Photothermoelectric Detection of Phase Transitions in Liquid Thermoelectrics

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Abstract: The recently introduced photothermoelectric technique (PTE) was applied to detect first order phase transitions in some liquid thermoelectrics (LTE). The investigated samples were based on dodecanol mixed with tetradodecylammonium nitrate (TDAN) and tetrabutylammonium nitrate (TBAN). It was demonstrated that the Seebeck effect, produced by a LTE, is an useful tool for the detection of phase transitions in the very same material. Additional photopyroelectric (PPE) measurements suported the obtained results.

Keywords: Photothermoelectric technique, photopyroelectric technique, liquid thermoelectrics, phase transitions, thermal parameters.

1. INTRODUCTION

A phase transition is a phenomenon associated with a break of the system's symmetry. Usually, in the critical region, the system passes from an ordered to a disordered phase. In the vicinity of the transition temperature, the order parameter (non-zero in the ordered phase) fluctuates and vanishes in the disordered phase. From theoretical point of view, the first and second derivatives of the thermodynamic potential can present anomalies in the critical region. If the first derivatives of the thermodynamic potential are discontinuous, the phase transition is of I-st order. If the first derivatives are continuous and the second are discontinuous, the phase transition is of II-nd order. Generally, II-nd order phase transitions have been more intensively studied due to their theoretical (fundamental) and applicative features [1]. As examples of II-nd order phase transitions we can count the magnetic, ferroelectric, etc. ones. As most common I-st order phase transitions we can identify meltings, vaporizations, etc. In any case, if one intends to detect and study a phase transition, he must be able to measure a quantity (parameter) presenting an anomaly at the critical point. These parameters can be specific for different class of materials (examples are: magnetic susceptibility for magnets, polarization for ferroelectrics, etc.), but they can also characterize all types of materials; among this last type of parameters we count the thermal parameters. Consequently, the methods (calorimetries) able to directly measure the thermal parameters are very suitable for phase transitions detection, due to their degree of generality(large range of materials possible to be investigated). Among these calorimetries, the photothermal techniques are of particular interest. For example, the photopyroelectric (PPE) method has been largely used in order to detect phase transitions in ferroelectric and magnetic materials [2,3], superconductors [4], liquid crystals [5,6], as well as to study I-st order transitions as meltings or glassy transitions [7-9]. On the other hand, recently, a new photothermal calorimetry, based on the so called photothermoelectric (PTE) effect, was proposed [11]. The method is rather similar with the PPE technique, but the pyroelectric sensor is replaced by a thermoelectric (TE) sensor. The physical mechanism in the case of the PTE technique relies to the Seebeck effect. It has been shown that this novel method allows for the determination of thermal parameters such as effusivity and diffusivity both for the material used as sensor and/or to another material used as a sample [11, 12]. Several applications on liquids and solids have been already reported [12, 13]. It has been also shown that solid TE materials can be suitable sensors for phase transitions investigations [12, 13].

In this paper we propose to use the Seebeck effect generated in a liquid thermoelectric (LTE) for the detection of the melting process in the same LTE. Dodecanol is a known alcohol involved in a solid/liquid phase transition at about 24^0C. Mixed with low concentration of tetradodecylammonium nitrate (TDAN) or tetrabutylammonium nitrate (TBAN) it becomes thermoelectric. The purpose of this paper is to detect the melting of two LTEs containing 10^{-3} mol/l TBAN and 10^{-3} mol/l TDAN respectively, by using the PTE signal generated by the LTE's themselves.

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2. THEORETICAL ASPECTS

For a LTE of thickness l, situated between two layers of air, and irradiated with a flux H of optical radiation, modulated with the frequency f, the PTE voltage is given by:

$$V = S_0[T(x=0) - T(x=l)] \tag{1}$$

where the temperature across the LTE is given by [14]:

$$T(x) = \frac{(1-R)H}{2k\sigma}\frac{\exp(-\sigma\, l) + \exp[-\sigma(2l-x)]}{1-\exp(-\sigma 2l)} \tag{2}$$

Using Eqs. (1) - (2) we obtain for the PTE signal:

$$V = S_0\frac{(1-R)H}{(1+\mathrm{i})(2\omega)^{1/2}\mathrm{e}}\frac{1-P^{-1}}{1+P^{-1}} \tag{3}$$

In Eqs. (1) – (3)

$$P = \exp(\sigma l); \sigma = (1+i)(\omega/2\alpha)^{\frac{1}{2}};$$

(1-R) represents the quantity of optical radiation absorbed by the LTE, $\omega = 2\pi f, i = \sqrt{-1}$, α and e represent LTE's thermal diffusivity and effusivity, respectively.

