

Phase Diagram of the LiBO_2 – CdO System, Phase Transition, and Structure of LiCdBO_3

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The phase diagram of the LiBO_2 – CdO system was studied by means of X-ray diffraction and thermal analysis. An intermediate compound LiCdBO_3 was formed by a peritectic reaction at $867 \pm 3^\circ\text{C}$ in this system. LiCdBO_3 exists in two polymorphic forms, the low temperature phase α - LiCdBO_3 and the high temperature phase β - LiCdBO_3 . The phase transition is reversible at $690 \pm 10^\circ\text{C}$. The phase transition processes of the crystal and of the amorphous states were studied. An obvious hysteresis phenomena was observed in the phase transition process of the crystal state. α - LiCdBO_3 belongs to the hexagonal $P\bar{6}$ space group with cell parameters $a = 8.307$, $c = 3.262 \text{ \AA}$, $Z = 3$, $D_0 = 4.55 \text{ g/cm}^3$, $D_x = 4.551 \text{ g/cm}^3$; β - LiCdBO_3 belongs to monoclinic system, $a = 10.509$, $b = 9.075$, $c = 10.862 \text{ \AA}$, $\beta = 92.97^\circ$, $Z = 16$, $D_0 = 4.57 \text{ g/cm}^3$, $D_x = 4.574 \text{ g/cm}^3$. By adding LiCl as flux into LiCdBO_3 , transparent crystals of β - LiCdBO_3 with dimensions of $2 \times 3 \times 5 \text{ mm}$ were grown from the melt above 730°C by cooling slowly. Crystals of α - LiCdBO_3 with dimensions of $2 \times 2 \times 3 \text{ mm}$ were grown below 650°C .

Introduction

Most crystals of anhydrous borates have a wide optical transparency range, good chemical stability, and high damage threshold that have led us to search for new nonlinear optical (NLO) crystals. The crystals of β - BaB_2O_4 (1) and LiB_3O_5 (2) are two excellent NLO materials with $[\text{B}_3\text{O}_6]^{-3}$ rings (3–5) and $[\text{B}_3\text{O}_7]^{-5}$ groups (6, 7) in their structure, respectively. α - LiCdBO_3 has another structure type with BO_3^{-3} groups in its structure (8), and has a large second harmonic generation (SHG) effect ($d_{\text{eff}} = 3$ rela-

tive to d_{eff} for powdered KH_2PO_4) (9). According to the $\text{Li}_2\text{B}_2\text{O}_4$ – CdO phase diagram (10), however, α - LiCdBO_3 cannot be grown. To find the reason for this, the phase diagram of the LiBO_2 – CdO system, the phase transition, and structure of LiCdBO_3 were investigated by means of X-ray diffraction and thermal analysis.

Experimental

Preparation of sample. All samples were made from Li_2CO_3 , H_3BO_3 , and CdCO_3 of analytical purity by solid state reaction in air. The LiBO_2 (11) was first obtained by fully grinding mixtures of Li_2CO_3 and H_3BO_3 , pressing into tablets, and then heating at 800°C for 7 days. The DTA result showed that LiBO_2 melts congruently at

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849°C and the X-ray powder diffraction pattern showed that it is α -LiBO₂ exactly. Seventeen binary samples were prepared by fully grinding the mixtures of LiBO₂ and CdCO₃, pressing into tablets, and then heating at 620°C. This procedure was repeated until no alterations would occur in the X-ray powder diffraction pattern. The total time of heating was more than 15 days.

Thermal analysis. All DTA thermal events and their temperatures were recorded on a PCR-II differential thermal analyzer with a heating rate of 10°C/min over the temperature range of room temperature to 950°C.

In most cases the extrapolated values at the start of the deviation point (onset) were adopted as the phase transition temperature. There were a few exceptions where the peak values of DTA were used due to the peak-broadening curves. In our DTA work, the Pt-PtRh thermocouple was used. Experiments of DSC with a heating rate of 10°C/min from room temperature to 550°C have been carried out on a DSC-4 apparatus (Perkin-Elmer) equipped with a computer data station.

X-ray work. A Guinier Lenné X-ray high temperature powder diffraction (XRHD) camera was used to observe the phase transition process of LiCdBO₃ over the temperature range of room temperature to 800°C. CuK α radiation ($\lambda = 1.54178 \text{ \AA}$, 36 kV/20 mA) was adopted. The width of the diffraction slot is 5 mm with a film moving rate of 5 mm/hr. The heating rate was about 0.7°C/min. A Guinier-II powder camera was used for the phase analysis at room temperature. The positions of reflections were measured from a Guinier X-ray powder diffraction film by an Abbe comparator. The data obtained from three measurements were averaged and Si ($a = 5.4304 \text{ \AA}$) was used as an internal standard. A trial and error computer program (12) on a VAX/785 computer was used to index the reflections. The relative intensities I/I_0 of reflections were obtained from a

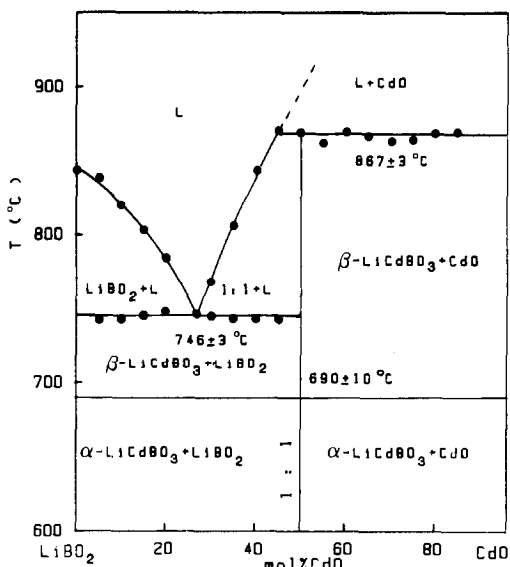


FIG. 1. The phase diagram of the LiBO₂-CdO system.

