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THERMAL BEHAVIOR OF UREA-(*D*) TARTARIC ACID AND UREA-(*DL*) TARTARIC ACID CRYSTALS

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Abstract

The thermal behavior of two new non-linear optical (NLO) materials, urea-(*D*) tartaric acid (UDT) and urea-(*DL*) tartaric acid (UDLT) were studied by using DSC, TG and TMA. The results show that: 1) The two crystals have different melting points but similar decomposition temperatures due to the influences of intermolecular forces, which is attributed to the stereo effects of (*D*)-tartaric and (*DL*)-tartaric acid molecules; 2) There was only thermal expansion and no thermal contraction when the UDT and UDLT crystals were heated; 3) There was no phase transition within the measured temperature range; 4) The thermal expansion of the UDT and UDLT crystals shows a small anisotropy; 5) The specific heats of UDT and UDLT change linearly with temperature in the measured temperature range and the value for UDT is 1.321 J g^{-1} K^{-1} at 320 K while the specific heat of UDLT is 1.357 J g^{-1} K^{-1} at the same temperature.

Keywords: organic inclusion compounds, thermal properties, urea-(*D*) tartaric acid and urea-(*DL*) tartaric acid

Introduction

Urea-(*D*) tartaric acid (UDT) (1) and urea-(*DL*) tartaric acid (UDLT) (2) are two new NLO materials. As new NLO materials, an understanding of their thermal properties and thermal behaviour is very important.

The aim of this work was to study the thermal properties of UDT and UDLT to provide helpful parameters for application of doubling frequency of laser beams.

Experimental

Materials

Both UDT and UDLT were grown from aqueous solution by the temperature-lowering method. Dimensions of the single crystals used in this work were

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Table 1 Crystal data of UDT and UDLT

	UDT	UDLT
Crystal class	orthorhombic	monoclinic
Point group	222	2
Space group	$P2_12_12_1$	$P2_1$
Lattice parameters	a = 17.229 Å b = 9.824 Å c = 5.056 Å v = 854.52 Å^3 z = 4	a = 7.697 Å b = 23.331 Å c = 4.873 Å β = 100.82° v = 859.51 Å^3 z = 2

45×19×19 mm^3 for UDT and 55×23×15 mm^3 for UDLT (for their crystal data see Table 1). UDT used for the TMA experiment was cut as a right prism with thickness of 3.08, 3.88 and 4.8 mm along a-, b- and c-oriented crystal, respectively. UDLT used for TMA experiment was manufactured as a right prism with thickness of 10.18, 2.68, 4.60 mm along X_1 (perpendicular to b and c), X_2 (twofold symmetry axis b) and X_3 (crystallization direction c) as well as a sample (4.16 mm thick) along the direction at 45° to the directions of the axes X_1 and X_3.

Experimental equipment and conditions

The DSC curves of UDT and UDLT were recorded by using a Perkin-Elmer DSC-2C differential scanning calorimeter. The conditions of DSC measurements were as follows: The standard average specific heat of sapphire, within the temperature range of 300 –350 K is 0.8270 J g^{-1}°C^{-1}, and the value measured in our laboratory is 0.8372 J g^{-1}°C^{-1}, with a relative standard deviation of 1.23%. This shows that the method of measuring the specific heat used in this work is reliable. The TG curves and TM curves of UDT and UDLT were obtained using Perkin-Elmer TGS-2 and TMA equipments.

Results and discussion

Figures 1 and 2 show the DSC curves of UDT and UDLT. The TG curves of UDT and UDLT are presented in Figs 3 should be turned over and 4. Figure 5 shows the temperature dependence of the specific heats of UDT and UDLT crystals measured from 310 to 370 K. The thermal expansion coefficients of UDT and UDLT are listed in Table 2. From Figs 1–5, the following conclusions can be drawn:

1) The melting point of the UDT crystal is 96.3°C, lower than those of its constituents, urea (132°C) and (*D*)-tartaric acid (170°C). However, the melting

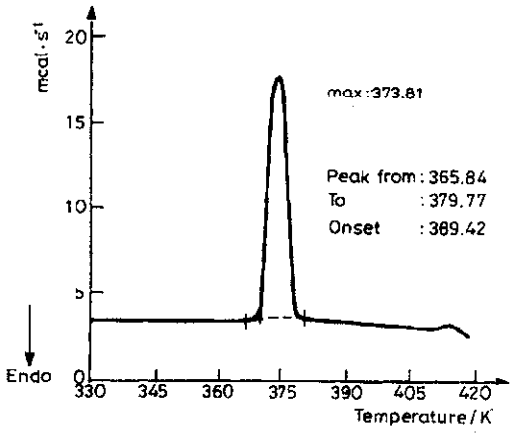

Fig. 1 DSC curve of UDT crystal. (Mass: 4.73 mg; scan rate: 20.0°C min^{-1})

