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The preparation and characterization of pyroelectric hybrid films containing C.I. Acid Red 29 (chromotrope 2R)

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Abstract

Pyroelectric hybrid materials were prepared from 4,5-dihydroxy-3-(phenyldiazenyl)naphthalene-2,7-disulfonic acid (*C.I. Acid Red 29*) and Nb or Ta alkoxides via a sol–gel process. The hybrid materials were analyzed and characterized using infrared spectrometry, atom force microscopy and thermal gravimetry differential thermal analysis. The dye was covalently linked to the inorganic network and organic–inorganic hybrid films had excellent pyroelectric character (average pyroelectric coefficient 1.79×10^{-6} C cm^{-2} K^{-1}) and high thermal stability; no phase separation was observed in the films.

Keywords: Pyroelectric; Organic–inorganic hybrid film; Sol–gel; Preparation

1. Introduction

Ferroelectric materials have wide applications, and they can be used as the micro-sensors, actuators, and semiconductor optical amplifier [1–6]. Recently, organic–inorganic hybrid materials have received more attention to prepare ferroelectric materials [7–9]. Such as organic–inorganic nonlinear optical materials, the inorganic network is densely and uniformly packed around the organic chromophores, and the interaction between the inorganic oxide and organic group will reduce the molecular motion during the glass transition. Therefore, hybrid materials can enhance the long-term organic nonlinear optical (NLO) stability and display the desired properties of both components [10–16]. NLO hybrid materials with the NLO chromophores are aligned in a noncentrosymmetric manner by the poling technique. These materials may possess ferroelectrics and pyroelectric properties. Like this aligned structure, these polymers are electrets materials that may possess ferroelectrics and pyroelectric properties [17].

On the basis of the above, metal alkoxide is a good choice of precursor to form polymeric matrix for sol–gel photonic material. However, it is very difficult to synthesize the special organic chromophores with D–π–A structure. So, in this study, simple molecular chromotrope 2R which contains azo group and conjugated structure was chosen as organic chromophore; the hybrid films were prepared via sol–gel process from the chromotrope 2R and metal alkoxide of Nb and Ta. The pyroelectric properties of the hybrid materials were investigated, and the results indicated that good pyroelectric properties had been achieved as a result of the designed network.

2. Experimental

2.1. Materials

All chemicals (analytically pure) were purchased and directly used as received unless otherwise stated. Tetrahydrofuran (THF) and ethanol were purified by distillation over anhydrous magnesium sulfate and dried further over molecular sieves before being used.

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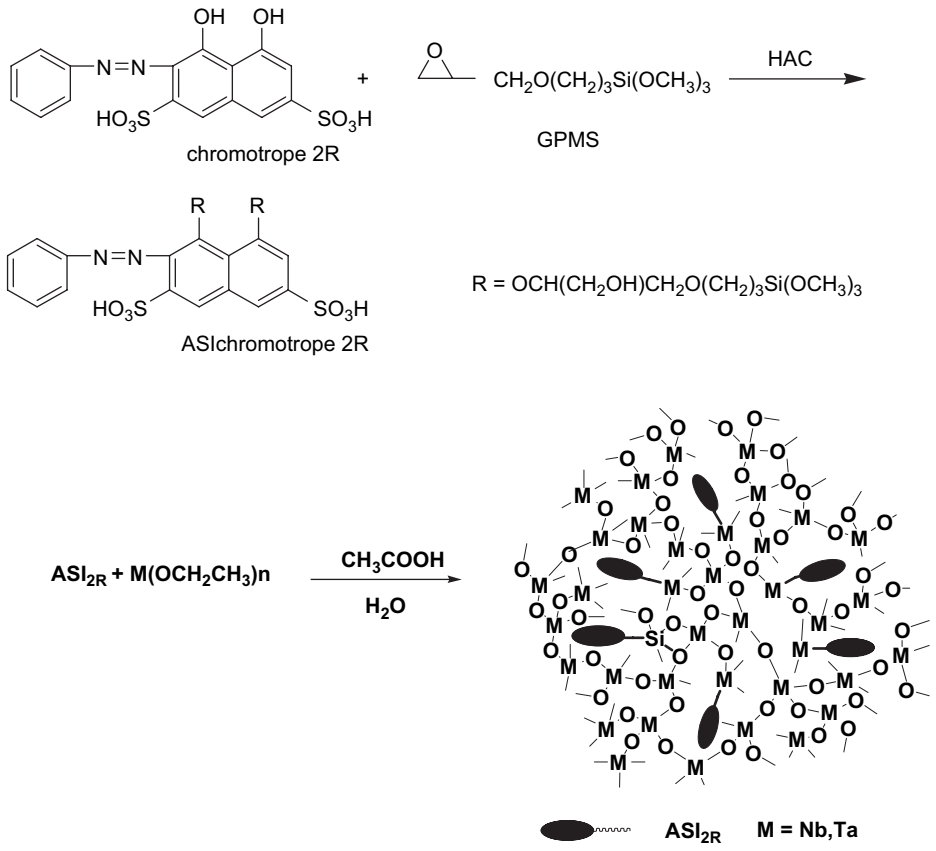

