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Pyroelectric figure of merit in alternating hemicyanine/NC Langmuir–Blodgett films incorporating barium ions

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Abstract

Pyroelectric properties in alternating hemicyanine (DAEP)/nitrogencrown (NC) Langmuir–Blodgett (LB) films and effects of incorporating barium cations on pyroelectric behaviors have been investigated. Its pyroelectric coefficient measured is found to be 58 $\mu C\,m^{-2}\,K^{-1}$ at 300 K. Their dielectric properties have been measured and used to determine the figures of merit in thermal devices. Relative permittivity (ε_r) and dielectric loss values ($\tan\delta$) of pyroelectric films (in the range of 1–100 KHz) are found to be 2.34–1.96 and 0.08–0.04, respectively. These data give a maximum pyroelectric figure of merit of 150 $\mu C\,m^{-2}\,K^{-1}$ in the alternating LB films incorporating barium ions. The effects of different deposition on pyroelectric properties are also discussed in this paper.

Keywords: Pyroelectricity; Langmuir–Blodgett films; Metallic cation; Dielectric property

1. Introduction

Pyroelectric materials show a temperature-dependent spontaneous polarization and have a lot of applications including uncooled thermal inaging device [1]. The pyroelectric effects in non-centrosymmetric Langmuir–Blodgett (LB) films has been widely reported. It has been known that LB films are well-organized thin organic assemblies capable of various functions if molecular compositions are suitably designed. For example: X- and Z-type LB films and alternating LB films consisting of two different amphilphiles (polar and/or non-polar) have non-centrosymmetric structure and are expected to show piezoelectric, pyroelectric, and various non-linear optical properties [2]. Since the beginning of the 1980s, more and more researchers focus on the pyroelectric effect of non-centrosymmetric LB films, for the reason that if the molecule is well-polarized, we need not apply an external electric field to remain the pyroelectricity of the conventional materials such as ferroelectric ceramic [3–5], i.e. the spontaneous polarization of an organic LB film has been firmly built into the organized molecular monolayers and/or multilayers structure without requirement of poling treatment before measuring pyroelectric coefficients. And LB films offers real advantages over poly-vinylidene fluoride (PVDF) and ceramic materials in terms of their lower dielectric constants and dielectric loss values. On the other hand, the multilayer structure and the pyroelectric effect of LB films could be improved by incorporating metal ion in the subphase [6]. Thereby, it is of important to investigate the effect on the pyroelectric properties of LB films of incorporation some metallic cations.

In the present paper, we report the fabrication, pyroelectricity and dielectric characterization of a alternating LB multilayer films made from the active materials (polar materials) hemicyanine (DAEP) and a novel disc-like amphiphilic materials (non-polar materials) nitrogencrown (NC) as well as the effects of incorporating the metallic cation (e.g. barium ions) on pyroelectric behaviors. The pyroelectric coefficient is up to be 58 $\mu C\,m^{-2}\,K^{-1}$ at room temperature. The dependence of relative permittivity (ε_r) and dielectric loss values ($\tan\delta$) on the frequency are described also.

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2. Experimental details

The chemical structures of DAEP and NC used in this work are shown in Fig. 1. The DAEP was synthesized in our laboratory and NC obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Science.

We fabricated four LB multilayers samples A, B, C and D, respectively, by using a computer-controlled KSV 5000 two-compartment Langmuir trough made in Finland. The DAEP and NC were spread from 10^{-3} mol l^{-1} chloroform solutions onto the aqueous subpahse in two separate compartments of the Langmuir trough. The subphase was deionized, doubly distilled water at 20 °C with pH value 5.5–6.0. For samples A, B and C, its are: pure NC Z-type, alternating DAEP/NC Y-type, pure DAEP Z-type multilayer films, respectively. The sample D is a alternating DAEP/NC LB multilayer films incorporating barium ions made by adding a few barium chloride of analytical-grade (10^{-4} mol l^{-1} concentration) in the subphase. The substrates were glass plates coated with an indium-tin-oxide (ITO) layer as the grounded lower electrode and treated to be hydrophilic surfaces. The multilayers were deposited during upstrokes and/or downstrokes at a constant pressure of 28 mNm^{-1}. The transfer ratio could be displayed and recorded automatically by the computer during deposition.

After deposition of LB films, an aluminum layer of 60 nm thickness and 0.25 cm^2 area were then evaporated on top of the films as the upper electrode to form sandwich structures (capacitors) ready for the measurements of pyrolelctric coefficient and their relative permittivity (ε_r) and dielectric loss values (tan δ).

