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Structural studies on the phase transition of rubidium formate[1]

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Abstract

The thermal phase transition of rubidium formate, observed at 363 K, was studied by means of thermal analysis and X-ray diffraction method. The transition was found to be a reversible first-order transition. In the phase transition, the orthorhombic phase ($Pca2_1$) with lattice constants a=9.229(1), b=4.630(2) and c=7.408(2) Å, was transformed to the monoclinic phase ($P2_1/m$) with one of a=4.6552(4), b=4.6528(7), c=7.5170(6) Å and γ=97.610(6)°. The values of the enthalpy, ΔH_{tr}, and entropy change, ΔS_{tr}, for the transition were 0.42±0.02 kJ mol^{-1} and 1.16±0.05 J K^{-1} mol^{-1}, respectively. Although the relative positions of rubidium atoms hardly changed in the phases before, and after, the transition, the orientation of formate ions differed in both the phases. The values of ΔH_{tr} and ΔS_{tr} seem to reflect a slight change of structure in the orientation of formate ions. © 1998 Elsevier Science B.V.

Keywords: Rubidium formate; Thermal analysis; Thermal phase transition; X-ray diffraction method

1. Introduction

Thermal properties of alkali metal formates have been studied by Shishido and Masuda [1–3]. These formates decomposed through two stages. In the first stage, the formates decomposed to form the respective carbonates and oxalates, and the oxalates thus formed decomposed to carbonates and carbon monoxide in the second stage. Although they described the decomposition process and the atmospheric effect on the decomposition in detail, they scarcely referred to the thermal phase transitions observed before melting of these formates.

Ferloni et al. [4] reported the values of enthalpy and entropy changes for alkali metal formates; however, they have not mentioned the structural changes of the phases obtained before, and after, the phase transitions.

Hashimoto et al. [5–9] studied the phase transitions of alkali metal formates by means of thermal analysis and powder X-ray diffraction measurement and determined the lattice parameters of both the phases before, and after, the transitions of these formates. However, they could not determine the crystal structure of each phase.

The crystal structures for both phases of cesium formate were determined by Masuda et al. [10] using the Rietveld analysis [11,12] of their X-ray powder

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diffraction profiles. They also discussed the relationship between the values of the enthalpy and entropy changes and the structural changes for the phase transition.

In this paper, the crystal structure of rubidium formate before transition is determined by means of the single-crystal X-ray diffraction method, and that after the transition is determined with the help of the Rietveld method [11,12] by analyzing the X-ray powder diffraction profiles. The relationship between enthalpy (ΔH_{tr}) and entropy (ΔS_{tr}) changes and the structural changes for the phase transition is discussed briefly.

2. Experimental

2.1. Materials

Rubidium formate was directly synthesized from formic acid and saturated aqueous solution of rubidium carbonate. After slow evaporation of the mixture, a residual crystalline material was obtained. This compound was recrystallized from distilled water and identified by means of TG and FT-IR measurements. The compound was so hygroscopic that it was kept in a desiccator under vacuum and dried in an oven above 373 K for one week before measurement.

The crystallized rubidium formate obtained from distilled water was a monohydrate, so the hydrate was heated over 373 K to obtain an anhydrous rubidium formate. This compound was recrystallized from methanol, and single crystals of rubidium formate were obtained.

2.2. Thermal analyses

TG and DTA were simultaneously recorded on a Rigaku Thermoflex TG8101D in vacuo (ca. 102 Pa). Nearly 10 mg of the sample were weighed into a platinum crucible, and α-alumina was used as a reference material. The measurement was performed at a heating rate of 5 K min^{-1}. The enthalpy changes for phase transition (ΔH_{tr}) and melting (ΔH_{fus}) were obtained from the DSC curves recorded on a Shinku-Riko DSC-1500 M5. About 10 mg of the sample were placed in an aluminum crucible, and α-alumina was used as a reference material. After the sample was set, the sample chamber was purged with dry nitrogen gas, and the measurements were carried out at a heating rate of 5 K min^{-1} under a closed system. The instrument was calibrated with enthalpy changes for the phase transitions of potassium nitrate (T_{tr}=400.9 K, ΔH_{tr}=5.4 kJ mol^{-1}) and potassium perchlorate (T_{tr}=572.7 K, ΔH_{tr}=13.8 kJ mol^{-1}) [13].

