

Phase Transition and Effect of Small Amount of Water Included in K_2ZnCl_4 Crystal

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(Received September 19, 1994)

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Absorption/desorption of small amount of water and its effects on the phase transition at 146 K in K_2ZnCl_4 were studied by FT-IR spectroscopy and adiabatic calorimetry. Existence of water molecule in absorbed crystal was substantiated by FT-IR spectra. It was verified by heat capacity measurements on single crystals of large size that the water is absorbed in the crystal. The reproducibility and reversibility of the absorption/desorption were confirmed by repeating heat/ventilation treatment and exposure of the sample to the laboratory atmosphere.

1. Introduction

K_2ZnCl_4 belong to a group of ferroelectrics with general formula A_2BX_4 ($A=K, Rb$; $B=Zn, Co$; $X=Cl, Br$) which have been extensively studied of the successive phase transitions¹⁾. The space group of the highest temperature phase (so-called "normal phase") and of low temperature ferroelectric phase (commensurate phase) are $Pmcn$ and $P2_1cn$, respectively, and the intermediate phase has an incommensurate structure with a wave vector $q = (1 - \delta) c^*/3^2$. The normal-incommensurate phase transition

and the incommensurate-commensurate phase transition (so-called "lock-in transition") occur at 553 and 403 K, respectively^{3),4)}. In K_2ZnCl_4 , another phase transition has been known at 146 K⁵⁾⁻¹²⁾, below which the structure is $Clc1$ ¹³⁾.

Recently heat capacities of K_2ZnCl_4 have been measured between 10 and 300 K by means of adiabatic calorimetry¹⁴⁾, and it has been found that the heat capacity anomaly due to the phase transition at 146 K is strongly influenced by the heat/ventilation treatment on the sample. The data of typical two series of measurements are shown in Fig.1. A broad anomaly

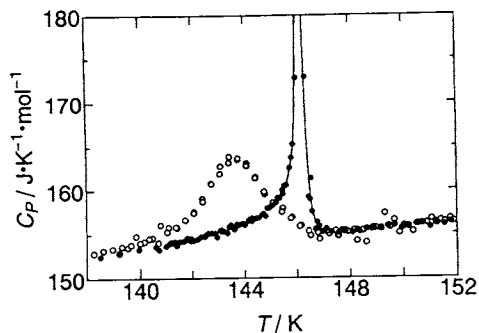


Fig.1 Heat capacity anomalies due to the phase transition in K_2ZnCl_4 . (○) as grown crystal, (●) ground and dried under vacuum at 370 K.

is seen with a maximum at about 144 K for the as-grown crystals from the aqueous solution (open circle in Fig.1), while a sharp anomaly due to the phase transition is observed at 146.24 K for the sample ground and dried under vacuum at 370 K (close circle). As such a drastic change of behavior at the phase transition was supposed to be caused by release of water from the sample, several series of measurements were made on the sample treated under various conditions. After the second series of measurements on the ground and dried sample, the specimen was exposed to the laboratory atmosphere (air-conditioned room) for 3 weeks. The exposure resulted in slight increase (0.01 g) in the weight of the sample (20 g), and then the third measurements showed a broad anomaly very similar to that of the as-grown crystals. Thereafter the sample was dried again under vacuum at 420 K (above the lock-in transition), and the fourth measurements showed a sharp anomaly due to the phase transition which coincided with the data of the second measurements. The final data of the heat capacities of K_2ZnCl_4 that was ground and dried under vacuum at elevated temperatures (irrespective of the temperature whether above or below the lock-in transition) are shown in Fig.2. The enthalpy and entropy of transition were determined as $57.16 \text{ J}\cdot\text{mol}^{-1}$, and $0.387 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.

