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Growth of ferroelectric crystals: 4-Aminopyridinium hydrogen maleate single crystals and their characterization

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Abstract

Single crystals of 4-aminopyridinium hydrogen maleate (4AM) were grown using the slow evaporation solution technique (SEST) from an aqueous solution of 4-aminopyridine and maleic acid at 303 K. Good optical quality single crystals of size $3 \times 7 \times 22$ mm^3 were grown in a period of 40 days. Single crystal and powder XRD confirmed the formation of the 4AM single crystal. FTIR confirmed the functional groups of the grown crystal. Thermal gravimetric analysis studied the thermal properties of the grown crystal. Dielectric study showed higher dielectric permittivity and lower dielectric loss in conventional grown 4AM crystal. The ferroelectric *P–E* hysteresis loop characteristics of the SEST grown 4AM crystal were studied and discussed in detail.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Single crystal; X-ray diffraction

1. Introduction

Ferroelectricity, which enables the electric changing of electric polarization, is attractive for versatile technical applications, such as ferroelectric random-access memories, ferroelectric field-effect transistors and infrared detectors [1]. After the anomalies of Rochelle salt (potassium sodium tartrate tetrahydrate) were first observed in the early twentieth century, the amino compounds have become of great interest due to their distinctive properties, especially their physical characteristics [2]. The anomalies of Rochelle salt were later called ferroelectricity. Ferroelectric layers are of importance in many advanced devices, such as tunable capacitors and ferroelectric random-access memory (FeRAM) [3]. The effectiveness and efficiency of ferroelectric devices depends greatly on the properties of the ferroelectric layer. In essence, each material has distinct properties, and thus is suitable for specific devices. At present, materials exhibit similar ferroelectric characteristics; in this fashion, the applications are limited. The connection between ferroelectric and organic molecules are still being studied now because they pose a new challenge to materials science, and they may find many applications, due to their flexibility and non-toxicity, in the emerging field of organic electronics [4]. After searching through the amino family, the complex of 4-aminopyridine with dicarboxylic acid usually results in heterosynthon [5], and 4-aminopyridine has also been used as a ligand in metal complex that shows nonlinear optical properties (NLO) [6]. The 4-aminopyridine cations incorporated into inorganic, organic–inorganic hybrid, networks may generate an acentric crystal lattice such as the [4-NH_2C_5NH][$SbCl_4$] complex that exhibits interesting ferroelectric properties [7]. 4-Aminopyridinium hydrogen maleate (4AM) possesses a non-centrosymmetrical architecture, and this generally leads to the ferroelectric property. In addition, 4AM single crystals exhibit non-linear optical behavior. However, studies on its ferroelectricity have been limited. The aims of this work were therefore to grow 4AM single crystals and to investigate their physical properties, especially the ferroelectricity.

2. Experimental procedure

The title compound was prepared by mixing equimolar portions of 4-aminopyridine and maleic acid in a 1:1 solution

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of DI water with $ZnSO_4$. In addition, the temperature of the solution was controlled in a water bath with an accuracy of ± 0.1 K throughout the growth process. The temperature was decreased gradually so the solution became saturated, and hence, the 4AM crystals grew. The temperature of the saturated solution was stabilized at about 303 K. Slow evaporation of the solvent enabled a perfect colorless single crystal of the block habit to grow from the saturated solution, as shown in Fig. 1.

3. Characterizations

4-AHM samples were prepared with similar prominent facets and identical thicknesses. Since surface damage generally influences the physical properties of crystalline samples, the defects from the cutting process were removed and minimized by polishing the surface with very fine grits and a lubricant. All the results were confirmed by repeating the characterizations. The microstructure of the crystals was identified using single crystal and powder X-ray diffraction spectroscopy. The functional groups of the crystals were investigated by Fourier-transform infrared spectroscope (FTIR). The thermal properties were studied by thermal gravimetric analysis. Dielectric measurement was performed to investigate the dielectric constant and dielectric loss of the 4AM crystal. The Sawyer-Tower circuit was operated at 273 K to measure the ferroelectric hysteresis of the crystals.

