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Photoacoustic detection of phase transitions

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The usability of the photoacoustic effect in studies of the phase transitions in the surface layers of various materials has been proved using an apparatus for continuous, automatic registration of the temperature dependences of the parameters (amplitude and phase) of the photoacoustic signal, built in our laboratory. The results obtained seem to be very promising to applied for studying the ageing processes in dielectrics, especially in polymers used for construction of insulating systems.

Keywords: photoacoustic, dielectrics, polymers, insulating systems.

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Introduction

In 1880 Alexander Graham Bell discovered that a material generates an acoustic signal when illuminated with periodically modulated light. This effect was named the photoacoustic effect (PA effect). In XX century this effect has gained much interest as an experimental tool in the studies of optical, thermal and spectral properties of liquid and solid state materials. The measured quantity in the photoacoustic technique is the pressure variation in the gas surrounding the sample. The pressure variation of the gas in the measuring chamber is caused by transfer of heat from the sample to gas. The frequency of the signal was identical to that of the modulation. This process was theoretically described by Rosencwaig and Gersho, McDonald and Wetzal and Korpiun and Tilger, who gave the analytical expression for the pressure variation in the gas that is in contact with the sample. The dependence of the photoacoustic parameters on the thermal properties of investigated matter permits to apply the photoacoustic technique to detecting those processes in which they are changed [1-7]. The results of systematic studies of the photoacoustic effect in the vicinity of phase transitions in condensed matter are presented in this communication.

I. Experiments

A photoacoustic spectrometer was constructed in our laboratory. This spectrometer enabling the simultaneous measurements the temperature dependencies of both the amplitude and phase of photoacoustic signal in the temperature interval ranging from room temperature to 750 K, at arbitrary chosen, constant heating rates ranging from 1 to 70 K/min.

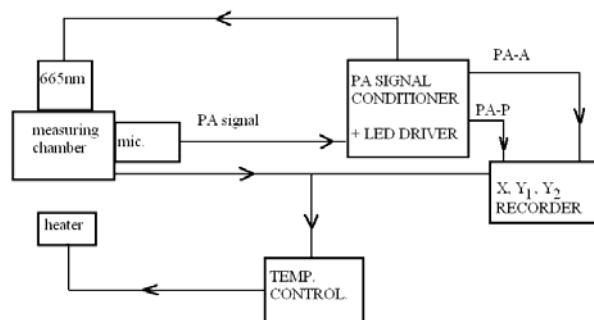


Fig. 1. Block diagram of the photoacoustic spectrometer.

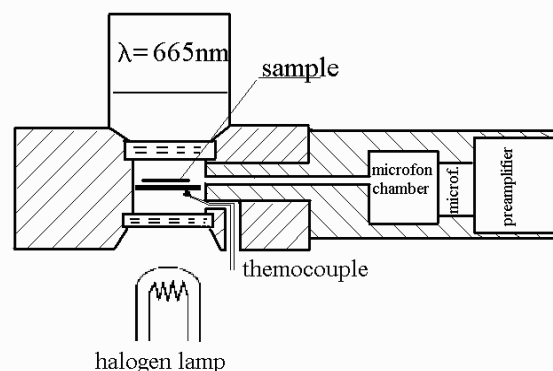


Fig. 2. Scheme of the photoacoustic cell.

A block diagram of the whole system for measuring the temperature dependence of the parameters of photoacoustic signal is shown in Fig. 1.

The scheme of the high temperature photoacoustic

cell is shown in Fig. 2.

The excitation of photoacoustic signal is made by light (665 nm) from the unit of electroluminescence diodes whose intensity is electrically modulated at a frequency of 403 Hz. The sample is placed in the measurement chamber on the heater. The sample is optically heated through light intensity control of halogen lamp. The temperature increases linearly. The pressure variation in the measuring chamber are detected by a capacitance microphone after transition through resonant cell. The value of voltage induced on microphone plates range from a few to over a dozen microvolts depends on the kind of sample. This voltage is given on the input of integral amplifier. The output signal from microphone amplifier is given on the input of band-pass filter. This filter selects a component with frequency equal to the frequency of light modulation (403 Hz). The photoacoustic (PA) signal on the filter output is free from noises and is directed to two blocks: analog – measure of the amplitude of PA signal, and digital – measure of the

phase of the photoacoustic signal for tin are represented in Fig. 3. The registered curves display a sharp peak in a temperature 504 K corresponding to the temperature of melting of investigated material.

