ELSEVIER

Thermochimica Acta 352–353 (2000) 61–67

thermochimica
acta

www.elsevier.com/locate/tca

Comparative study on the thermal phase transitions of rubidium and cesium formates

Yoshio Masuda[a,*], Wataru Morita[b], Xiaou Wang[b], Yasuhiko Yukawa[a]

[a] *Department of Environmental Science, Faculty of Science, Niigata University, Niigata 950-2181, Japan*
[b] *Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan*

Received 2 June 1999; received in revised form 30 July 1999; accepted 25 August 1999

Abstract

The thermal phase transitions of HCO_2Cs and HCO_2Rb were found to be reversible, first-order transitions. Through the transitions, the orthorhombic phase(*Pbcm*) of HCO_2Cs transformed to the cubic phase (*P*3*m*3) , and the orthorhombic phase (*Pca*21) of HCO_2Rb transformed to the monoclinic phase (*P*21/*m*).

From the viewpoint of the orientation of formate ion, the thermal phase transitions of HCO_2Rb and HCO_2Cs could be classified as order–order and order–disorder transitions, respectively. The ΔH_{tr} and ΔS_{tr} values for the transition of HCO_2Cs were lager than those of HCO_2Rb, which was predictable from the difference of the orientational changes of formate ions in both the transitions.

When compared with the space around the formate ion for the phase after transitions of both the formates, the space for HCO_2Cs is larger than that for HCO_2Rb, and the formate ion of HCO_2Cs could move more easily than that of HCO_2Rb. This finding appears to reflect the difference of ionic radii of Rb^+ and Cs^+ ions.

Keywords: Thermal phase transition; Rubidium and Cesium formates

1. Introduction

The thermal decomposition of alkali-metal formates has been studied by Masuda and Shishido [1–3]. These formates decomposed through two stages. In the first stage, the formates decomposed to form the respective carbonates and oxalates. The oxalates formed in the first stage decomposed to carbonate and carbon monoxide in the second stage. However, only a few papers have been reported on the thermal phase transitions of these formates [4–8]. In the course of the thermal analysis of alkali metal formates, we found that they transformed before melting [6–8].

In the present paper, the thermal phase transitions of HCO_2Cs and HCO_2Rb were studied by means of X-ray diffraction method and thermal analysis, and the difference of the transitions was discussed from the viewpoint of the orientational change of formate ion through the transition in connection with the difference of the ionic radii of Cs^+ and Rb^+ ions.

2. Experimental

2.1. Thermal analysis

TG and DTA were simultaneously recorded on a Rigaku Thermoflex TG8101D in vacuo (ca 100 Pa). About 10 mg of sample was weighed into a platinum

---

[*] Corresponding author.

0040-6031/00/$ – see front matter
PII: S0040-6031(99)00438-4

crucible, and α-alumina was used as a reference material. The enthalpy changes for melting (ΔH_{fus}) and phase transition (ΔH_{tr}) were obtained from DSC curves recorded on a Shinku-Riko DSC-1500 M5. About 10 mg of the sample was 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 measurement was 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}=127.8°C, ΔH_{tr}=5.4 kJ mol^{-1}) and potassium perchlorate (T_{tr}=299.6°C, ΔH_{tr}=13.8 kJ mol^{-1}) [9].

2.2. X-ray diffraction

The crystal structure of the phase before transition of HCO_2Rb was determined by the single-crystal method [8]. All measurement were performed on a Rigaku AFC5R diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ=0.7107 Å). The data were collected using the $\omega-2\theta$ scan technique to a maximum 2θ value of 70.0°. A total of 591 reflections was collected, and 323 of the reflections having intensities three times larger than the standard conditions were used for the structural analysis. The observed intensities were corrected for the Lorentz polarization and absorption effects.

The crystal structures of the phase after transition of HCO_2Rb, and the phases before, and after, the transition of HCO_2Cs were determined using the Rietveld method to analyze the powder X-ray diffraction data [7,10,11]. X-ray powder 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 2θ range from 20 to 70° with a step-scan width of 0.02° and fixed time (10 s) counting procedure in vacuo (ca 10^{-1} Pa). Cu$K\alpha$ radiation (λ=1.5418 Å) was monochromatized at the counter side using a graphite monochrometer.

