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THE LOW TEMPERATURE THERMAL PROPERTIES OF POTASSIUM TANTALATE NIOBATE CRYSTAL

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Abstract

The thermal properties of KTN crystal were investigated at low temperatures by DSC and TM. The phase transition enthalpies and the average specific heats of the crystal were measured. Results are analyzed and discussed.

Keywords: DSC and TM methods, KTN crystal, phase transition

Introduction

Potassium tantalate niobate ($KTa_{1-x}Nb_xO_3$, KTN) crystal, a perfect solid-solution of potassium niobate ($KNbO_3$) and potassium tantalate ($KTaO_3$), has important applications in the field of nonlinear optics for its excellent electrooptic and photorefractive properties. When cooled from high temperature, KTN crystal exhibits different phases in a sequence of cubic–tetragonal–orthorhombic–rhombohedral. The phase transition temperatures of KTN crystals vary with the different Nb contents x. According to Hellermann *et al.* [1], KTN crystals are in cubic phase at the room temperature when $x<0.4$, in tetragonal when $0.4\leq x<0.57$ and in orthrohombic when $x>0.57$. The KTN crystal used in our experiment has a Nb content $x=0.37$, in other words, its composition is $KTa_{0.63}Nb_{0.37}O_3$.

Many physical properties change abruptly near the phase transition temperatures. Therefore, the phase transition behaviours can be investigated by monitoring its various properties. It has been reported in [2] that the phase transition behaviours of KTN crystals have been studied by measuring its dielectric properties. The phase transition and thermal properties of KTN crystals have never been studied by means of DSC and TM so far. In this paper, we report the results of phase transition enthalpies and the average specific heats of KTN crystal, and compare the results obtained from DSC and those from TM.

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Experimental

The KTN crystal used in our experiment was grown by the flux pulling method. A smooth face of the plate sample was polished to ensure good contact with the sample holder. Similar samples were used in both DSC and TM.

The instruments used are the Perkin-Elmer DSC-2C differential scanning calorimeter and TMS-2 thermomechanical analyzer (equipped with a 3600 data station). The experiment was carried out within the temperature range of 110–310 K with liquid nitrogen as the cooling medium. The sample was heated at a rate of 10 deg·min^{-1} under a dynamic helium atmosphere (20 ml·min^{-1}).

The instruments were calibrated with cyclohexane and standard sapphire before experiments.

Results and discussion

1. The standard average specific heat of sapphire, within the temperature range of 110–310 K, is 0.5305 J/g·K [3], and the value measured in our laboratory is 0.5246 J/g·K, with a relative deviation of 3.0%. The specific heat curve measured is shown in Fig. 1.

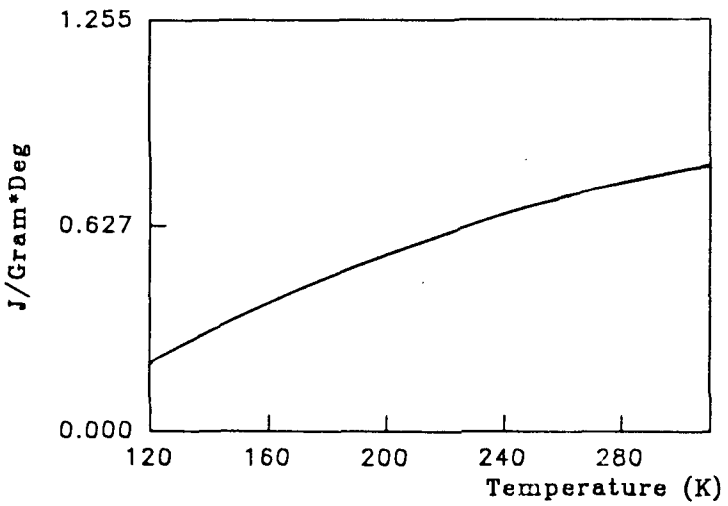

Fig. 1 The specific heat curve of sapphire

The DSC curve of cyclohexane is shown in Fig. 2. There are two phase transitions within the temperature range of 110–310 K: one is a solid–solid phase transition and another is melting. The phase transition temperatures and enthalpy values measured on our instrument are listed in Table 1 together with the standard ones [4].