The first order phase transitions in multicomponent metallic alloys (Pb-Sn, Zn-Al, Zn-Al-Cu) have been measured too. The results obtained in this study corroborate the usefulness of the photoacoustic technique for determination of the phase diagrams of multicomponent metallic systems (solid-liquid, solid-solid, melting phase transitions).

Observations of the photoacoustic effect accompanying the solid-solid (polymorphic) phase transitions in silver salts were performed. The high-temperature phases of this salts are known as solid electrolytes or superionic conductors. The investigated materials were: silver iodide (AgI), silver selenide (Ag₂Se), silver sulphide (Ag₂S), silver telluride (Ag₂Te). The control measurements were performed by DSC (differential scanning calorimetry) using the NETZCH

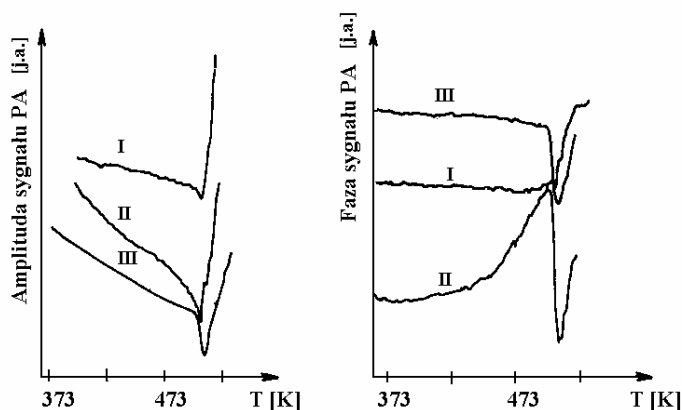


Fig. 3. The temperature dependencies of the amplitude and phase in tin. I, II, III – the next heating cycle the same sample. The heating rate – 24 K/min.

phase of PA signal. The complete apparatus description is given in [8].

Using this apparatus, the temperature dependencies of both the amplitude and phase of photoacoustic signal have been measured for various substances, exhibiting the first and the second order phase transitions in the temperature interval Rt-750 K.

The testing of apparatus we began from investigation of the melting of metals and metallic alloys. We study the photoacoustic effect accompanying the phase transitions in a wide range of materials [9-15].

II. Results

The measurements we started from investigation in pure metals. It had been measured: tin, indium, bismuth, lead. The temperature dependencies of the amplitude and

DSC 404/3/F differential scanning calorimeter with Pt-PtRh measuring head and platinum sample pans. All measurements were performed at the heating rate 10 K/min, under ambient pressure.

The stable form of silver telluride at room temperature is hexagonal structure. Polymorphic phase transitions to the face-centered cubic structure occurs at 410K. The anomalies on the DSC, PAA, PAP curves well coinciding with the temperature of phase transition of Ag₂Te. The temperatures of phase transitions for AgI, Ag₂Se, Ag₂S determined from measurements agree well with the literature data on the temperature at which transition of investigated materials to the state of superionic conductivity.

The temperature dependences of the amplitude of photoacoustic signal with control measurements by the DSC from vanadium oxide V₂O₄ have been measured.

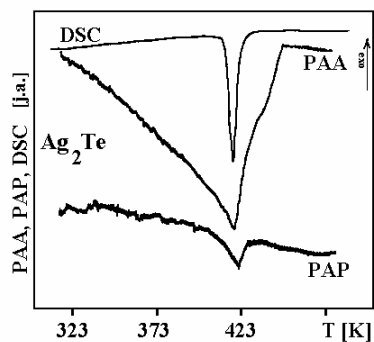


Fig. 4. Temperature dependences of the DSC signal amplitude PAA and phase PAP of photoacoustic signal for Ag_2Te .

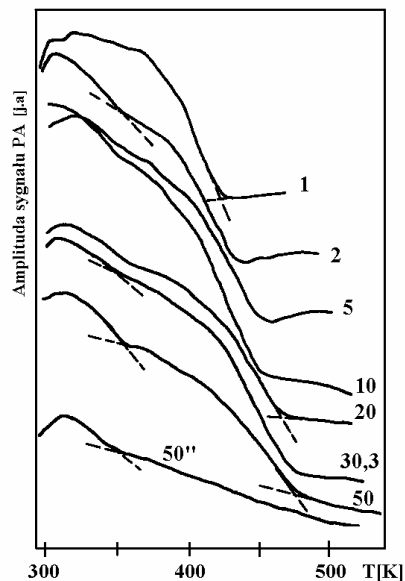


Fig. 5. The temperature dependences of the amplitude of photoacoustic signal registered in the first heating run for V_2O_4 . Heating rate 10 K/min.