The PTE voltage expressed in Eq. (3) is a complex quantity, both the amplitude and the phase of the signal depending on LTE's thermal diffusivity and effusivity. At a phase transition both thermal parameters mentioned above present anomalies. Consequently, both sources of information (the amplitude and the phase of the PTE voltage) can be used for phase transitions detection.

3. EXPERIMENTAL

The experimental set-up used for PTE detection of phase transitions in LTEs was largely described elsewhere [7, 14, 15]. It contains a radiation source, a detection cell, a lock-in amplifier for signal processing and a computer for automatization and data analysis. In the following we give only some specific details. The radiation source was a 200 mW YAG laser, modulated from the internal generator of a SR 830 lock-in amplifier, used also for data processing. The detection cell [7] was provided with Peltier elements (coupled to a thermostatic bath) for temperature scans. The temperature variation rate was 600 mK $\mathrm{min}^{-1}$and the temperature range 8^0C–32^0C included the melting point of the investigated samples. The data acquisition and data processing were computer controlled.

The sample filled the space between two thin (100 µm) metallic foils acting in the same time as electrodes for the PTE signal (see Figure **1**)). The irradiated foil is blackened to assure a good optical absorption. The spacers' thickness (practical the sample's thickness) is 800 µm. As demonstrated in previous works [17, 18] at this thickness, for a chopping frequency of 0.3 Hz, both PTE amplitude and phase are saturated. In the meantime at this frequency the two metallic layers are thermally thin and, consequently, from theoretical point of view, the LTE material can be considered as being bordered by two layers of air.

The supporting PPE investigations have been performed in the front detection configuration [15, 16]. The pyroelectric sensor was a 500 µm thick and

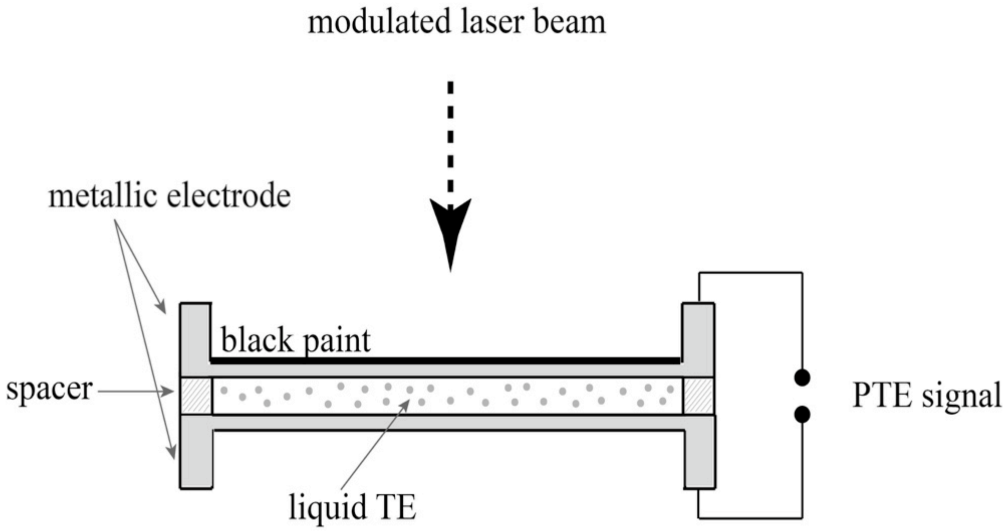

Figure 1: Schematic view of the irradiated LTE sample.

1.5x1.5 cm^2 area $LiTaO_3$ single crystal provided with CrAu electrodes on both sides.

The samples under investigation were produced by mixing and dissolving salts of tetradodecylammonium nitrate - TDAN and tetrabutylammoniumnitrate - TBAN, (Sigma Aldrich, purity ≥ 99.0%) at concentration c = 10^{-3} mol/l in 1-dodecanol (Sigma Aldrich, purity ≥98.0%) at ambient temperature. The mixtures were stirred and heated at around 40 °C during 15 minutes to improve salt solubility.