The reproducibility and reversibility of the heat/ventilation and the exposure effects have been thus confirmed on the phase transition phenomena in K_2ZnCl_4 . However, there have still been some open questions; existence of water in the powder sample and

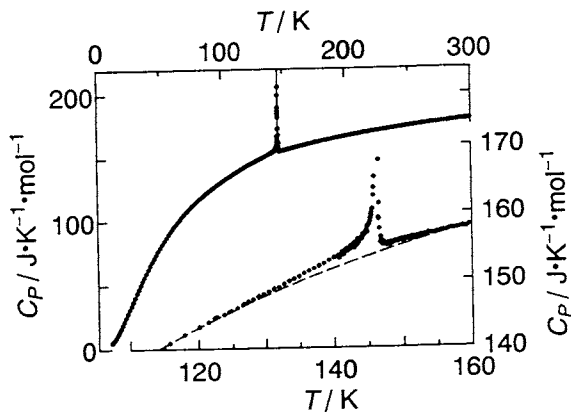


Fig.2 Molar heat capacity of K_2ZnCl_4 ground and dried under vacuum at 370 K. Dashed line in the inset denotes the base-line for estimating the transition entropy.

effects of grinding the sample. The purpose of the present study is to detect the water in the powder sample by FT-IR experiments and to see the phase transition phenomena by heat capacity measurements on large crystals without grinding.

2. Experimental

Sample preparation

K_2ZnCl_4 crystals were grown in an aqueous solution of KCl and $ZnCl_2$ by slow evaporation of water at 35°C ¹⁴. The colorless and transparent single crystals exhibited obvious crystal habit in the shape. The as-grown crystals were ground and treated in a similar manner to the previous experiments of heat capacity measurement¹⁴, and used for the present FT-IR experiments. On the other hand, the as-grown crystals of large size (5-15mm) were used without grinding for the present study by heat capacity measurements.

Infrared spectroscopy

FT-IR experiments were carried out by using a Fourier Transform Infrared Spectrometer (FT-IR-3, JASCO Corporation) at room temperature. The powdered sample was pressed into the sample holder (10 mm in diameter and 2 mm in thickness), which was then treated under various conditions. To avoid the deliquescent effects the holder loaded with sample was set into the FT-IR apparatus quickly in an atmosphere of dried air and each experiment was carried out in 2 hours in the air-conditioned room.

After the first measurements, the loaded holder was dried under vacuum at 370 K (below the lock-in transition) and then used for the second measurements. The third measurements were made on the sample treated under vacuum at 420 K (above the lock-in transition). To confirm the reproducibility and reversibility of absorption/desorption of water, the loaded holder was exposed to the laboratory atmosphere for 1 day and then used for the fourth measurements.

Heat capacity measurements

Heat capacity measurements were made by using a home-made adiabatic calorimeter. The details of the apparatus and the procedure of the experiments are available¹⁵⁾. The calorimeter vessel was newly constructed for the use of large size of crystals, and thus the as-grown crystals of K_2ZnCl_4 of 5-15 mm could be loaded for the present study. After the first series of measurements on the as-grown crystals, the sample was dried under vacuum at 370 K for 1 week without grinding and used for the second series of measurements.

3. Results and discussion

The FT-IR transmission spectra obtained at room temperature for the powdered sample of K_2ZnCl_4 are shown in Fig.3. In the first measurements ((a) in Fig.3), the absorption bands caused by water included in the sample are clearly seen at 3500 cm^{-1} assigned

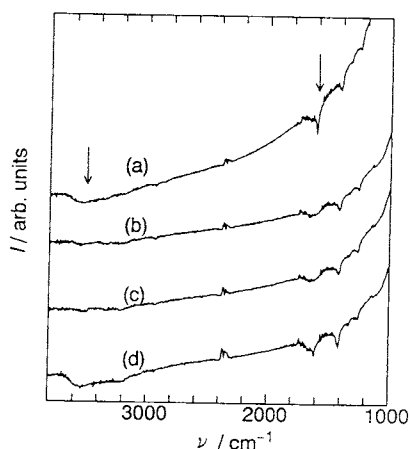


Fig.3 FT-IR transmission spectra of powdered K_2ZnCl_4 at room temperature. (a) as-grown sample, (b) dried under vacuum at 370 K, (c) dried under vacuum at 420 K, (d) exposed to laboratory atmosphere.