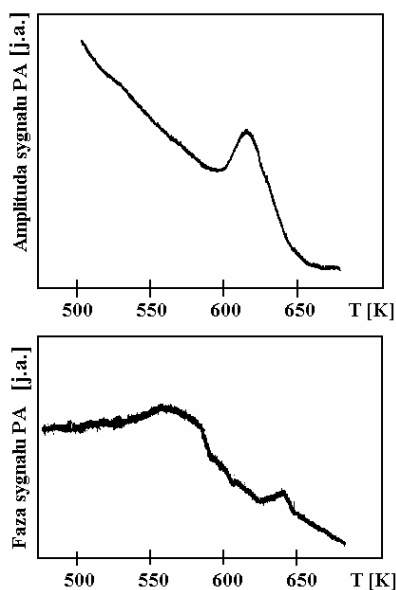


Fig. 6. The temperature dependences of amplitude and phase of the photoacoustic signal from nickel.

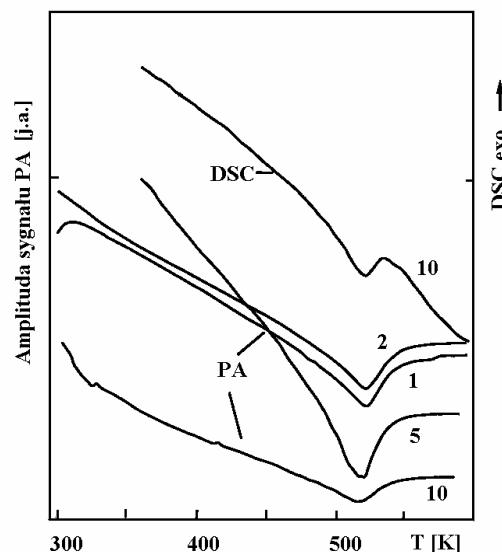


Fig. 7. The temperature dependences of amplitude of the PA signal in NiO .

The low temperature anomalies (~ 340 K) coincides well with the DSC endotherm. Its position does not depend on the heating rate and can be reproduced in the second and subsequent heating runs. Therefore we ascribed this anomaly to metal-nonmetal phase transition (literature data on the temperature of this transition – 340 K). The position of high temperature anomaly (~ 440 K) strongly depends on the heating rate, and disappears after the first heating run. It should be ascribed to the irreversible thermally activated transformation in the investigated material (most probably desorption of gases).

It has been studied the phase transitions

(polymorphism (orientational disordering) – II order and melting – I order phase transitions) in organic materials: pure n-alkanes and paraffin waxes. The phase transition temperature measured by this technique are in good agreement with those obtained from others methods.

The magnetic second order phase transitions have been studied; the ferromagnetic- paramagnetic phase transition in pure Ni at the Curie point, the antiferromagnetic- paramagnetic phase transition in NiO at the Neel point. In Fig. 6 the temperature dependences of amplitude and phase of the photoacoustic signal from nickel was shown. The temperature dependences the

amplitude of the photoacoustic signal in nickel oxide is shown in Fig. 7.

The thermal stability and crystallization kinetics of amorphous selenium have been studied by too. The temperature position of the anomalies on the temperature dependencies of the amplitude and phase of the PA signal depends on the heating rate thus enabling the activation energy for the crystallization process to be determined by the Ozawa's method.

Conclusions

As a whole, the results of the performed experiments demonstrate the usefulness of the proposed photoacoustic technique as a thermoanalytique method. It seems, that the photoacoustic technique can be applied for studying the ageing processes in dielectrics, especially in polymers used for construction of insulating systems. The works devoted to the selection of insulating polymers, whose ageing degree could be evaluated by the proposed method, are in progress.

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Фотоакустичне виявлення фазових переходів

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Застосовність використання фотоакустичного явища в дослідженнях фазових переміщень в поверхневих шарів різноманітних матеріалів доведено використанням установки для неперервної, автоматичної реєстрації температурних залежностей параметрів (амплітуда і фаза) фотоакустичного сигналу, яка була створена в нашій лабораторії. Отримані результати, здається, є багатообіцяючими в застосуванні у вивченні процесів старіння в діелектриках, особливо в полімерах, які використовуються в конструюванні ізоляційних структур.