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DSC, DTA and TG studies on structural phase transitions in Tl_2ZnCl_4

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Abstract

Among A_2BX_4-type compounds belonging to the pseudo-hexagonal β-K_2SO_4 structure known to form incommensurate (IC) phases at low temperatures, the phase transition sequence in Tl_2ZnCl_4, where Rb^+ ions in the representative compound Rb_2ZnCl_4 were substituted by Tl^+ ions with a similar ionic radius, was investigated by the differential thermal analysis (DTA) and the differential scanning calorimetry (DSC). The composition of a hydrous compound which was obtained by keeping under the atmosphere was determined to be $Tl_2ZnCl_4 \cdot 1.5H_2O$ by the thermogravimetric (TG) analysis.

Keywords: Tl_2ZnCl_4; Phase transition; Sr_2GeS_4 structure; β-K_2SO_4 structure; Hydration

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1. Introduction

A_2BX_4-family compounds containing isolated tetrahedral BX_4^{2-} ions form orthorhombic β-K_2SO_4 (*Pnma*, $Z=4$) or monoclinic Sr_2GeS_4 ($P2_1/m$, $Z=2$) structures. Many compounds with the β-K_2SO_4 (*Pnma*, $Z=4$) structure undergo phase transitions to incommensurate (IC) phases at low temperatures [1]. Previously, we reported ^{133}Cs NMR results in Cs_2CdBr_4, Cs_2HgBr_4 [2], Cs_2CdI_4 [3] and Cs_2HgCl_4 [4], which take the β-K_2SO_4 (*Pnma*, $Z=4$) structure, and discussed the lattice dynamics in IC phases and the mechanism of phase transitions concerning with the difference in interionic interactions. On the other hand, all compounds of Sr_2GeS_4 ($P2_1/m$, $Z=2$) type have no IC phase. Some of the latter compounds transform from α phase with the Sr_2GeS_4 structure to β phase with the β-K_2SO_4 structure, so-called the α–β phase transition at a high temperature $T_{\alpha-\beta}$ [5–7]. Below $T_{\alpha-\beta}$, the Sr_2GeS_4 structure is stable than the β-K_2SO_4 type, but often the latter can exist as a supercooled metastable state [8]. We have discussed that the difference between Cs_2MX_4 compounds with Sr_2GeS_4 and β-K_2SO_4 structures was induced by the partial covalency, which has been qualitatively estimated from values of NMR chemical shift and spin-lattice relaxation time T_1 [9].

Tl_2ZnCl_4 is a compound in which Tl^+ substitutes for Rb^+ with a close ionic radius in the representative incom-

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mensurate compound Rb_2ZnCl_4 [1,10,11]. The former compound was reported to show the possibility of an interesting phase transition sequence containing α–β phase transitions into incommensurate [12] and ferroelectric phases in the low-temperature range [13]. In the present study, Tl_2ZnCl_4 is investigated by measuring differential thermal analysis (DTA), X-ray powder diffraction, differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis.

2. Experimental

Tl_2ZnCl_4 crystals were grown by cooling a molten mixture containing stoichiometric amounts of TlCl (purity 99.999%) and $ZnCl_2$ (purity 99.9%) purchased from Aldrich and Wako Pure Chemical Industries, respectively. The crystalline powder obtained was dried in vacuo and then sealed in glass tubes with nitrogen gas for the differential thermal analysis (DTA), which was measured between 100 and 450 K on a heating rate of about 3 K/min to determine possible phase transition temperatures. The sample temperature was determined within ±0.2 K using a chromel–constantan thermocouple. The X-ray powder diffraction was measured for an as-grown sample at 300 and 400 K and for the other sample obtained by keeping under the atmosphere at room temperature by Rigaku 1100S and 2500VHF and Phillips X'Pert PW3050/00 diffractometers. The DSC measurement was performed for an as-prepared sample with a Rigaku DSC8230 in the range of 130–420 K at a heating rate of 5 K/min. The TG–DTA measurement was performed for the sample kept under the ambient atmosphere with a Rigaku TG8120 in the range of 300–520 K on a heating rate of 5 K/min.