2.3. Determination of the crystal structure.

A 0.5×0.4×0.3 mm specimen was sealed in a glass capillary, and measurements were performed on a Rigaku AFC5R diffractometer with graphite monochromated MoK_α radiation (λ=0.7107 Å). The data were collected using $\omega-2\theta$ scan technique to a maximum 2θ value of 70.0°. A total of 591 reflections were collected, and 323 of the reflections, having intensities three times stronger than the standard ones, were used for the structural analysis. The observed intensities were corrected for the Lorentz-polarization absorption effects. The liner absorption coefficient, μ, was 153.6 cm^{-1} and the transmission factors were in the interval 0.86–1.00.

Powder X-ray diffraction data were collected using a Rigaku Geigerflex RAD-3R diffractometer equipped with a high-temperature sample holder. The sample was set on a platinum plate in a grove pack filled with dry nitrogen gas. The data were collected in the $20 < 2\theta < 70°$ range with a step-scan width of 0.02° and fixed time (10 s) counting procedure in vacuo (ca. 10^{-1}Pa mm. CuK_α radiation (λ=1.5418 Å) was monochromatized at the opposite side using a graphite monochrometer.

3. Results and discussion

The DTA curves are shown Fig. 1. Although there was no weight change on the TG at temperatures below the melting point (446 K), an endothermic peak was confirmed at 363 K. Fig. 2 shows the powder X-ray diffraction patterns measured before, and after, the endothermic peak. The different diffraction profiles indicate that the endothermic peak corresponds to a phase transition. When the samples were heated to 403 K and then cooled gradually to 293 K, an exothermic peak was recognized at just below the temperature of the endothermic peak, 341 K. This phenomenon is

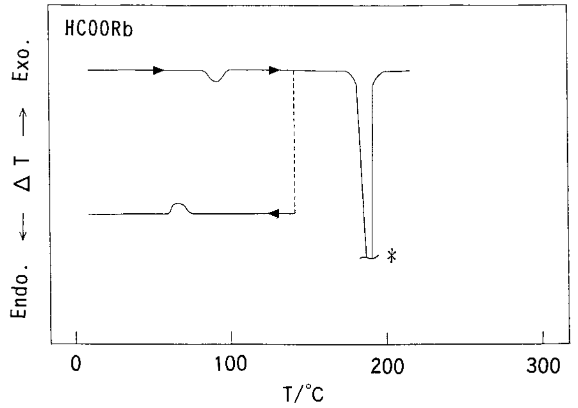

Fig. 1. DTA curves of rubidium formate. The asterisk indicates melting.

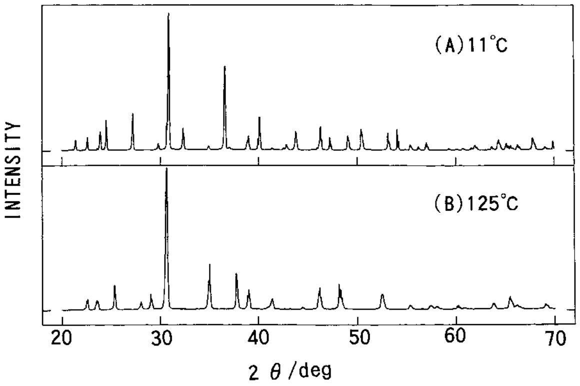

Fig. 2. X-ray powder diffraction patterns measured before, and after, the endothermic peak. (A), before transition; and (B), after transition.

referred to as a thermal hysteresis, and the phase transition classified as a reversible and first-order transition.