Scheme 1. The synthesis route and structure of chromotrope 2R, and hybrid material.

2.2. Preparation of the hybrid material

The synthesis route for the organic silicone-modified dye (*C.I. Acid Red 29*) ($ASI_{chromotrope\ 2R}$) is shown in Scheme 1. Dye (0.4 g, 0.9 mmol), (3-glycidoxypropyl)trimethoxy-silane (GPMS) (0.2 g, 0.7 mmol), and THF (20 ml) were added into a three-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and reflux condenser, and five drops of glacial acetic acid (HOAc) were used as catalyst. The mixture was refluxed for 12 h under nitrogen atmosphere. Then a solution of $Nb(OC_2H_5)_5$ (0.7 g) and HOAc (1.4 g) in THF (15 ml) was added dropwise and the mixture was stirred 10 h at room temperature. Finally, certain amounts of silicone glass resin (SGR), which is the auxiliary agent for the formation of the film, was introduced and the organic–inorganic hybrid sol containing chromotrope 2R and Nb (SNb_{2R}) was

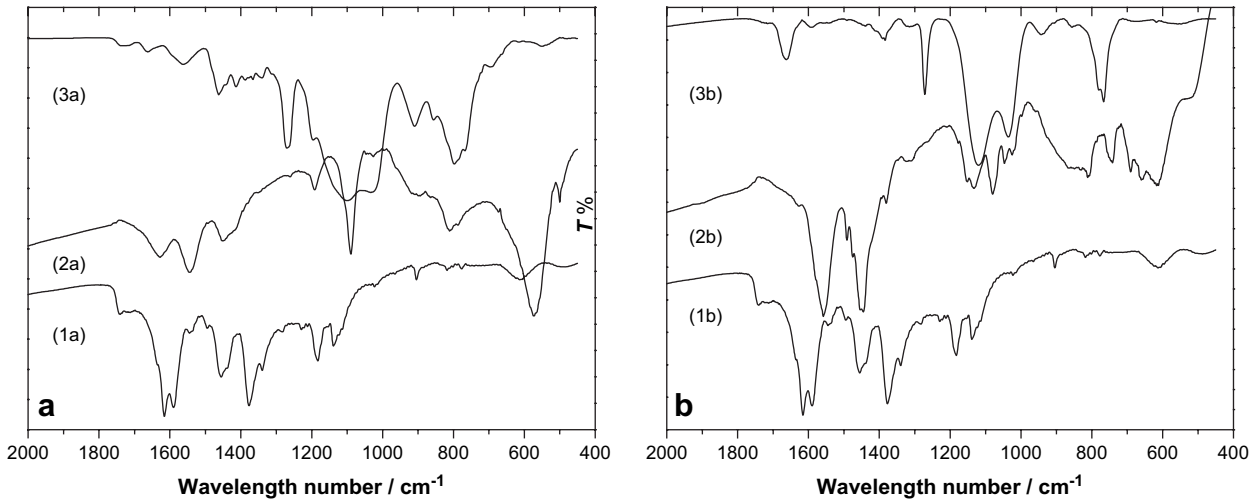

Fig. 1. FT-IR spectra: (a) MNb_{2R}; (b) MTa_{2R}. (1a) chromotrope 2R, (2a) $Nb(OC_2H_5)_5$, (3a) MNb_{2R}, (1b) chromotrope 2R, (2b) $Ta(OC_2H_5)_5$, (3b) MTa_{2R}.