The pyroelectric coefficient of the samples was performed at various temperatures by the method of pyroelectric voltage measurement, as shown in Fig. 2. The measuremental principle [7,8] is: the devices were mounted onto a semiconductor cooler system and a platinum resistance thermometer (PRT) was used to measure the temperature. The electroded samples were heated and cooled in a triangular wave fashion (amplitude 1 K, frequency 0.06 Hz) about a mean temperature that could be varied from −10 to 60 °C by adjusting the drive current of the current source. The electroded were connected together via a sensitive electrometer (Keithley 614). The output from the electrometer and PRT form the input to a storage-oscilloscope by a luck-in amplifier (SR 630), which enables the temperature variation and resulting pyroelectri signal to be recorded. The pyroelectric effect results in the generation of a current flow when the temperature changes and follows the relation: $Ipp = pA(dT/dt)$, where p is the pyroelectric coefficient, A the area of overlap of the upper and lower electrodes and dT/dt the temperature rate of change of temperature. Therefore, with knowledge of the value of A and dT/dt, a measurement of the pyroelectric current allows the pyroelectric coefficient to be attained [8].

The dielectric properties, relative permittivity (ε_r) and dielectric loss values (tan δ), were obtained using a Hewlett Packard 4194A impedance/gain-phase analyzer with a frequency range from 1 to 100 KHz.

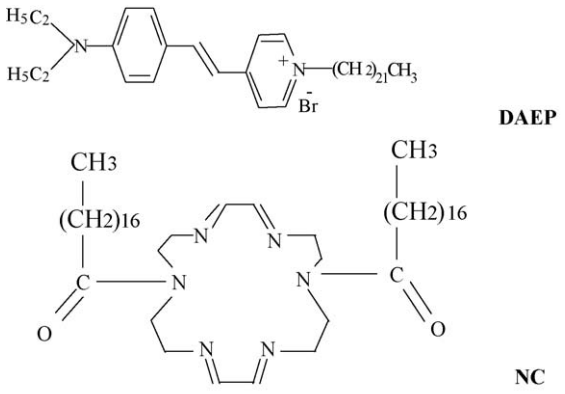

Fig. 1. The molecular structure of hemicyanine dyes and nitrogencrown used in the experiment.

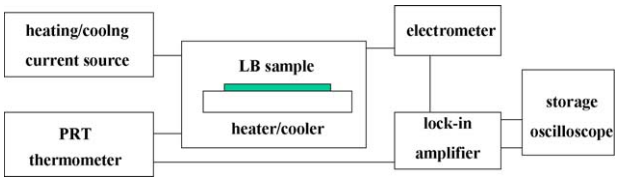

Fig. 2. The experimental set-up for pyroelectric coefficients measurement.

3. Results and discussions

The variation in pyroelectric coefficient with temperature for Sample A, B, C and D was given in Fig. 3. It can be seen that the coefficients increase with temperature monotonically and the values of p for sample A, B, C and D are 4, 6, 12 and 58 μC m^{-2} K^{-1} at room temperature, respectively.

Compared sample A and C, it is found that the pyroelectric coefficient of sample A is less that that of sample C. It is reason that the former is a non-polar molecules and there is almost not polarity. On the contrary, the later is polar molecules and there is larger dipole moment in the later than the former. It results in the fact that the stronger the polarity of materials, the larger the pyroelectric coefficient in LB films.

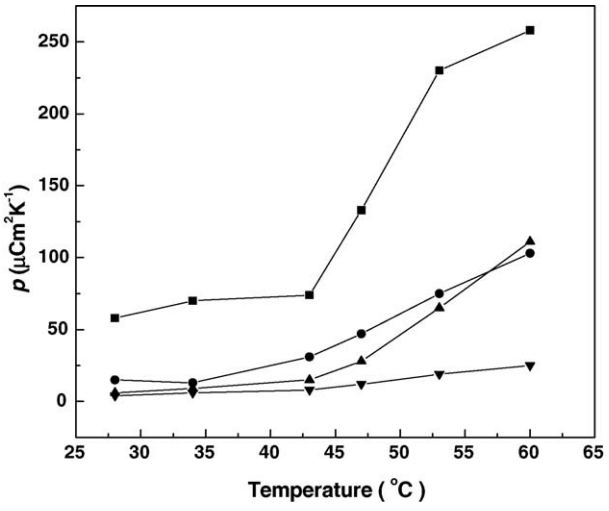

Fig. 3. Temperature dependences of pyroelectric coefficients of sample: A (▼); B (▲); C (●) sample D (■).