

Short Communication

**USE OF A SUMMATION TECHNIQUE FOR EVALUATION
OF THE PHASE TRANSITION IN LEAD GERMANATE,
 $\text{Pb}_5\text{Ge}_3\text{O}_{11}$**

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A computer technique is outlined to increase the signal: noise ratio of DSC results for transformations involving small changes of energy. The method is applied to determine the transformation temperature of the ferroelectric-paraelectric transformation of lead germanate, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, either pure or doped with Nd^{3+} or with $\text{Nd}^{3+} + \text{K}^+$.

Compared with classical calorimetric techniques, e.g. adiabatic calorimetry, in DSC the amount of sample material and the duration of the experiment are greatly reduced. These advantages are offset by a loss in resolution and in the accuracy of the results. These drawbacks become increasingly evident in the study of transformations with a wide transition interval and/or a small transition energy. Here we describe a technique to improve the results of DSC by computer evaluation of a series of measurements.

The method is exemplified on lead germanate, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, a ferroelectric crystal with a transition temperature $T_C = 451$ K [1]. This material can be used as a laser host to be doped with neodymium. The transformation temperature not too far from room temperature allows study of the interactions of stimulated emission with the ferroelectric transformation. Therefore, one needs to know exactly the T_C of pure and doped crystals. The transformation at T_C is of second thermodynamic order and its thermal effect is hardly discernible.

Experimental

Single-crystals were grown by the Czochralski technique from melts of compositions $\text{Pb}_{5(1-3x/2)}\text{Nd}_{5x}\text{Ge}_3\text{O}_{11}$ ($x = 0$ and 0.005) and $\text{Pb}_{5-2x}\text{Nd}_x\text{K}_x\text{Ge}_3\text{O}_{11}$ ($x = 0.025$), as described previously [2, 3]. For the Nd-doped material we found a distribution coefficient during growth of $k = 0.6$, i.e. the crystal had a composition with $x = 0.003$. Spectroscopic results suggest that Nd^{3+} ions occupy different lattice positions, presumably of Pb^{2+} ions by substitution [2].

Differential scanning calorimetry was carried out on ~ 100 mg powdered samples in a DuPont 910 DSC cell in air atmosphere. Non-hermetically crimped aluminium pans were used, with an empty pan as reference. The experiments, at a heating rate of 10 deg/min^{-1} , were performed from 403 to 523 K. ΔT was measured with chromel-constantan thermocouples and then calculated to Δq . The temperature scale was calibrated using ICTA standards.

To improve the evaluation of DSC data, we made use of a summation technique described previously in connection with the low-temperature DTA of mercury(I) halides [4]. The differential scanning calorimeter was connected to an HP 9825 table calculator. In the DuPont instrument there is no other external output except the built-in $X+Y+Y'$ coordinate recorder, so the compensational voltages corresponding to the positions of both pens are brought out. These analog signals were digitized via the interface equipment developed in the Development Workshop of the Czechoslovak Academy of Sciences and then fed to the computer. A pair of values corresponding to the X and Y coordinates of the position of the pen were treated in the computer so that the first datum represented the sample temperature and the second one the heat difference Δq . A set of data was taken every 3 s and then recorded on magnetic tape. A program was carried out which enabled us to sum up curves of several DSC measurements and in this way to eliminate noise and incidental effects.

Results and discussion

From the DSC curves recorded directly with the DuPont thermal analyzer, the determination and evaluation of the effect is hardly possible: the effects are small and merge into the background. The improvement achieved through the summation of repeated measurements is evident from a comparison of Figs 1 and 2. It is now possible to determine Curie temperatures as the extrapolated onset. Traces of admixtures have a great influence on the temperature of the phase transition. We

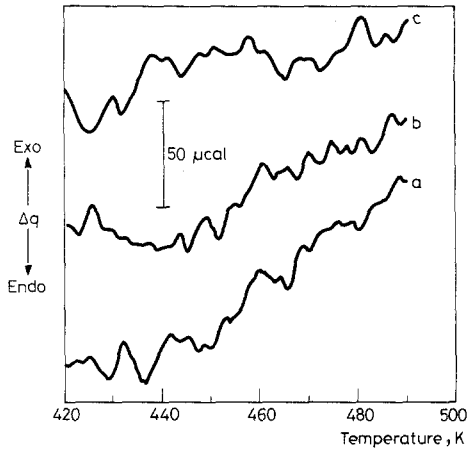


Fig. 1 Single curves of the measurements from the HP 9825 calculator. Curve a) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$; b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ doped with Nd^{3+} ; c) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ doped with $\text{Nd}^{3+} + \text{K}^+$

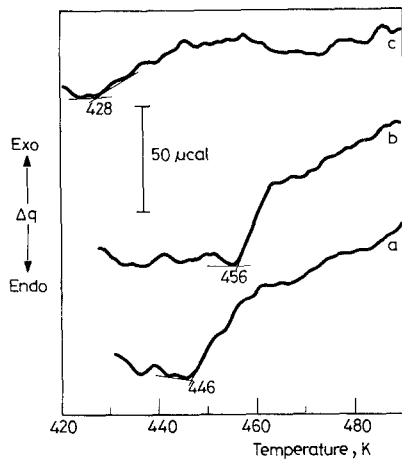
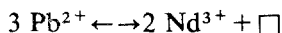


Fig. 2 Summation curves from the HP calculator curve. a) $\text{Pb}_5\text{Ge}_3\text{P}_{11}$; b) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ doped with Nd^{3+} ; c) $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ doped with $\text{Nd}^{3+} + \text{K}^+$

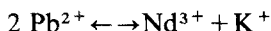
found that pure lead germanate exhibits a phase transition at $T_c = 446$ K, while that doped with neodymium displays a shift to $T_c = 456$ K. On the other hand, the addition of potassium plus neodymium decreases the transition temperature to $T_c = 428$ K and the effect as a whole is less sharp and less distinct.

The different shifts of T_c by Nd^{3+} and by $\text{Nd}^{3+} + \text{K}^+$ doping may be due to different types of substitution in the crystal lattice of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$. In the first case

2 Nd^{3+} ions have to substitute for 3 Pb^{2+} ions, thereby creating one Pb^{2+} vacancy in the lattice:



In the second case we assume a coupled substitution of 2 Pb^{2+} ions by Nd^{3+} and K^+ :



Thus, the two types of substitution are distinguished by either K^+ ions or vacancies at lead positions, giving rise to different changes in the crystal field of the lead germanate lattice. A broadening of the transformation interval, at least for the $\text{Nd}^{3+} + \text{K}^+$ -doped sample, can account for the smaller effect of this material.

Conclusions

The results demonstrate that the summation technique provides a suitable improvement of DSC for the evaluation of small effects. The signal-to-noise ratio is distinctly increased even by the summation of as few as 5 to 20 DSC curves. In this way the high accuracy and resolution of adiabatic calorimetry are not attained, but the material and time requirements remain relatively small.

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Zusammenfassung — Eine Computermethode wird angegeben, die es erlaubt, das Signal: Rausch-Verhältnis bei DSC-Messungen von Umwandlungen mit geringer Energie zu erhöhen. Diese Methode wird verwendet, um die Temperatur der Umwandlung ferroelektrisch-paraelektrisch an Bleigerminat $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, rein oder dotiert mit Nd^{3+} oder mit $\text{Nd}^{3+} + \text{K}^+$, zu bestimmen.