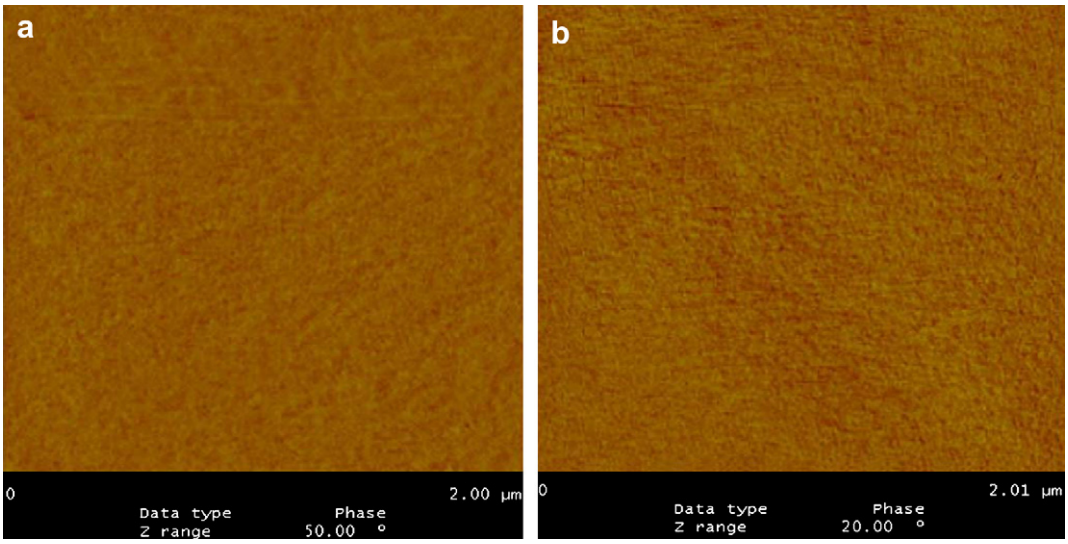

Fig. 2. AFM of hybrid film: (a) 93-nm-thick MNb_{2R}; (b)95-nm-thick MTa_{2R}.

obtained. In the same way, we obtained hybrid sol containing chromotrope 2R and Ta (STa_{2R}) which were prepared from $ASI_{chromotrope\ 2R}$ and $Ta(OC_2H_5)_5$.

2.3. Preparation of the poling hybrid films

Hybrid films containing chromotrope 2R and Ta (MNb_{2R}) were prepared by spin-coated onto clean SiO_2 glass substrates and Ag/Si(100) substrates with their respective sol, and in the same way, hybrid films containing chromotrope 2R and Ta (MTa_{2R}) were prepared. These hybrid films were dried in a vacuum oven at ambient temperature for 1 day. These films were electrically poled by a corona discharge poling method using a device designed by ourselves to align the chromophores into the three-dimensional inorganic network. They were poled at 100 °C under 9–12 kV cm^{-1} electric field for 30 min.

2.4. Characterization

Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin–Elmer spectrometry in the region of 4000–400 cm^{-1} using KBr pellets. The decomposition temperature of the obtained materials was determined on a TA Instruments Perkin–Elmer X with the heat rate of 10 °C min^{-1} under nitrogen atmosphere. The surface morphology of films was recorded with an atom force microscope (AFM) and tapping mode was used in all the measurements.

The thickness of hybrid films was measured by WJZ-II spectral ellipsometer manufactured by ZHEJIANG OPTICAL INSTRUMENT CO., LTD. The dielectric properties were measured by HP-4292A low-frequency impedance analyzer. The relative permittivity could be calculated by using the equation [18]: $\varepsilon_r = Ct/\varepsilon_0 A$, where C is the capacitance determined from impedance analyzer; t is the thickness of the film, in our experiments the values of t is fit to 9.45×10^{-8} m; ε_0 is vacuum dielectric permittivity, $\varepsilon_0 = 8.85 \times 10^{-12}$ (Fm^{-1}); A is the efficient square of the sample, $A = 7.85 \times 10^{-7}$ m^{-2}.

The pyroelectric coefficient was obtained by digital integral method using the DH-1 digital charge instrument made by Guangzhou Liheng electronic equipment workshop and Sun Yat-Sen University after hybrid films were polarized. The pyroelectric coefficient (P) could be calculated by using the following equation [19]: $P=(\delta Q \Delta N)/(A(T_2 - T_1))$, where δQ is the quantity of discharge per times, $\delta Q = 10^{-11}$ C; $\Delta N = (N_+ - N_-)$, N_+, N_- are the times of discharge shown in positive and negative counter, respectively; T is the temperature; A is the efficient square of the sample.