3. Results and discussion

The DTA curves of HCO_2Cs and HCO_2Rb are shown in Fig. 1. Small endothermic peaks without any weight change were observed at 36 and 90°C on the DTA curves of HCO_2Cs and HCO_2Rb, respectively. The difference between the powder X-ray diffraction profiles measured before, and after, these endothermic peaks showed that the peaks corresponded to phase transitions. When the samples were heated above the temperatures of endothermic peaks and cooled gradually, exthothermic peaks were observed just below the temperatures of the endothermic peaks (Fig. 1). These results show that both the transitions can be classified as reversible, first-order transitions. The endothermic and exothermic peaks of HCO_2Cs had discernible shoulders; however, no intermediate phases were detectable by careful diffraction analyses.

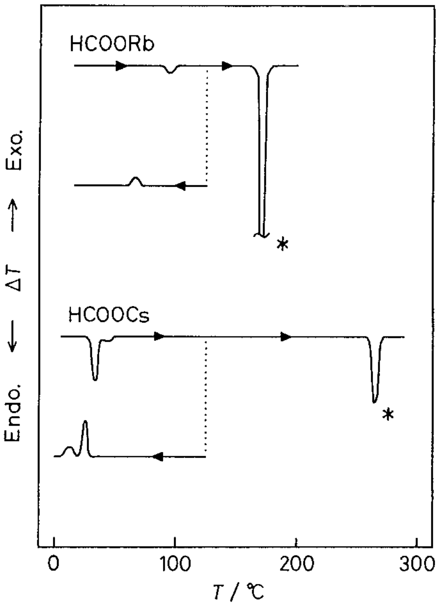

Fig. 1. DTA curves of HCO_2Rb and HCO_2Cs. Heating at 5 K min^{-1} and cooling spontaneously.

The values of enthalpy (ΔH_{tr}) and entropy (ΔS_{tr}) changes for the phase transitions and the fusions (ΔH_{fus} and ΔS_{fus}) were given in Table 1 [3,14]. It is worth noting that ΔS_{tr} of HCO_2Cs is larger than ΔS_{fus}, and that the ΔH_{tr} and ΔS_{tr} of HCO_2Cs are larger than those of HCO_2Rb. Therefore, a violent structural change, such as the melting, seems to take place through the phase transition of HCO_2Cs.

The lattice parameters of the phases before, and after, transitions were also shown in Table 2. The

Table 1
The values of enthalpy and entropy changes for the transitions of rubidium and cesium formates

		T (°C)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
HCO_2Rb	phase transition	90	0.42 ± 0.02	1.16 ± 0.05
	melting	173	12.5 ± 0.5	28.0 ± 1.1
HCO_2	Cs phase transition	36	6.87 ± 0.28	22.2 ± 0.90
	melting	263	8.11 ± 0.33	15.1 ± 0.6

Table 2
Lattice parameters before, and after, phase transitions of HCO_2Cs and HCO_2Rb

	Before transition		After transition	
HCO_2Cs	crystal system orthorhombic (*Pbcm*)	a=4.785(1) Å b=9.553(2) Å c=15.927(2) Å z=8	crystal system cubic (*P*3*m*3)	a=4.500(2) Å z=1
HCO_2Rb	crystal system orthorhombic (*Pca*21)	a=9.229(1) Å b=4.630(2) Å c=7.408(2) Å z=4	crystal system monoclinic (*P*21/*m*)	a=4.6522(4) Å b=4.6528(7) Å c=7.5170(6) Å γ=97.610(6) z=2

orthorhombic phase (*Pca*21) of HCO_2Rb transformed to the monoclinic phase (*P*21/*m*) through phase transition.

The crystal structures of both the phases before, and after, transition of HCO_2Rb are shown in Figs. 2 and 3, respectively. Although the position of the hydrogen atom could not be determined, the atom was placed in the position expected from the form of formate ion [12,13]. In both the phases, the rubidium ions situated on the x–y planes at z=0 and 0.5, and the formate ions also situated on the x–y plane at z=0.25 and 0.75. Fig. 4 shows the three-dimensional frameworks connecting the eight Rb^+ ions for both the phases before, and after, transition. Because a drastic change was not observed for the dimensions of the frameworks of the phases before, and after, transition, the relative position of Rb^+ ions appears to be scarcely changed through the transition. Therefore, the structural

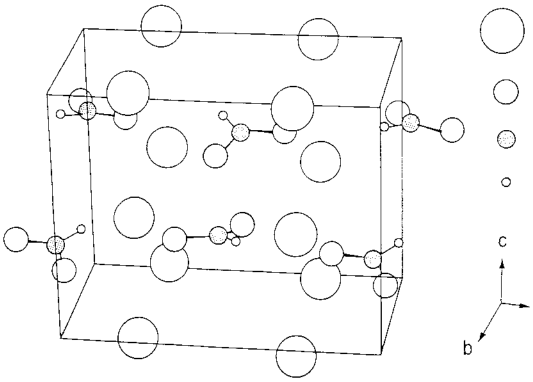

Fig. 2. Crystal structure of phase before transition of HCO_2Rb.