The enthalpy and entropy changes for phase transition and the fusion are listed in Table 1. The values obtained in the present work are larger than those reported by Ferloni et. al.; however, the values obtained are the average of measurements repeated ten times and have an accuracy of better 5%. The values of enthalpy, ΔH_{tr}, and entropy changes, ΔS^{tr}, for the phase transition are much smaller than the ones for fusion. This fact suggests that such a drastic structural change as that of fusion is not to be expected for the present phase transition.

Table 1
Value of enthalpy and entropy changes for the phase transition and fusion of rubidium formate

	T/ (°C)	ΔH/ (kJ mol^{-1})	ΔS/ (J K^{-1})
Phase transition	90	0.42±0.02	1.16±0.05
	95[a]	0.25[a]	0.67[a]
Melting	173	12.5±0.5	28.0±1.1
	170[a]	11.9[a]	26.8[a]

[a] P. Ferloni et al., Z. Naturforsch. 30a (1995) 1447.

The structure of the phase before the transition was solved using the heavy-atom Patterson method. The space group and the lattice parameters are shown in Table 2. The rubidium atoms were refined anisotropically, while the rest were refined isotropically. The position of hydrogen atom could not be determined by the X-ray diffraction method, but hydrogen atom was placed in the position expected from the form of the formate ion. The final positional parameters are listed in Table 2 with the thermal parameters. The conventional R factor, $R = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}|/\Sigma|F_{\mathrm{o}}|$, and the weighted R_{w} factor

$$R_{\mathrm{w}} = \sqrt{(\Sigma w(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2/\Sigma w|F_{\mathrm{o}}|^2)}$$

Table 2
Crystal data for the phase before the phase transition of rubidium formate

Space group	$Pca2_1$ (orthorhombic)
lattice constants	a=9.229(1) Å b=4.630(2) Å c=7.408(2) Å
Z	4

Positional (*x,y,z*) *and isotropic thermal* (*B*) *parameters*)

atom	x	y	z	B/(Å^2
Rb	0.2478	0.0608	0.0	1.44(3)[a]
O(1)	0.822(1)	0.447(2)	0.264(8)	2.1(2)
O(2)	1.005(1)	0.145(2)	0.241(5)	1.8(3)
C	0.951(2)	0.385(3)	0.269(5)	1.5(3)
H	1.0193	0.5372	0.2942	5.0

Reliability factor
R=8.6(%) R_{w}=11.0(%)

[a]
$$B_{eq} = \frac{8}{3}\pi^2(B_{11}(aa^*)^2 + B_{22}(bb^*)^2 + B_{33}(cc^*)^2 + 2B_{12}aa^*bb^*\cos\gamma + 2B_{13}aa^*bb^*\cos\beta + 2B_{23}bb^*cc^*\cos\alpha)$$

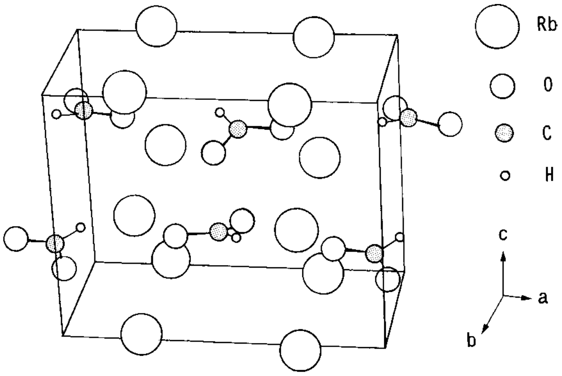

Fig. 3. Crystal structures of the phase before transition.

were 0.086 and 0.110, respectively, where $|F_o|$ is observed structural factor, $|F_c|$ is the calculated one. Fig. 3 shows the crystal structure before the transition. In this phase, all the rubidium atoms were situated on the x–y planes at z=0.0 and z=0.5, and the formate ions are located on the planes situated between the planes formed by rubidium atoms.

