitable, even at medium-low temperatures, for the investigation of phase transitions in the condensed phase, as long as the cooling of the measurement system is sufficiently stable. At the same time, it is clear that the time domain method is to be preferred to measurements with rates not equal to zero.

**Literature:**


**Publishing Note:**

This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 7. See www.mt.com/ta-usercoms