Optical and Thermal Tools for the Phase Transitions Detection in the Guanidine Compounds

P Brągiel, M Piasecki, I Kityk

Institute of Physics, Jan Długosz University, Armii Krajowej 13/15 42-200 Częstochowa, Poland

e-mail: m.piasecki@ajd.czest.pl

Abstract: In the Reference 1 it was established that single crystals of guanidine compound \([\text{C(NH}_2\text{)}_3\text{]}\text{Cl}_2\text{SO}_4\) possess two structural phase transitions of the first order at \(T = 352\) K (to the intermediate orthorhombic) and \(T = 356\) K (to the paraelectric tetragonal). In this report we present results of DSC measurements in heating-cooling regime with relatively low temperature rates- 0.3 K/min and 0.1 K/min. We compare the measured by us the DSC results with temperature dependent photo induced second harmonic generation (PISHG) data. The investigations show that at lowest heating temperature changes velocity (0.1 K/min) we obtain two wide peaks temperature separated. We conclude from this DSC measurement that \([\text{C(NH}_2\text{)}_3\text{]}\text{Cl}_2\text{SO}_4\) single crystals undergo a two-step phase transitions. We have received a similar temperature splitting of the observed phase transformations and a 15 K shift between the temperature PISHG dependences and the principal DSC maxima.

1. Introduction

Differential scanning calorimetry (DSC) and its modulated DSC (MDSC) version are known to be sensitive tools for studies of phase transitions, especially in the cases of strong electron-phonon anharmonic interactions in vicinity of critical temperature points. As DSC/MDSC methods are convenient in practice they are widely used: polymer transformations, crystallization – melting features, resins curing, protein denaturation, glass transitions are among fields of this methods application [1-4].

At the same time the optical methods are able to indicate also transformations connected with interactions of phonon modes with excited states. Due to this reason the optical and especially nonlinear optical methods become more and more popular for detection of different phase transitions [5,6]. The higher order optical effects are more sensitive than this of lower order a two-photon absorption and a third harmonics generation [7]. However, there is a strong shortcoming for the third harmonic generation: a dozens of samples, including semiconductors and even dielectrics, are non-transparent for the tripled frequency wavelengths. The other effect depending on third rank polar tensor is also optical second harmonic generation (SHG). A limitation in this case presents randomly oriented samples or centro-symmetrical crystals. A solution, in this case may be an optical poling or a photoinduced second harmonic generation (PISHG) [8,9].

The main goal of this paper is to compare the results of DSC and PISHG measurements and to discuss a capability of both these methods to detect properly phase transition temperature and its kind for ferroelectrics.

At first a brief description of DSC scans for the pyridazine perchlorate single crystals is given to prove with earlier permittivity data, that when used with extremely small heating rates is able to indicate transition temperatures very precisely. After this both DSC and PISHG methods are applied to study tetraguanidine dichloro-sulfate: \([\text{C(NH}_2\text{)}_3\text{]}\text{Cl}_2\text{SO}_4\) single crystals. The discrepancies between the temperature-dependent pictures obtained from the both sets are then compared and discussed together with some generalizing remarks.
Possible temperature shift between the DSC, PISHG are discussed within the framework of the local heating during the photo-induction processes.

2. Experimental

2.1. Non-linear optical set-up

The principal scheme of the non-linear optical set-up is given in figure 1.

Figure 1. Principal experimental set-up for the PISHG measurements.

The photoinducing pulsed Nd :YAG laser providing the 1,06 µm wavelength operates with a pulse duration of 40 ps and a pulse repetition rate about 100 Hz. The optical SHG is generated by a single phase-matched KTiOPO₄ (KTP) crystal. The pumping laser beams consist of a combination of the fundamental and the doubled frequency wavelengths. The ratio of their intensities is changed from 15 to 70 by varying the KTP crystal angle from 3 to 17 degree with respect to the incident fundamental beam. A beam-splitter (BS) is used for the independent control of the incident light from the fundamental Nd :YAG laser. The polarisations of the incident bicolour coherent light on the sample are performed with the Glahn polariser (P). A synchronisation of the chopper (Sh) with the Nd-YAG laser is ensured for a simultaneous light interruption. At the same time, the light source supplies a probing non-mono-chromatic beam slavered to the chopper whose pulse frequency can attain 100 kHz. The polarisation of the incident light is done with the polariser before irradiation of the sample (S). The monitoring of changes in the optical transmission spectrum is performed with the monochromator PM of about 2 nm spectral resolution directly connected with the CCD camera.