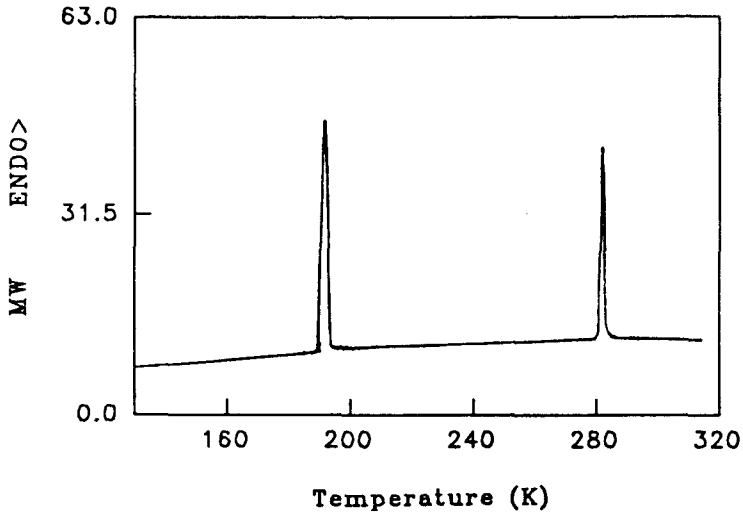

Fig. 2 DSC curve of cyclohexane

Table 1 The measured and standard values of the phase transition temperature and enthalpy of cyclohexane

Transition type	Transition temperature /K			Enthalpy /J·g^{-1}		
	Standard	Measured	Deviation %	Standard	Measured	Deviation %
Solid-solid	186.1	187.93	−1.0	79.58	85.94	−7.9
Melting	279.7	278.41	0.5	31.25	32.72	−4.7

From the comparison between the measured and standard values of these two materials, we can conclude that our instruments possess good reliabilities.

2. DSC is an important method for investigating crystal phase transitions and their thermal properties. The phase transition temperatures and enthalpies of $KTa_{0.63}Nb_{0.37}O_3$ were measured within the temperature range of 110–310 K. The instrument and experimental conditions were the same as above except that the heating and cooling rates were 20 deg·min^{-1}. The heating and cooling DSC curves are shown in Figs 3 and 4, respectively. The phase transition temperatures and enthalpies are listed in Table 2.

The phase transition temperatures measured are consistent with those obtained by measuring the dielectric constant [5]. It is obvious that all three phase transitions are of the first order.

As a perfect solid-solution crystal, the composition of KTN changes as its growing temperature was lowered. Therefore, the composition of its crystal as grown is difficult to be determined exactly from the composition of the starting materials; it is also difficult to be measured exactly by chemical analysis which

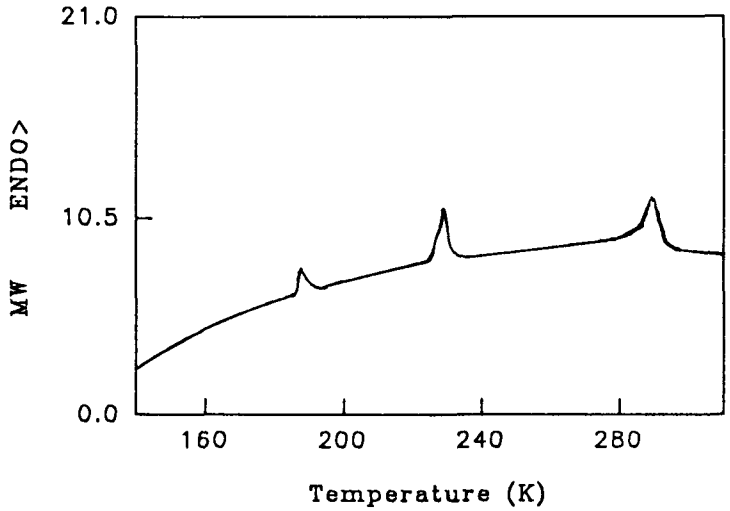

Fig. 3 Heating DSC curve of KTN

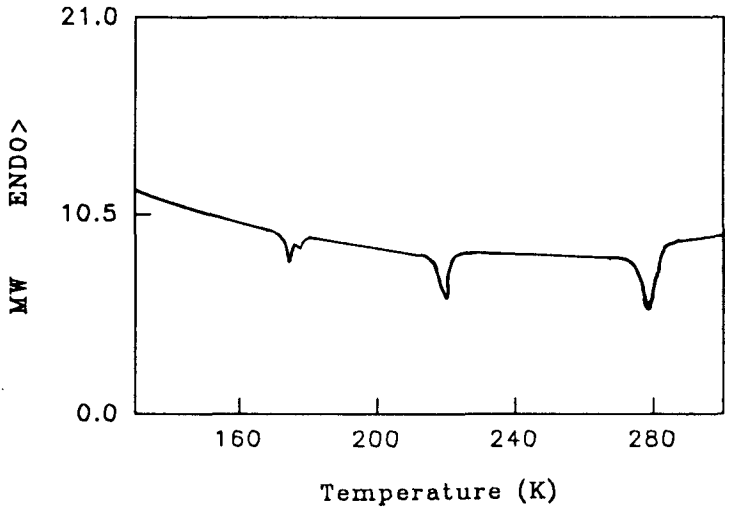

Fig. 4 Cooling DSC curve of KTN

are often found to be too complicated. However, it can be calculated basing on the linear relationship between the Nb content and the Curie temperature, i.e., $T_c(K)=676x+32$ [6], where T_c is determined by DSC. This method for determining the composition of KTN crystal is thought to be simple and prompt, and the results are satisfactorily reliable.