3. Results and discussion

3.1. Preparation and characterization of the hybrid films

The FT-IR spectrum of MNb_{2R} and MTa_{2R} hybrid films are shown in Fig. 1. In Fig. 1(a), the characteristics absorption

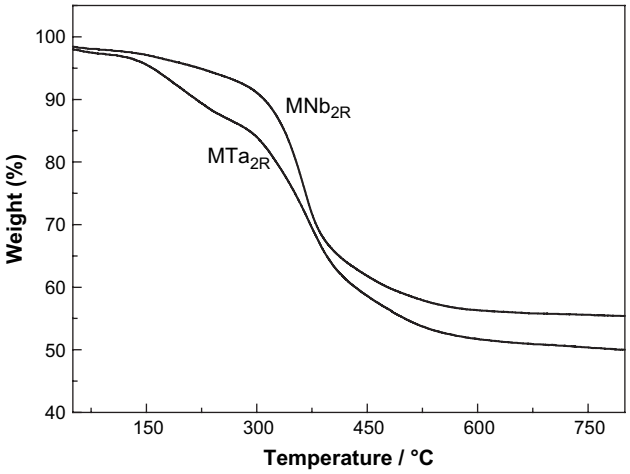

Fig. 3. The TGA of hybrid film.

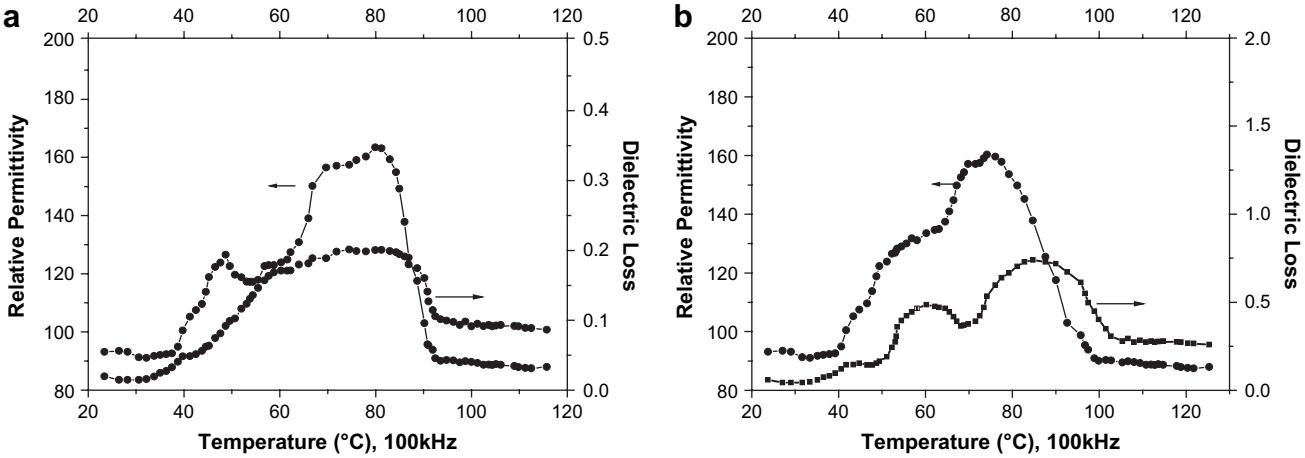

Fig. 4. Variation of ε_r and tan δ of films with temperature: (a) MNb_{2R}; (b)MTa_{2R}.

peaks at 1031 cm^{-1}(C–O–Nb) and 930 cm^{-1}(Si–O–Nb) were observed [20]. The stretching peak of Si–O–Ta at 1035 cm^{-1} was also observed in Fig. 1(b). These results indicated that the dye had been equally distributed into the inorganic network.

As seen in Fig. 2, no phase separation between the organic and inorganic component was observed in AFM images. The results strongly suggested that *C.I. Acid Red 29* was covalently linked to the inorganic network, which can lead to the better pyroelectric property.