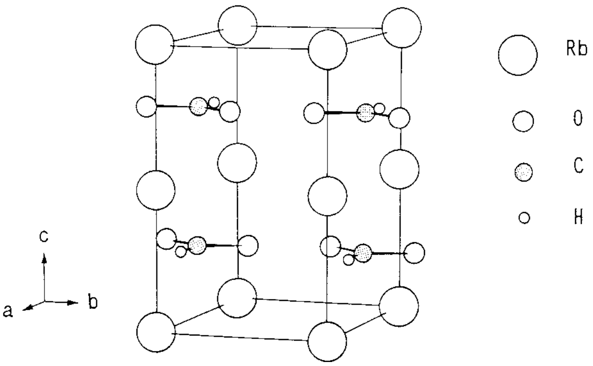

Fig. 3. Crystal structure of phase after transition of HCO_2Rb.

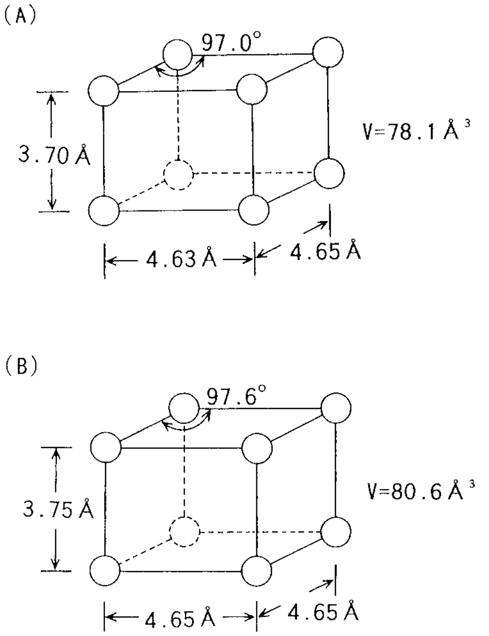

Fig. 4. Framework of Rb^+ ions of HCO_2Rb. (A) before, and (B) after transition.

change must be due to the orientation of the formate ion in the respective phases. The formate ions, however, moved slightly on the x–y planes through the transition as shown in Fig. 5, and the small values of ΔH_{tr} and ΔS_{tr} seem to correspond to the slight change of the orientation of the formate ions.

In the phase transition of HCO_2Cs, the orthorhombic phase (*Pbcm*) transformed to the cubic phase (*Pm*3*m*) (Table 2). The crystal structures of the phases before, and after, the transition are shown in Figs. 6 and 7, respectively. Fig. 8 shows the three-dimensional frameworks connecting the eight Cs^+ ions for both the phases before, and after, transition. As well as the case of HCO_2Rb, little difference was noted in volumes of both the frame-works. The most remarkable change must be due to the orientation of the formate ion in both the phases. The formate ion occupies a specific position in the structure before the transition and the orientational freedom is thought to be unity. Whereas, in the phase after transition, the configuration of the formate ion is not determined, the orientational freedom is estimated to be 12, as shown in Fig. 9. The value of entropy change calculated on the basis of the

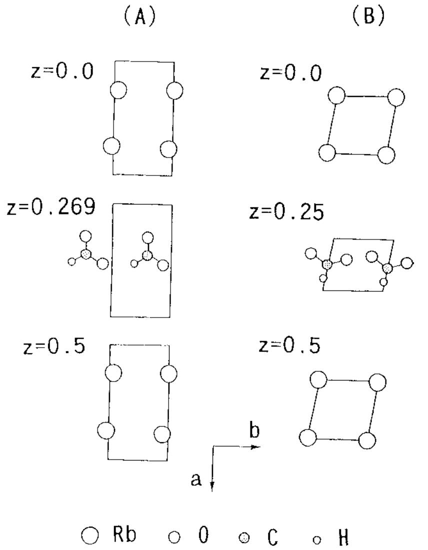

Fig. 5. Stacking sequences of layers along c-axis of HCO_2Rb. (A) before, and (B) after transition.