3. Results and discussion

A large and a small endothermic anomaly at 329 and 365 K, respectively, were detected in the DTA measurement for an as-grown sample on the first heating run up to 400 K after cooling from room temperature to 100 K. In this process, the thermal anomaly around 330 K disappeared and a new anomaly appeared at 169 K on the following heating process in the temperature range of 100–400 K. The small anomaly at 365 K remained in this process. These results agree well with recently reported DTA and dielectric results [13]. The phase transition sequence obtained is discussed below. The large anomaly around 330 K in the first heating is considered to be a so-called α–β phase transition as observed in some of the A_2BX_4 family substances with the Sr_2GeS_4 structure [5–7]. Since the α–β transition was reported to have strong nature of the first-order transition [14], the sample is expected to show a supercooled phase transition sequence. The anomalies at 169 and 365 K is considered to indicate lock-in and normal-incommensurate phase transitions, respectively. Supercooled crystals of Tl_2ZnCl_4 indicate (ferroelectric commensurate)–incommensurate–(β-K_2SO_4 structure normal phase) transition sequence from the analogy to that in Rb_2ZnCl_4.

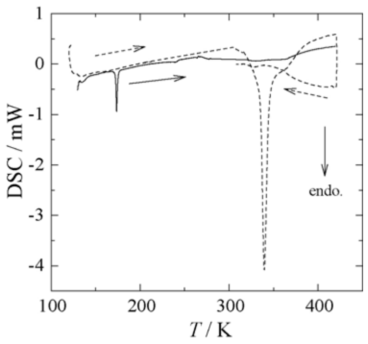

Fig. 1. DSC curves for the as-grown sample (dashed line) and the annealed one (solid line). The sample temperature was increased at a rate of 5 K/min and the negative heat flow is endothermic.

Similar results were also observed in the DSC measurement shown in Fig. 1. Phase transition temperatures, enthalpies ΔH and entropies ΔS are estimated as 330 ± 5 K, ca. 2.3 kJ mol^{-1} and ca. 7 J K^{-1} mol^{-1} for the α–β phase transition and 170 ± 2 K, 0.20 ± 0.03 kJ mol^{-1} and 1.2 ± 0.2 J K^{-1} mol^{-1} for the lock-in one, respectively.

The X-ray diffraction patterns in the as-grown sample at 300 K and that heated up to 400 K are shown in Fig. 2(a) and (b). These patterns (a) and (b) were attributable to Sr_2GeS_4 and β-K_2SO_4 structures, respectively. This result supports the above interpretation of the phase-transition sequence.

We found that the X-ray powder diffraction pattern of the sample kept under the ambient atmosphere for several days shown in Fig. 2(c) was different from (a) and (b) in the as-grown sample. This result indicates that Tl_2ZnCl_4 is hydrated by the absorption of the atmospheric water. In the TG analysis of this hydrated sample, the decrease of about 4% in weight with the dehydration was observed as shown in Fig. 3. The composition of the hydrated compound kept under the ambient atmosphere was determined to be $Tl_2ZnCl_4 \cdot 1.5H_2O$.

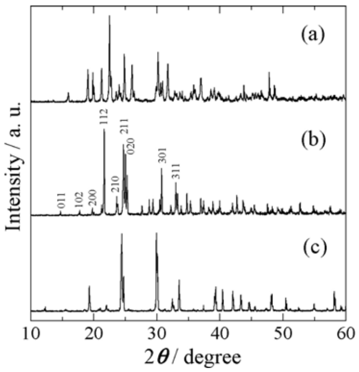

Fig. 2. X-ray diffraction patterns of the as-grown sample measured at 300 (a) and 400 K (b) and the hydrated samples at room temperature (c). Miller indices of several representative peaks of β-K_2SO_4 structure are indicated.

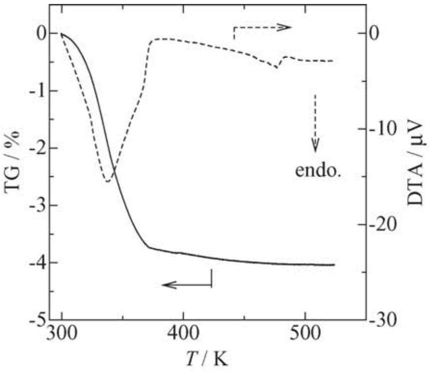

Fig. 3. TG–DTA curves of the hydrated sample on heating. The dashed and solid lines correspond to TG and DTA curves, respectively. The sample temperature was increased at a rate of 5 K/min and the negative TG and negative DTA values indicate the decrease in weight and endothermic, respectively.

Acknowledgments

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