3.2. Thermal properties of hybrid material

The thermal stability of 93-nm-thickness MNb_{2R} and 95-nm-thickness MTa_{2R}, which were dried in a vacuum oven at ambient temperature for 1 day, was investigated. The TGA curves as shown in Fig. 3 reveal that there is bulky mass decrease to the hybrid films in the region from 250 °C to 600 °C. The decomposition temperature for MNb_{2R} and MTa_{2R} are estimated to be 360 °C and 375 °C for the 93-nm-thickness MNb_{2R} and 95-nm-thickness MTa_{2R}, respectively.

3.3. Dielectric properties of hybrid films

Fig. 4 shows the changes of relative permittivity (ε_r) and dielectric loss (tan δ) versus the change of temperature of 93-nm-thick MNb_{2R} and 95-nm-thick MTa_{2R}, measured at a frequency of 100 kHz. In Fig. 4(a), there is a broad peak of relative permittivity between 40 °C and 90 °C. There are also other two peaks of the dielectric loss in the same region, which may be caused by the relaxation of domain wall movement of organic components in the hybrid film [21,22]. The average ε_r and tan δ of MNb_{2R} were estimated to be132.8 and 0.18 at 100 kHz between 40 °C and 90 °C, respectively. A strong broad peak of the relative permittivity was observed between 40 °C and 100 °C in Fig. 4(b). The dielectric loss also exhibited two peaks in this region. The average ε_r and tan δ were 122.5 and 0.033 at 100 kHz between 40 °C and 100 °C, respectively.

3.4. Pyroelectric properties of hybrid films

Fig. 5 show the changes of pyroelectric coefficient (p) of 93-nm-thick MNb_{2R} and 95-nm-thick MTa_{2R}, respectively. In Fig. 5(a), there is a broad peak occurred between 80 °C

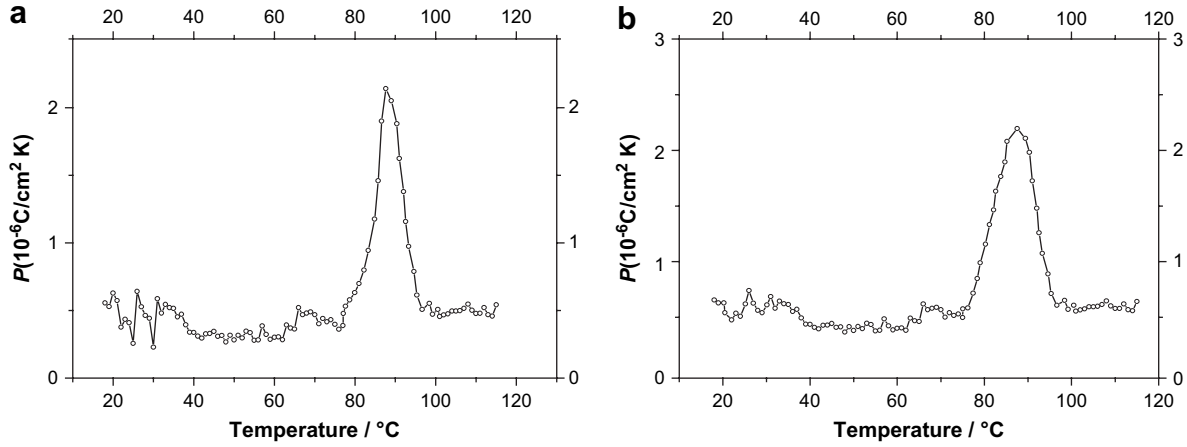

Fig. 5. Variation of the pyroelectric coefficient of films with temperature: (a) MNb_{2R}; (b)MTa_{2R}.

and 100 °C, and the maximal peak appeared at 85 °C with a value of 2.17×10^{-6} C cm^{-2} K^{-1}. The average value of p was calculated to be about 1.82×10^{-6} C cm^{-2} K^{-1} in the region from 80 °C to 100 °C. In the case of 95-nm-thick MTa_{2R} hybrid material, the average value of p was 1.79×10^{-6} C cm^{-2} K^{-1} as shown in Fig. 5(b).

4. Conclusions

The novel organic–inorganic hybrid pyroelectric materials were prepared by sol–gel method. The organic chromophoric group, chromotrope 2R, was covalently bonded to inorganic gel network testified by the combination of IR and AFM measurements. The hybrid films were poled in electric field and showed low relative permittivity, low dielectric loss, and high pyroelectric coefficient. These results suggested that the obtained organic–inorganic hybrid films may be useful as pyroelectric materials.

Acknowledgments

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