Boltzmann equation

$$\Delta S_{tr} = R \ln\left(\frac{n_{after}}{n_{before}}\right)$$

where R is the Universal Gas Constant, and n_{after} and n_{before} the orientational freedom of formate ion for the phase after, and before, transition, respectively. The calculated ΔS_{tr} in accordance with this equation,

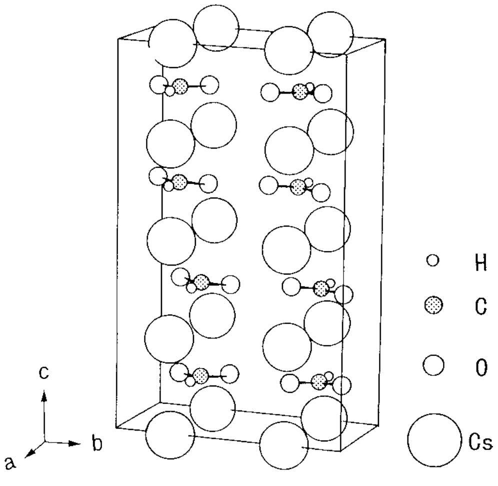

Fig. 6. Crystal structure of phase before transition of HCO_2Cs.

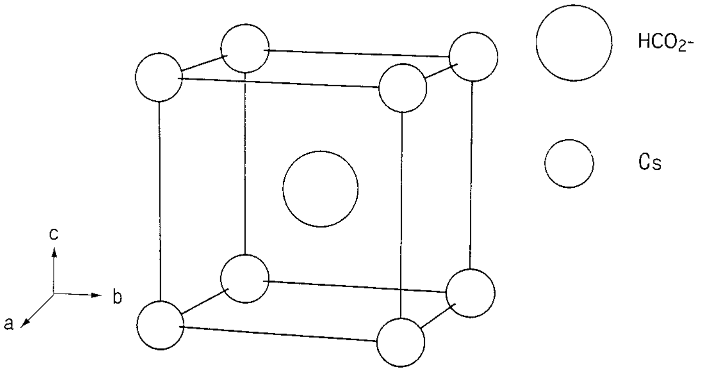

Fig. 7. Crystal structure of phase after transition of HCO_2Cs.

20.7 J K^{-1} mol^{-1}, is in fair agreement with the observed one, 22.2 ± 0.9 J K^{-1} mol^{-1}. Therefore, the phase transition of HCO_2Cs can be classified as an order–disorder transition from the viewpoint of the orientation of formate ion. On the other hand, the formate ion of HCO_2Rb occupy specific positions in both the phases before, and after, transitions, so the transition is classified as an order–order transition.

It is reasonable that the values of ΔH_{tr} and ΔS_{tr} for the order–order transition of HCO_2Rb are much smaller than those for the order–disorder transition of HCO_2Cs, because the relative positions of Rb^+ and Cs^+ ions were scarcely changed in both the transitions and the large portions of the ΔH_{tr} and ΔS_{tr} are ascribable to the orientational change of the formate ion. Why does the difference between the phase transitions of HCO_2Cs and HCO_2Rb arise? One of the reasons could be discussed as follows on the basis of the difference of the ionic radii of Rb^+ and Cs^+ ions. Fig. 5 shows the projections of the crystal structure before, and after, the transitions of HCO_2Rb. In the phase before transition, the carbon atom of formate ion is situated approximately at the center of the three-dimensional lattice consisting of Rb^+ ions. After the transition, the carbon atom moves to the plane formed by the Rb^+ ions, and then the surrounding space of the formate ion seems to become more narrow than that of the phase before transition (Figs. 10 and 11). In the phase before transition in case of HCO_2Cs, the carbon atom of formate ion is situated on the plane parallel to the planes formed by Cs^+ ions. After the transition, the carbon atom moves to the center of the three-dimensional lattice consisting of the Cs^+ ions (Figs. 10 and 11).