3. The specific heats of the KTN crystal were measured under the same conditions as the DSC measurements except that the heating rate is 10 deg·min^{-1}. The results are shown in Fig. 5.

Table 2 The phase transition temperatures and enthalpies of KTN crystal

	Cubic-tetrag.		Tetrag.-ortho.		Ortho.-rhomb.	
	T/K	Enthalpy /J·g^{-1}	T/K	Enthalpy /J·g^{-1}	T/K	Enthalpy /J·g^{-1}
Heating	284.34	0.33	226.80	0.13	186.33	0.04
Cooling	281.86	–0.29	220.52	–0.13	175.63	–0.08

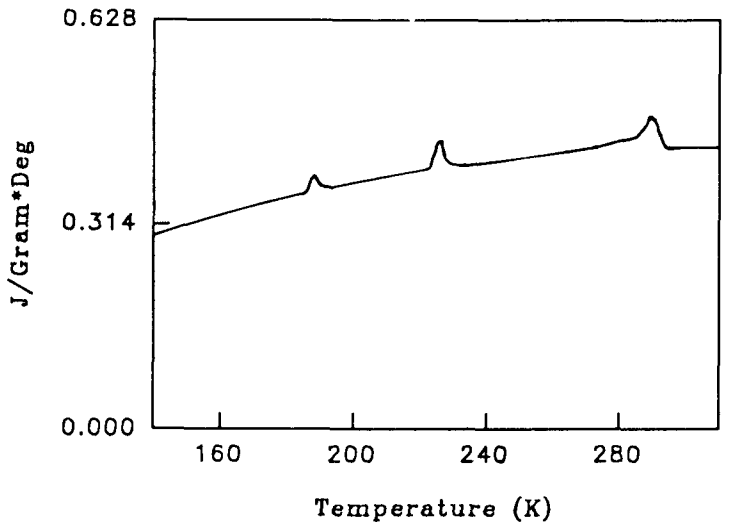

Fig. 5 The specific heat curve of KTN

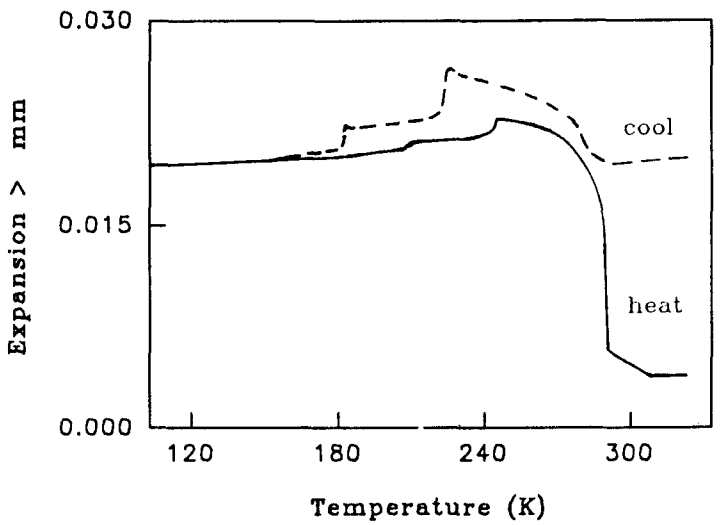

Fig. 6 TM curves of KTN

According to the measurements and calculations, the average specific heats of the KTN crystal in phases are 0.451 J/g·K (cubic), 0.436 J/g·K (tetragonal), 0.405 J/g·K (orthorhombic) and 0.381 J/g·K (rhombohedral), respectively. The specific heat is an important physical property and is a valuable reference for the study and application of KTN crystal.

4. For further study of the phase transitions of KTN crystal at low temperatures, its linear expansion was measured and the results are shown in Fig. 6.

In Fig. 6, the solid line is the heating curve and the dotted line is the cooling curve. It is evident that three abrupt changes occur in both curves, indicating three phase transitions within this temperature range. The phase transition temperatures measured on this figure are approximately identical with those measured by DSC. It is well known that TM method is also one of the important means which can be employed to study the phase transitions of materials.

Conclusion

Both DSC and TM are important means for the study of crystal phase transitions. The results obtained by these methods indicate that all the three solid–solid phase transitions of KTN crystal are of the first order. These methods can be used to determine the Curie temperature of KTN crystal, and as a result, its composition can be obtained in a prompt and convenient way.

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Zusammenfassung — Mittels DSC und TM wurden bei niedrigen Temperaturen die thermischen Eigenschaften von KTN-Kristallen bestimmt. Die Phasenumwandlungsenthalpien und die mittleren spezifischen Wärmen der Kristalle wurden gemessen. Die Ergebnisse wurden ausgewertet und diskutiert.