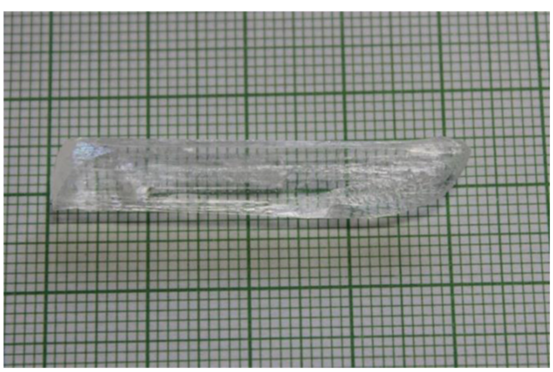

Fig. 1. 4-Aminopyridinium hydrogen maleate crystal.

3.1. Single crystal and powder X-ray diffraction analysis

Single crystals of 4AHM were studied using a BRUKER X-ray diffractometer with Cukα radiation of wavelength 1.54184 Å. A suitable crystal was selected and placed on the diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2 [8], the structure was solved with the ShelXS [9] structure solution program using Direct Methods and refined with the Olex2.refine [10] refinement package using Gauss–Newton minimization. It was observed that the 4AM crystal belongs to the monoclinic, space group $P2_1$, $a=8.149(2)$ Å, $b=5.4689(16)$ Å, $c=10.975(3)$ Å, $\beta=97.47(1)^{\circ}$, $V=485.0(2)$ Å^3, $Z=2$, which was in close agreement with a reported value [11], 1140 reflections measured ($29.5 \leq 2\Theta \leq 121.26$) 928 unique ($R_{int}=0.0357$, $R_{sigma}=0.0735$) points that were used in all calculations. The final R_1 was 0.0755 ($I \geq 2u(I)$) and wR_2 was 0.1930 (all data). The structure of the 4AM single crystal is shown in Fig. 2. The powder X-ray diffraction (PXRD) patterns of the grown 4AM single crystal were recorded over the range 10–70 by employing a BRUKER Diffractometer with Cukα radiation at room temperature. As shown in Fig. 3, the PXRD result reveals that the dominant plane in this 4AM crystal is a (101) plane, and some small peaks can also be observed in the spectrum. These very sharp peaks may show that the 4AM sample is a perfect single crystal; however, some split peaks may reflect a few defects at the surface of the sample or inside the crystal.

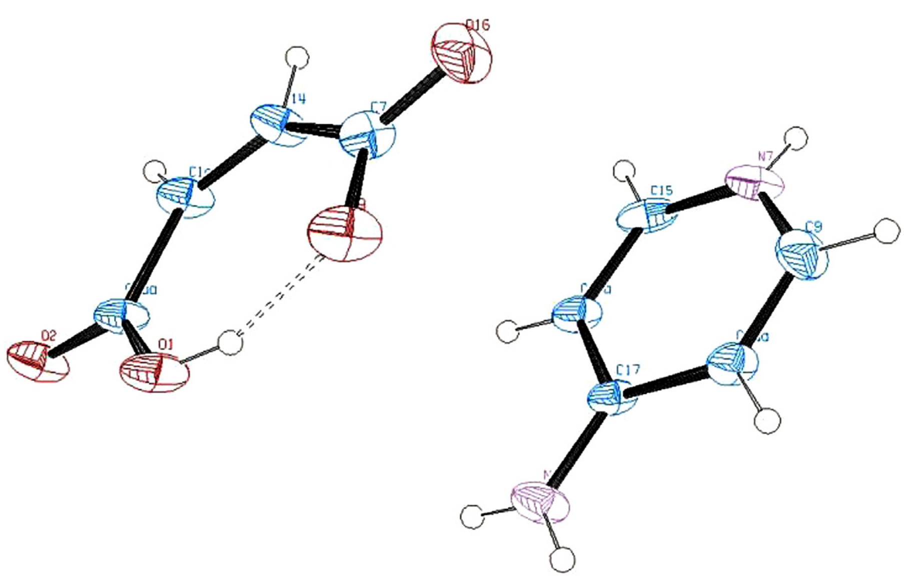

Fig. 2. Structure of 4-aminopyridinium hydrogen maleate single crystal.