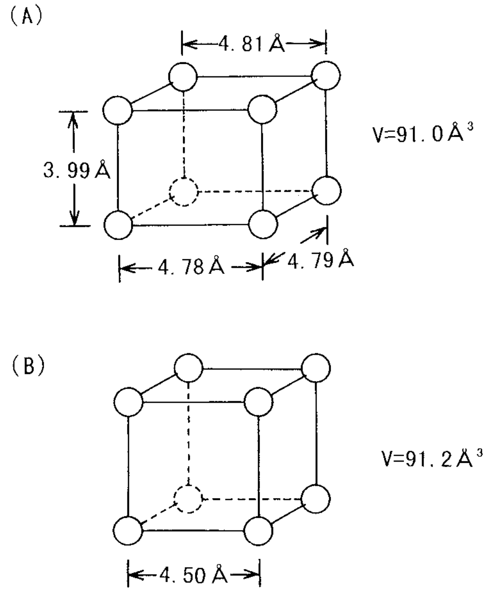

Fig. 8. Framework of Rb^+ ions of HCO_2Cs. (A) before, and (B) after transition.

Fig. 11 shows a comparison of the spaces around the carbon atoms of formate ions for the phases after transitions of both the formates. The space for HCO_2Cs is larger than that for HCO_2Rb, and then the formate ion in the phase of HCO_2Cs seems to be able to move more easily than that of HCO_2Rb. The ionic radius of Cs^+ ion, 1.81 Å, is larger than that of Rb^+ ion, 1.66 Å [14], and the difference of the ionic radii of both the ions appears to affect the dimensions

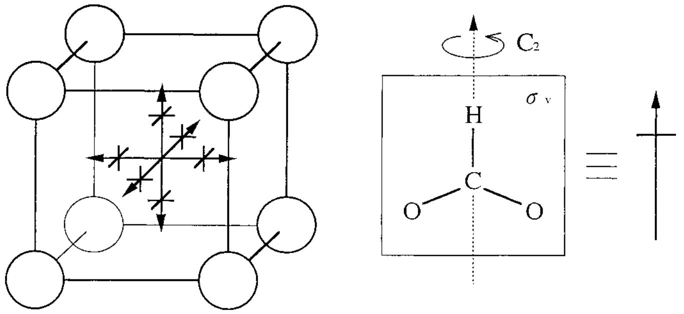

Fig. 9. Orientational freedom of formate ion for the phase after transition of HCO_2Cs.

of the framework formed by the respective metal ions. The dimension of the framework formed by Cs^+ ions is larger than that formed by Rb^+ ions. The critical condition, whether a formate ion can move easily in the phase after transition or not, seems to depend on the dimension of the framework formed by metal ions. Therefore, the condition of the order–order or the order–disorder transitions appears to result from the mobility of the formate ion in the phase after transitions.

4. Conclusions

The thermal phase transitions of HCO_2Cs and HCO_2Rb were found to be a reversible and first–order transition by means of thermal analysis and X-ray diffraction method. Through the transitions, the orthorhombic phase(*Pbcm*) of HCO_2Cs transformed to the cubic phase (*P*3*m*3), and the orthorhombic phase (*Pca*21) of HCO_2Rb transformed to the monoclinic phase (*P*21/*m*).