Table 3
Crystal data for the phase after phase transition of rubidium formate

Space group	$P2_1/m$ (monoclinic)
lattice constants	a=4.6522(4) Å b=4.6528(7) Å c=7.5170(6) Å γ=97.610(6)°
Z	2

Positional (x,y,z) *and isotropic thermal* (B) *parameters*

atom	x	y	z	B/Å^2
Rb	0.0	0.0	0.0	2.42
O(1)	0.42(1)	0.26(1)	0.25	6.02
O(2)	0.35(1)	−0.26(1)	0.25	6.02
C	0.50(3)	0.0	0.25	0.08
H	0.70	0.0	0.25	0.72

Reliability factor
R_I [a]=9.005(%) R_F [b]=5.79(%)

[a] $R_I = \sum_k |I_k(o) - I_k(c)| / \sum_k I_k(o)$.
[b] $R_F = \sum_k |[I_k(o)]^{1/2} - [I_k(c)]^{1/2}| / \sum_k [I_k(o)]^{1/2}$

The diffraction peaks observed for the phase after transition were indexed on the monoclinic cell with lattice constants of a=4.6522(4) , b=4.6528(7), c=7.5170(6) Å and γ=97.610(6)°. Only one extinction rule was held for the special reflections, namely 00l : l=2n+1. Therefore, the space group were presumed to be $P2/m$ or $P2_1/m$. The diffraction profile observed is more compatible with that for the crystal structural model on the basis of $P2_1/m$ than the one calculated for $P2/m$, as shown in Fig. 4. Table 3 and Fig. 5 show the refined structural parameters and the crystal structure, respectively. In the phase, all rubidium atoms were situated on the x–y planes at z=0.0 and z=0.5, and the formate ions also form the layer structures situated on the x–y planes at z=0.25 and z=0.75.

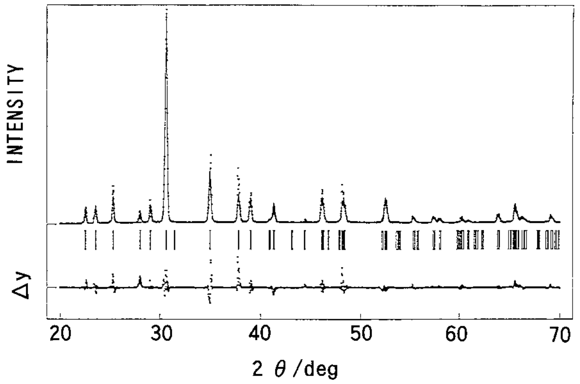

Fig. 4. Observed (· · ·), calculated (———), and difference (Δy, lower (· · ·) line) X-ray powder diffraction profiles of the phase after transition. Reflection positions are indicated by vertical bars.

Fig. 6 shows the three-dimensional frameworks connecting the eight rubidium atoms for both the

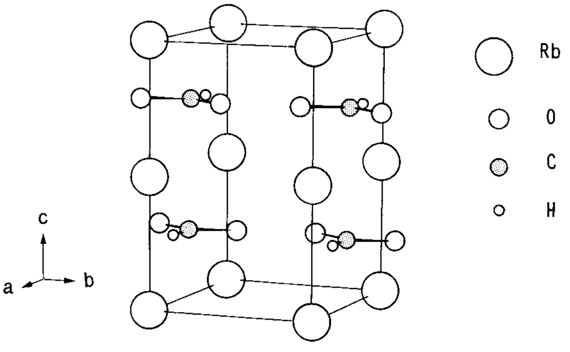

Fig. 5. Crystal structure of the phase after transition.