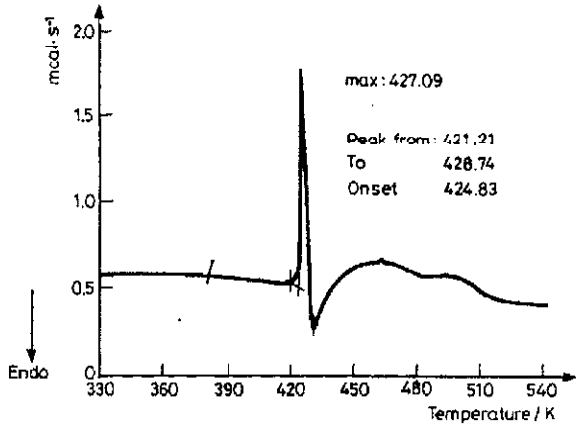

Fig. 2 DSC curve of UDLT crystal. (Mass: 3.01 mg; scan rate: 10.0°C min^{-1})

Table 2 Thermal expansion coefficients of UDT and UDLT

	α_{ij}	Values($\times 10^{-5}$ K^{-1})
UDT	α_{11}	5.23
	α_{22}	3.86
	α_{33}	3.57
UDLT	α_{11}	2.75
	α_{22}	4.95
	α_{33}	7.28
	α_{13}	2.34

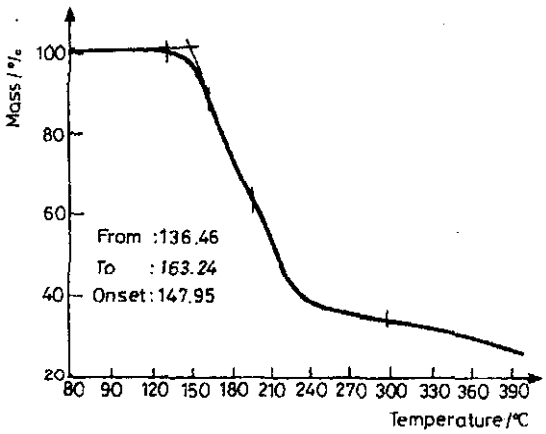

Fig. 3 TG curve of UDT crystal. (Mass: 3.14 mg; scan rate: 10.00°C min^{-1})

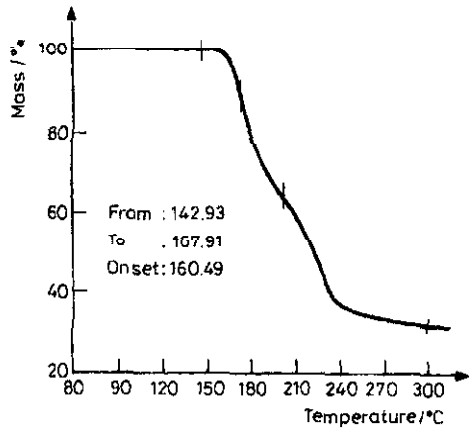

Fig. 4 TG curve of UDLT crystal. (Mass: 1.98 mg; scan rate: 10.00°C min^{-1})

point of the UDLT crystal is 151.7°C, lower than that of (*DL*)-tartaric acid but higher than that of urea, and 55.4°C higher than that of the UDT crystal. The difference in melting point can be ascribed to the difference in the hydrogen-bond strengths in (*D*)-tartaric acid and (*DL*)-tartaric acid molecules;

2) The decomposition temperatures of UDT and UDLT are 148.0 and 160.5°C, respectively. The shapes of the TG curves of UDT and UDLT are similar;

3) There is no water of crystallization in UDT and UDLT in spite of the fact that (*DL*)-tartaric acid usually contains one water of crystallization;

4) The specific heats of UDT and UDLT change linearly with temperature in the measured temperature range and the value for UDT is 1.321 J g^{-1} K^{-1} at 320 K while the specific heat of UDLT is 1.357 J g^{-1} K^{-1} at the same temperature;

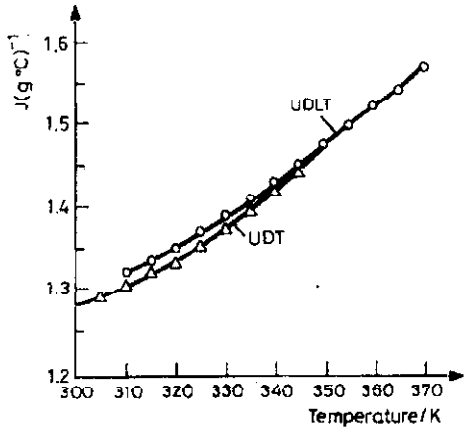

Fig. 5 Temperature dependence of the specific heat of UDT and UDLT crystal. (Mass: 9.23 and 9.70 mg; scan rate: 10.00°C min $^{-1}$)

5) There was only thermal expansion and no thermal contraction when the UDT and UDLT crystals were heated;

6) There was no phase transition within the measured temperature range;

7) The thermal expansion of the UDT and UDLT crystals show a small anisotropy.

From the data of UDT and UDLT crystals given above, we have the impression that the UDLT crystal which has a higher melting point, is better than UDT crystal in respect of thermal stability. The experiment shows that the thermal expansion is uniform over the measured temperature range. The expansion coefficients coincide with the DSC results indicating that there is no phase transition within the temperature range shown. Thanks to its larger specific heat, UDLT absorbs more energy when a laser beam is focused on it, which helps maintain a smaller thermal gradient inside it.

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