

05.1-8 THE POLYMORPHISM PHASE TRANSITION OF  $\text{LiIO}_3$  CRYSTAL AND THE RELATIVE STABILITY OF  $\alpha$ ,  $\beta$  AND  $\gamma$  PHASE. By Liang Jingkui and Rao Guanghui, Institute of Physics, Academia Sinica, Beijing, China.

$\text{LiIO}_3$  exhibits very complex polymorphism phase transition. There exist 8 phase structures in various temperature ranges (Liang Jingkui, Zhang Yuming, Acta Physica Sinica, 1984, 33, 69. Liang Jingkui, Zhang Yuming, J. Structural Chemistry, 1983, 2, 81). At room temperature the  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{LiIO}_3$  can coexist for a long time without changing into each other. The  $\alpha$  and  $\beta$ - $\text{LiIO}_3$  can be grown independently from the aqueous solution under different conditions. The  $\gamma$ -phase, however, can not be obtained directly from  $\alpha$  or  $\beta$  phases. It can only be obtained through melting and middle transition phase by special heat treatment technology.  $\alpha$ - $\text{LiIO}_3$  with its space group  $P6_3$  is a non-ferroelectric polar crystal having excellent non-linear optical and piezoelectric properties.  $\beta$  and  $\gamma$  phases belong to the tetragonal and orthorhombic systems, respectively. The specific heats  $C_p$  of  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{LiIO}_3$  in the temperature ranges of  $-100$ – $400^\circ\text{C}$  and the latent heat of phase transition are measured by the M- and L-type SH-3000 adiabatic scanning calorimeter, and fitted in terms of the 5th order polynomial by least-square method:

$$C_p = aT^5 + bT^4 + cT^3 + dT^2 + eT + f.$$

The coefficients of  $C_p$  and latent heats for various phase are shown in Table 1.

The entropies, enthalpies and Gibbs free energies of  $\alpha$ ,  $\beta$  and  $\gamma$  phases have been derived. From the change of free energy curves vs temperatures, it is shown that  $\alpha$  phase is stable below  $200^\circ\text{C}$ , while  $\beta$  phase is stable above  $300^\circ\text{C}$ , the  $\gamma$  phase is stable in the range of  $200$ – $300^\circ\text{C}$ . This result agrees with the phase relation of  $\alpha$ ,  $\beta$ , and  $\gamma$  phases after a long time heat treatment at constant temperature. The phase transition mechanism of  $\text{LiIO}_3$ , the thermodynamic factor and the existence of complex polymorphism are discussed from the thermodynamic and structural viewpoints.

Table 1

phase	$\alpha$		$\gamma$		$\beta$
Temp. ( $^\circ\text{C}$ )	-100-306	306-400	-100-310	310-400	-100-400
$a(10^{-14})$	-6.32993	-1.87651	-38.0230	-4.72794	0.097504
$b(10^{-11})$	5.83600	0.839213	52.9126	2.19111	-0.118268
$c(10^{-9})$	-4.01201	1.66700	-277.362	6.50558	0.253882
$d(10^{-5})$	-1.14090	0.618594	6.80859	1.26435	-0.105184
$e(10^{-3})$	4.97045	-3.05538	-6.81319	-7.95366	1.44737
$f(10^{-1})$	-1.21988	2.69969	5.87136	3.21469	1.92522
$T_c$ ( $^\circ\text{C}$ )	248	306	310		
$\Delta H(\text{J/g})$	+11.4 ( $\alpha \rightarrow \gamma$ )	-4.84 ( $\gamma \rightarrow \beta$ )	-4.74 ( $\beta \rightarrow \beta$ )		

05.1-9 STUDIES ON PHASE TRANSITION OF  $\text{LiCdBO}_3$ . By Zhou Zicang, Huang Qingzhen, Liang Jingkui, Lin Wei, Yin Xiande, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, China.