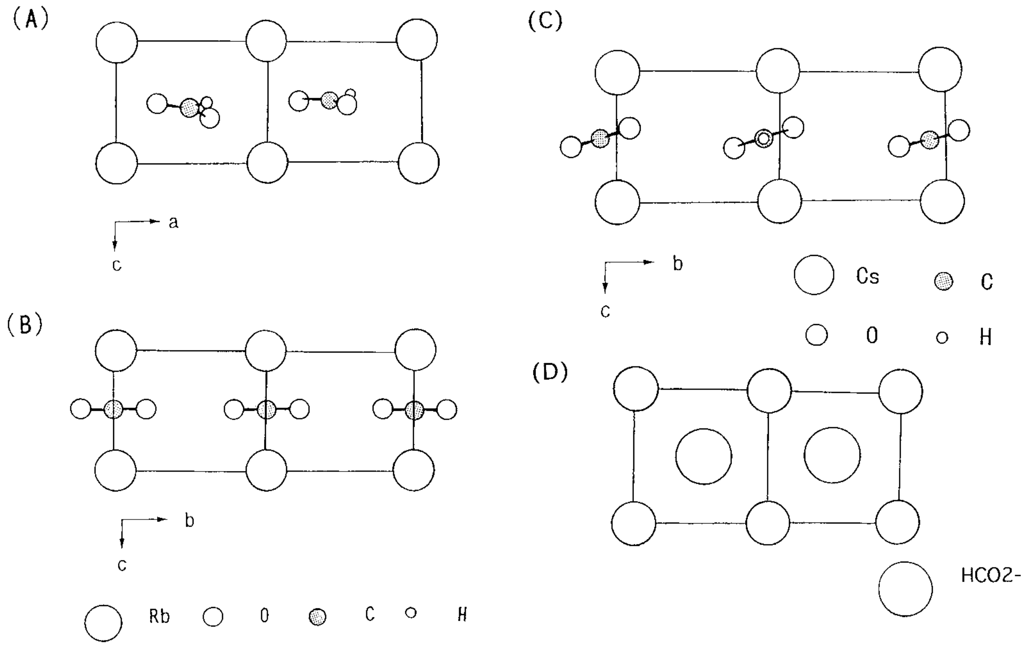

Fig. 10. Projections of the crystal structures of HCO_2Rb and HCO_2Cs. (A) before trasnsition of HCO_2Rb; (B) after transition of HCO_2Rb; (C) before trasnsition of HCO_2Cs; and (D) after transition of HCO_2Cs.

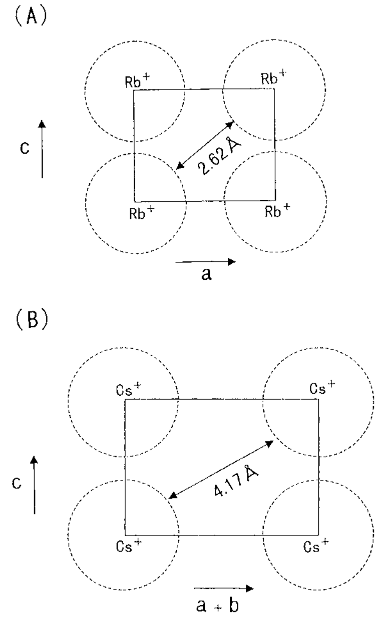

Fig. 11. Spaces around formate ion of phase after transition. (A) HCO_2Rb, and (B): HCO_2Cs.

In both the transitions, the relative positions of metallic ions hardly changed and most of the structural changes could be attributable to the orientational changes of formate ions. The transitions of HCO_2Rb and HCO_2Cs could be classified as order–order and order–disorder transitions, respectively, from the viewpoint of the orientation of formate ion. The ΔH_{tr} and ΔS_{tr} values for the transition of HCO_2Cs were larger than those of HCO_2Rb, which was predictable from the difference of the orientational changes of formate ions in both the transitions.

On comparing the space around the formate ion for the phase after transition of both the formates, the space for HCO_2Cs is larger than that for HCO_2Rb, and the formate ion of HCO_2Cs could move more easily than that of HCO 2Rb. This finding appears to reflect the difference of ionic radii of Rb^+ and Cs^+ ions.

References

[1] S. Shishido, Y. Masuda, Nippon Kagaku Zasshi 92 (1971) 309.
[2] S. Shishido, Y. Masuda, Nippon Kagaku Kaishi (1973) 185.
[3] S. Shishido, Y. Masuda, Nippon Kagaku Kaishi (1976) 66.
[4] P. Ferloni, M. Sansei, P. Franzosini, Z. Naturforsh. 30a (1975) 1147.
[5] M. Braghetti, G. Bercheisie, Ann. Meeting, Chim. Inorg. (1969) 101.
[6] Y. Masuda, K. Hashimoto, Y. Ito, Thermochim. Acta. 163 (1990) 171.
[7] Y. Masuda, A. Yahata, H. Ogawa, Inorg. Chem. 34 (1995) 3130.
[8] Y. Masuda, W. Morita, A. Yahata, Y. Yukawa, Thermochim. Acta 318 (1998) 39.
[9] Kagaku Binran Kisohen II (Handbook of Chemistry), 3rd Edition, The Chemical Society of Japan (Edited), Maruzen, Tokyo 1984, 267 pp.
[10] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[11] F. Izumi, H. Asano, H. Murata, N. Watanabe, J. Appl. Crystallogr. 20 (1987) 411.
[12] J.W. Bats, H. Fuess, Acta Cryst. B36 (1980) 1940.
[13] P.L. Markila, S.J. Retting, J. Trotter, Acta Cryst. B31 (1975) 2927.
[14] Kagaku Binran Kisohen II (Handbook of chemistry), 4th Edition, The Chemical Society of Japan (Edited), Maruzen, Tokyo 1993, 725 pp.