05.1-8 THE POLYMORPHISM PHASE TRANSITION OF $LiIO_3$ CRYSTAL AND THE RELATIVE STABILITY OF α, β AND γ PHASE.
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$LiIO_3$ 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 α, β and γ-$LiIO_3$ can coexist for a long time without changing into each other. The α and β-$LiIO_3$ can be grown independently from the aqueous solution under different conditions. The γ-phase, however, can not be obtained directly from α or β phases. It can only be obtaind through melting and middle transition phase by special heat treatment technology. α-$LiIO_3$ with its space group $P6_3$ is a non-ferroelectric polar crystal having excellent non-linear optical and piezoelectric properties. β and γ phases belong to the tetragonal and orthorhombic systems, respectively. The specific heats C_p of α, β and γ-$LiIO_3$ in the temperature ranges of -100—400 °C and the latent heat of phase transition are measured by the M- and L-type SH-3000 adiabic 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 α, β and γ phases have been derived. From the change of free energy curves vs temperatures, it is shown that α phase is stable below 200°C, while β phase is stable above 300°C, the γ phase is stable in the range of 200-300°C. This result agrees with the phase relation of α, β, and γ phases after a long time heat treatment at constant temperature. The phase transition mechanism of $LiIO_3$, the thermodynamic factor and the existence of complex polymorphism are discussed from the thermodynamic and structural viewpoints.

Table 1

phase	α		γ		β
Temp. (°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 (°C)	248	306	310		
ΔH (J/g)	+11.4 ($\alpha \rightleftharpoons \gamma$)	-4.84 ($\gamma \to \beta$)	-4.74 ($\gamma \to \beta$)		

05.1-9 STUDIES ON PHASE TRANSITION OF $LiCdBO_3$.
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The pseudo-binary system $LiBO_2$-CdO has been studied by means of thermal analysis and X-ray diffraction. Only one new compound $LiCdBO_3$ has been formed in the system, which forms by peritectic reaction at 867±3 °C. There exist two polymorphic forms in $LiCdBO_3$, i.e. high temperature phase β and low temperature phase α, and inversion temperature is 690±10 °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 °C/min, the phase transition process of β-$LiCdBO_3$ was found to be $\beta \xrightarrow{520°C} \beta+\alpha \xrightarrow{690°C} \beta$, but no phase transition of α-$LiCdBO_3$ was observed. For the same reason, no heat effect of phase transition was observed by DTA analysis with heating rate 10 °C/min for both polymorphic forms.

By quenching the samples after isothermal heat treatment at 1300 °C for ten minutes, the amorphous samples were obtained. The high temperature diffraction analysis shows that the crystallization process of amorphous is:
amorphous state $\xrightarrow{320°C} \beta \xrightarrow{520°C} \alpha \xrightarrow{690°C} \beta$, 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 β phase into α phase have been studied by DSC method.

A powder SHG test shows that the SHG effect in α-$LiCdBO_3$ is about three times as large as that of ADP($NH_4H_2PO_4$), but β-$LiCdBO_3$ has no SHG effect.

The indexing of X-ray powder diffraction pattern indicates that α-$LiCdBO_3$ is just same as $LiCdBO_3$-II (Соколова Е. В. et al, Докл. АН СССР., 1979, 246, 1126). It belongs to the hexagonal system with the unit cell dimension: a=b=8.307Å, c=3.262Å, Z=3, the space group is $P\bar{6}$. But β-$LiCdBO_3$ is different from $LiCdBO_3$-I (Соколова Е. В. et al, Кристаллография, 1980, 25, 1185). β-$LiCdBO_3$ belongs to monoclinic system, and only the reflections hkl with h+k=2n are observed while the reflections h0l with odd l are absent. The unit cell parameters of $LiZnBO_3$, $LiMnBO_3$ (Бондарева О. С. et al, АН СССР. Кристаллография, 23, 487) and β-$LiCdBO_3$ 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 $LiCdBO_2$-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% CdO and treated them according to their experimental conditions, but can not repeat their results. Furthermore, we have found that the dark red color CdO was separated out for the samples with the composition more than 45 mol% CdO when temperature was higher than 867 °C, that shows that CdO and liquid coexist in the system when the temperature is above 867 °C, i. e. $LiCdBO_3$ is formed by peritectic reaction. The cause of the inconsistency has been discussed.

Table 1. The unit cell parameters of $LiRBO_3$, R=Cd, Mn, Zn.

Compound	Space Group	a (Å)	b (Å)	c (Å)	β	Z
$LiZnBO_3$	C2/c	5.094	8.806	10.374	91.09°	8
$LiMnBO_3$	C2/c	5.188	8.952	10.367	91.75°	8
$LiCdBO_3$	C2/c	5.253	9.072	10.875	92.97°	8