The pseudo-binary system  $\text{LiBO}_2$ - $\text{CdO}$  has been studied by means of thermal analysis and X-ray diffraction. Only one new compound  $\text{LiCdBO}_3$  has been formed in the system, which forms by peritectic reaction at  $867 \pm 3^\circ\text{C}$ . There exist two polymorphic forms in  $\text{LiCdBO}_3$ , i.e. high temperature phase  $\beta$  and low temperature phase  $\alpha$ , and inversion temperature is  $690 \pm 10^\circ\text{C}$ . Because of the hysteresis of phase transition, when the X-ray powder diffraction was carried out by using Guinier Lenne high temperature camera with heating rate  $0.7^\circ\text{C}/\text{min}$ , the phase transition process of  $\beta$ - $\text{LiCdBO}_3$  was found to be  $\beta \xrightarrow{520^\circ\text{C}} \beta + \alpha \xrightarrow{690^\circ\text{C}} \beta$ , but no phase transition of  $\alpha$ - $\text{LiCdBO}_3$  was observed. For the same reason, no heat effect of phase transition was observed by DTA analysis with heating rate  $10^\circ\text{C}/\text{min}$  for both polymorphic forms.

By quenching the samples after isothermal heat treatment at  $1300^\circ\text{C}$  for ten minutes, the amorphous samples were obtained. The high temperature diffraction analysis shows that the crystallization process of amorphous is: amorphous state  $\xrightarrow{320^\circ\text{C}} \beta \xrightarrow{520^\circ\text{C}} \alpha \xrightarrow{690^\circ\text{C}} \beta$ , and no phase transition hysteresis was observed. This result agrees with that of experiment by DTA. The kinetic process of both the crystallization of amorphous and phase transition from  $\beta$  phase into  $\alpha$  phase have been studied by DSC method.

A powder SHG test shows that the SHG effect in  $\alpha$ - $\text{LiCdBO}_3$  is about three times as large as that of  $\text{ADP}(\text{NH}_4\text{H}_2\text{PO}_4)$ , but  $\beta$ - $\text{LiCdBO}_3$  has no SHG effect.

The indexing of X-ray powder diffraction pattern indicates that  $\alpha$ - $\text{LiCdBO}_3$  is just same as  $\text{LiCdBO}_3$ -II (Соколова E. B. et al, Докл. АН СССР., 1979, 246, 1126). It belongs to the hexagonal system with the unit cell dimension:  $a=b=8.307\text{\AA}$ ,  $c=3.262\text{\AA}$ ,  $Z=3$ , the space group is  $P6_3$ . But  $\beta$ - $\text{LiCdBO}_3$  is different from  $\text{LiCdBO}_3$ -I (Соколова E. B. et al, Кристаллография, 1980, 25, 1185).  $\beta$ - $\text{LiCdBO}_3$  belongs to monoclinic system, and only the reflections  $hk\ell$  with  $h+k=2n$  are observed while the reflections  $h0\ell$  with odd  $\ell$  are absent. The unit cell parameters of  $\text{LiZnBO}_3$ ,  $\text{LiMnBO}_3$  (Бондарева O. C. et al, АН СССР, Кристаллография, 23, 487) and  $\beta$ - $\text{LiCdBO}_3$  are listed in Table 1. The comparison of the unit cell parameters and the indexing results of these three compounds suggest that they are isostructural compounds with the space group  $C2/c$ .

Because the phase diagram of pseudo-binary system  $\text{LiCdBO}_2$ - $\text{CdO}$  (Лудов Н. Т. et al, Журнал Неорганической Химии, 1985, 30, 1523) is inconsistent with present work, we chose four samples with composition 15, 25, 45, 50 mol%  $\text{CdO}$  and treated them according to their experimental conditions, but can not repeat their results. Furthermore, we have found that the dark red color  $\text{CdO}$  was separated out for the samples with the composition more than 45 mol%  $\text{CdO}$  when temperature was higher than  $867^\circ\text{C}$ , that shows that  $\text{CdO}$  and liquid coexist in the system when the temperature is above  $867^\circ\text{C}$ , i. e.  $\text{LiCdBO}_3$  is formed by peritectic reaction. The cause of the inconsistency has been discussed.

Table 1. The unit cell parameters of  $\text{LiRBO}_3$ ,  $R=\text{Cd, Mn, Zn}$ .

Compound	Space Group	a ( $\text{\AA}$ )	b ( $\text{\AA}$ )	c ( $\text{\AA}$ )	$\beta$	Z
$\text{LiZnBO}_3$	$C2/c$	5.094	8.806	10.374	$91.09^\circ$	8
$\text{LiMnBO}_3$	$C2/c$	5.188	8.952	10.367	$91.75^\circ$	8
$\text{LiCdBO}_3$	$C2/c$	5.253	9.072	10.875	$92.97^\circ$	8