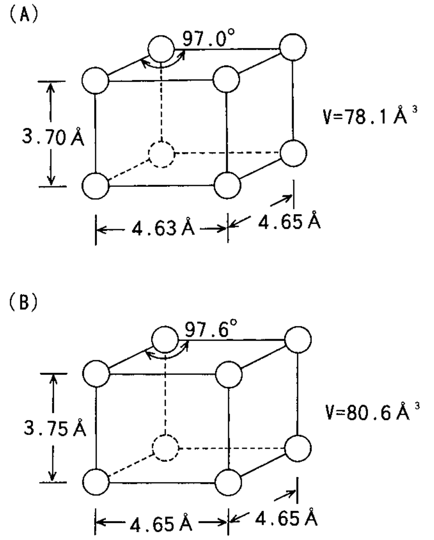

Fig. 6. The frameworks of rubidium atoms of rubidium formate. (A), before transition; and (B), after transition.

phases before, and after, transition. Both the dimensions of the frameworks of the phases before, and after, transition seem to agree fairly well with each other. Therefore, the relative positon of rubidium atoms for both the phases barely changed in the transition. On the other hand, the orientation of formate ions is clearly changed in both the phases as shown in Fig. 7. A structural change through the phase transition seems to be mostly attributable to the change of orientation of the formate ions. The small values of ΔH_{tr} and ΔS_{tr} are consistent with the slight change of structure as the orientation of formate ions through the present phase transition.

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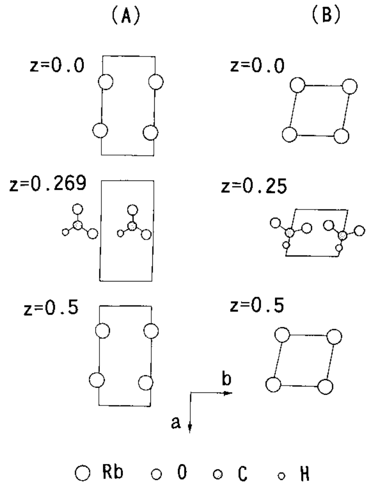

Fig. 7. The stacking sequences of layers along the *c*-axis of rubidium formate. (A), before transition; and (B), after transition.

References

[1] S. Shishido, Y. Masuda, Nippon Kagaku Zasshi 92 (1971) 309.
[2] S. Shishido, Y. Masuda, Nippon Kagaku Kaishi, 185 (1973).
[3] S. Shishido, Y. Masuda, Nippon Kagaku Kaishi, 66 (1976).
[4] P. Feroni, M. Sansei, P. Franzosini, Z. Naturforsch. 30a (1975) 1447; M. Braghetti, G. Bercheisie, Ann. Meeting, Chim. Inorg., 101 (1969).
[5] Y. Masuda, K. Hashimoto, Y. Ito, Thermochim. Acta 163 (1990) 171.
[6] K. Hashimoto, Y. Ito, Y. Masuda, 59th Annual Meeting of the Chemical Society of Japan, preprint 2F508, 1990.
[7] A. Yahata, Y. Ito, Y. Masuda, 26th Annual Meeting of The Japan Society of Calorimetry and Thermal Analysis, preprint, 1990, pp. 200–201.
[8] A. Yahata, K. Hashimoto, Y. Ito, Y. Masuda, 61th Annual Meeting of The Chemical Society of Japan, preprint 3A310, 1991.
[9] A. Yahata, Y. Ito, Y. Masuda, 27th Annual Meeting of The Japan Society of Calorimetry and Thermal Analysis, preprint, 1991, pp. 80–81.
[10] Y. Masuda, A. Yahata, H. Ogawa, Inorg. Chem. 34 (1995) 3130.
[11] H.M. Ritveld, J. Appl. Crystallogr., 65–71 (1969).
[12] F. Izumi, H. Asano, H. Murata, N. Watanabe, J. Appl. Crystallogr. 20 (1987) 411.
[13] The Chemical Society of Japan, Kagaku Binran Kisohen II (Handbook of Chemistry), 3rd edn., Maruzen, Tokyo, 1984, p. 267.