to the ν_1 or ν_3 mode of H_2O molecule and at 1600 cm^{-1} assigned to the ν_2 mode, which are in fairly good agreement with the previous reports on single crystal of K_2ZnCl_4 by Zhang *et al.*¹⁶⁾. The second measurements made on the sample dried under vacuum at 370 K showed no absorption bands due to H_2O ((b) in Fig.3). The spectrum of the sample dried at higher temperature 420 K (the third measurements, (c) in Fig.3) is the same as that of the second measurements. After exposure to the laboratory atmosphere for 1 day, the absorption bands of water molecule were observed again as shown in (d) in Fig.3 (the fourth measurements). Therefore, the FT-IR spectroscopy substantiated the existence of water in the as-grown crystals from the aqueous solution. The release of water from the sample by heat/ventilation treatment and the reproducibility and reversibility of the phenomena were also confirmed. Thus, all the results of the present FT-IR experiments are compatible with those of the previous heat capacity measurements¹⁴⁾ (see Figs.1 and 2).

However, such phenomena described above might be caused by some effects of grinding the crystals; water might be not absorbed in the crystals but adsorbed on the surface of the fine powder of K_2ZnCl_4 and the phase transition might be affected by electric field and/or stress induced by the adsorbed water molecules. To answer this final question, heat capacity measurements were made on as-grown crystals of large size (5-15 mm); several pieces of crystals which were colorless and transparent with obvious crystal habits. The amount of sample used for the first series of measurements was 2.46236 g (0.00862784 mol) which contributed about 14% to the total heat capacity including that of the calorimeter vessel. After the first series of measurements, the crystals were dried under vacuum at 370 K for 1 week without grinding, and then the second series of measurements was made. Any change such as a crack did not occur in the crystals during the heat treatment. The results of the two series of measurements are shown in Fig.4. A broad anomaly is seen with a maximum at about 144 K for the as-grown crystals, and a sharp anomaly is observed in the second series of measurements. These results coincide with those of the previous study on powdered sample. Now it turned out that water is

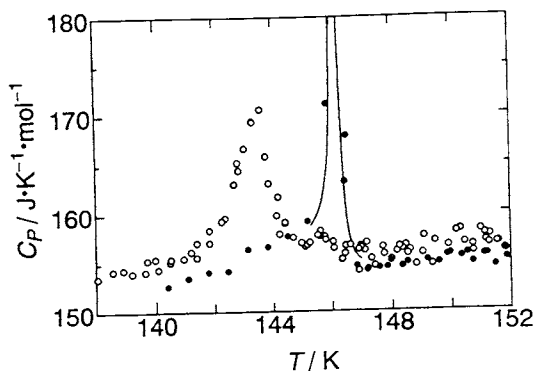


Fig.4 Heat capacity anomalies due to the phase transition in large size (5-15 mm) crystals of K_2ZnCl_4 . (○) as-grown crystal, (●) dried under vacuum at 370 K without grinding.

absorbed in the crystals of K_2ZnCl_4 . There should be many domain walls in the crystals¹⁷⁾, and the water molecule might be mobile in the boundaries.

In conclusion, the phase transition at 146 K in the crystal of K_2ZnCl_4 is strongly influenced by small amount of water included in the crystal. The existence of water molecule in as-grown crystal was substantiated by FT-IR spectroscopy. It was verified by the heat capacity measurements on single crystals of large size that the water is not adsorbed on the surface but absorbed in the crystal. The reproducibility and reversibility of the absorption/desorption phenomena have also been confirmed. The desorption is realized by drying the sample under vacuum at elevated temperatures irrespective of the temperature whether above or below the lock-in transition.

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要 旨

K_2ZnCl_4 における微量の水の吸収・脱離と146Kの相転移への影響をFT-IRおよび断熱型熱量計によって調べた。結晶中の水分子の存在はFT-IRスペクトルによって明らかになった。大きな粒径の結晶を用いた熱容量測定によって、水は結晶内に吸収されることがわかった。熱処理と試料を室内の雰囲気にとらす実験をくり返すことによって、吸収・脱離の再現性と可逆性を確かめた。