4. RESULTS AND DISCUSSIONS

The results obtained for the amplitude and phase of the PTE signal are presented in Figures **2** and **3**. An anomalous behavior for both amplitude and phase are observed around 24^{0}C. For such low TBAN and TDAN concentrations, no clear shift of the melting point of the mixtures, compared with the melting point of pure dodecanol, was observed. In fact, the liquid/solid transition region is rather large, typical for I-st order phase transitions. Figure **2** contains also the PTE signal obtained for pure dodecanol, which is zero, as expected, because pure dodecanol is not a thermoelectric material.

In order to support the PTE results, classical PPE investigations, in front detection configurations have been performed. The results for the phase of the PPE signal are displayed in Figure **4**. Clear anomalies have been found both for pure dodecanol and for the mixtures around 24^{0}C.

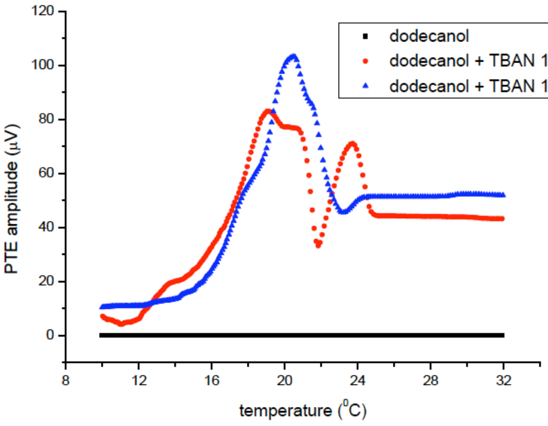

Figure 2: The temperature dependence of the PTE amplitude of the investigated samples in the temperature region including the melting point. The behavior for pure dodecanol is also displayed.

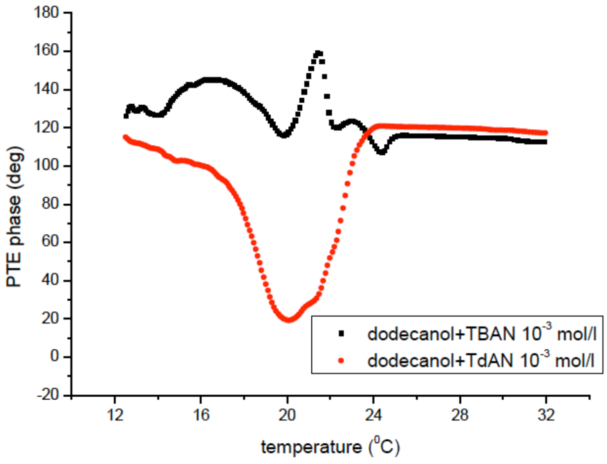

Figure 3: The temperature dependence of the PTE phase of the investigated samples in the temperature region including the melting point.

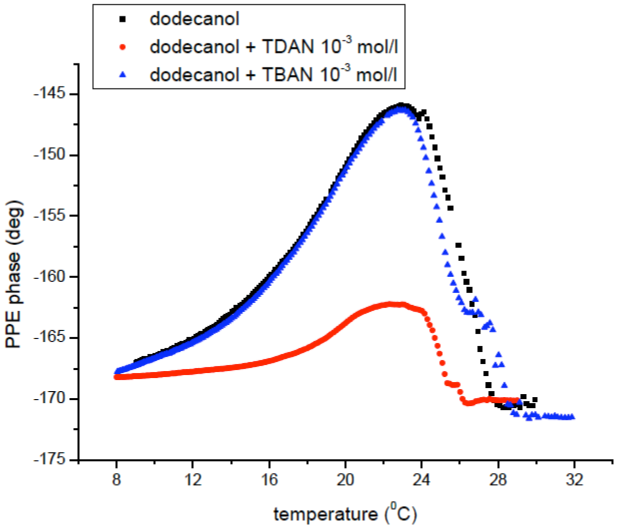

Figure 4: The temperature dependence the PPE phase of the investigated samples in the temperature region including the melting point. The behavior for pure dodecanol is also displayed.

CONCLUSIONS

In this paper, the PTE technique, in a particular configuration, was applied for the first time for detection of phase transitions in liquid thermoelectrics. The main novelty of the paper is the *particular detection configuration*, which consists in using the Seebeck effect, produced by a LTE, for the detection of the phase transition (melting) in the *very same material*. Dodecanol mixed with 10^{-3} mol/l TBAN and TDAN respectively, have been used as samples. Additional photopyroelectric (PPE) measurements supported the obtained PTE results.

Work is in progress with PTE investigations of the phase transition in the same mixtures with different TBAN and TDAN concentrations and with the study of critical behavior of static and dynamic thermal parameters and Seebeck coefficient.

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