2.2. DSC measurement

DSC measurements were done with the commercial Netzsch Simultaneous Thermal Analyzer STA409C with 32-bit controller. High temperature furnace together with a sample carrier suitable for C₅ measurements and Al₂O₃ crucibles were used. Apparatus was calibrated both for temperature and for sensitivity with melting temperatures and melting enthalpies of the pure metals: Ga, In, Sn, Zn, Al, Ag, Au. All the recordings were in argon (5N) atmosphere to prevent samples from oxidation. Heating rates were 0.1, 0.3, 0.5, 1, 2, 3 and 5K per minute.

3. Results and discussion

Several DSC measurements of single crystal of guanidine compound [C(NH₂)₃]₄Cl₂SO₄ made with a standard values of heating rate shows (see fig. 2) very broad huge anomaly which suggested presence of a few overlapping peaks which is consistent with DTA plots [1].
Next we decrease heating rate to 0.1 K/min and as a result obtain - during heating cycle- two sharp maxima - at 356.2 K and 362 K. In the cooling run the DSC behaviour of the crystal shows single peak (see Fig. 3) occurred in 354.4 K. From the Fig 3 it is easy to see that start of lower phase transition in heating process is correlated with phase transformation temperature in cooling regime.
Generally the Fig 2 and Fig. 3 show that total transition enthalpy (corresponding with peak area) in heating (divided into two peaks: first bigger than second) is greater compared to those obtained in cooling.

The photoinduced SHG is determined by anharmonic phonons described by polar third rank tensors and forming so-called optically induced non-centrosymmetry. When the given phase is more disordered there exists a larger opportunity to form additional non-centrosymmetry. Following the results presented by Szafranski [1] one can see that there exists several temperature ranges with the lattice unstable structure which give the possibility to form additional non-centrosymmetry.

Figure 4. Temperature dependence of the PISHG with temperature rate 0.1 K/min for the 1.06 µm/53 µm. First cycle within cooling and heating

Figure 5. Temperature dependence of the PISHG for the XZ-crystal cut.

Comparing the obtained DSC and PISHG data one can conclude a high sensitivity of these methods to the observed phase transformations caused by the displacements of the guanidine cations from their high-symmetry sites in the tetragonal phase together with local re-ordering of the sulphate and chlorum groups [1]. Because there exists a relatively large amount of the disordered phase manifestation of the PISHG would be more prominent. In this case principal role should play the crystalline anisotropy. We observe clear temperature anisotropic maxima of the second order optical susceptibilities. Such anisotropy confirms principal role of the particular structural clusters in the observed phase transformations, and in particular of the ferroelectrics ones. However, more striking is the observed temperature shift of the PISHG with respect to the DSC, despite the corresponding temperature split is similar. The existence of the close hysteresis split similar for the DSC and the PISHG may reflect the same origin of the studied order-disordered phase transformations. However, at low temperature shift for the PISHG may indicate an appearance of several photo-thermal heating favouring additional electron-phonon anharmonicities necessary for the phase transformation observations.
The data obtained from the performed measurements are well correlated with those from DSC scanning. The shift of temperatures for the phase transitions may be caused by locally higher temperatures during PISHG photo-treated process. Pumping laser beam locally heat the surface from which we obtain measurement reflecting SHG. Constant difference - nearly 15 K - between described DSC and PISHG in guanidine compound \([\text{C(NH}_2\text{)}_3]\text{Cl}_2\text{SO}_4\) measurements temperatures of phase transitions may be an additional confirmation of this prediction. High sensitivity makes SHG applicable also in the cases in which DSC is not sufficient due to too weak signal.

4. Conclusions

The SHG signal was found to be extremely sensitive for detection of structural phase transitions in guanidine compound \([\text{C(NH}_2\text{)}_3]\text{Cl}_2\text{SO}_4\). Two sequences of first order phase structural transitions caused by heating are considered: first one - from orthorhombic with space group \(\text{Cmc}_2_1\) (ferroelectric order) to intermediate orthorhombic and second to tetragonal with space group \(\text{I4}_2\text{m}\) (paraelectric order). It is demonstrated that albeit both methods gives an evidence of the transitions the optical one is much more sensitive. Even for a centrosymmetrical materials joined with optical poling SHG is an efficient tool for phase transition indication.

Information obtained from these methods are well correlated. The observed temperature shift between the PISHG and DSC maxima may be related to the local photo-thermal overheating.

There are limitations too. Namely, the SHG method is proper for this kind of transitions which generate “soft” phonon modes. SHG does not provide us with any energy data but kinetics of the transformation may be established from an incremental SHG signal increase within peak area.

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