D/max-rA/200 powder diffractometer (Rigaku) with CuK α radiation and the powder samples for this experiment were passed through a 320 mesh sieve. A colorless single crystal of β -LiCdBO₃ with a dimension of 0.2 × 0.5 × 0.6 mm was selected for X-ray data collection on an Enraf-Nonius CAD-4 four-circle diffractometer. The unit cell parameters were refined from a least-squares analysis of 25 reflections in the range $28^\circ < 2\theta < 30^\circ$.

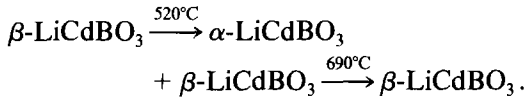
Results and Discussion

Phase Diagram of the LiBO₂-CdO System

The phase diagram of pseudobinary system LiBO₂-CdO is shown in Fig. 1. Only one intermediate compound LiCdBO₃ was formed by a peritectic reaction at $867 \pm 3^\circ\text{C}$ in this system. There exists a eutectic horizontal from LiCdBO₃ to LiBO₂ at $746 \pm 3^\circ\text{C}$, the composition of the eutectic point is 27 mol% CdO.

Phase Transition of LiCdBO₃

1. *Crystalline state.* By heating LiCdBO₃ at 520°C for 50 hr, the low temperature phase α -LiCdBO₃ was obtained. The high temperature phase β -LiCdBO₃ can be obtained by heating α -LiCdBO₃ for 20 hr in air at 780°C and cooling quickly to room temperature. No thermal effect of the phase transition for either of the polymorphic forms of LiCdBO₃ can be observed by using DTA with a heating rate of 10°C/min from room temperature to 950°C. XRHD experiments over the temperature range of room temperature to 800°C with a heating rate of 0.7°C/min were performed for both α - and β -LiCdBO₃ showing



No phase transition was observed for α -LiCdBO₃ using the same experimental condition. A sample consisting of α - and β -phase results in an obvious transition from α - to β -phase observed at 690°C on XRHD film. This means that α -LiCdBO₃ can also be transformed into β -LiCdBO₃ quickly above 690°C if there are some β -phase nuclei to introduce.

2. *Amorphous state.* By quenching liquid samples consisting of less than 45 mol% CdO after treatment at 1300°C for 10 min, transparent samples which are completely amorphous to X-ray diffraction were obtained. The XRHD analysis showed the crystallizing process of the amorphous sample to be

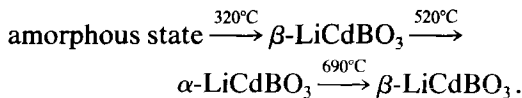


Figure 2 shows the DSC curves of amorphous samples with compositions of 33 mol% CdO (a), 40 mol% CdO (b), and LiBO₂ (c). The shape of the curves could be explained by comparison with the XRHD re-

sults. The amorphous state softens at 311°C and crystallizes at 364°C (peak value). The thermal event at 539°C is the exothermic effect of the phase transition from β -LiCdBO₃ to α -LiCdBO₃. The temperatures of all thermal events on curve b are lower than that on curve a. That is because of the different composition in these amorphous samples. LiBO₂, as an impurity, has some influence on the crystallization process. The thermal event at 430°C on the DSC curves is an exothermic effect of the crystallization of LiBO₂, but the temperature is lower than that in a pure LiBO₂ amorphous sample (Fig. 2c) because of the influence of LiCdBO₃.

In the process of the crystallization, β -LiCdBO₃ forms first at 320°C, and exists up to 520°C, then transforms into α -LiCdBO₃. There is no obvious hysteresis in any of these transformations. This means that the nuclei of the β -phase can be formed very easily in the process of crystallization. Quenched amorphous samples after treatment in a DTA furnace for 8 hr at 450 and 490°C respectively and analysis by X-ray powder diffraction confirmed that β -LiCdBO₃ formed first. However, α -LiCdBO₃ was observed after heat treatment at 500°C for 50 hr. This indicates that β -LiCdBO₃ exists as an intermediate phase from 320 to 520°C in the crystallization process and that the structure of the amorphous state is much more similar to β -LiCdBO₃ than to α -LiCdBO₃. Thus β -LiCdBO₃ was formed first despite the fact that α -LiCdBO₃ is the stable phase below 690°C.

Structure of LiCdBO₃

The X-ray powder diffraction data of α - and β -LiCdBO₃ at room temperature are listed in Tables I and II. Indexing of powder reflections indicates that the α -LiCdBO₃ belongs to the hexagonal *P6* space group and β -LiCdBO₃ belongs to the monoclinic system. Their crystallographic parameters are listed in Table III.

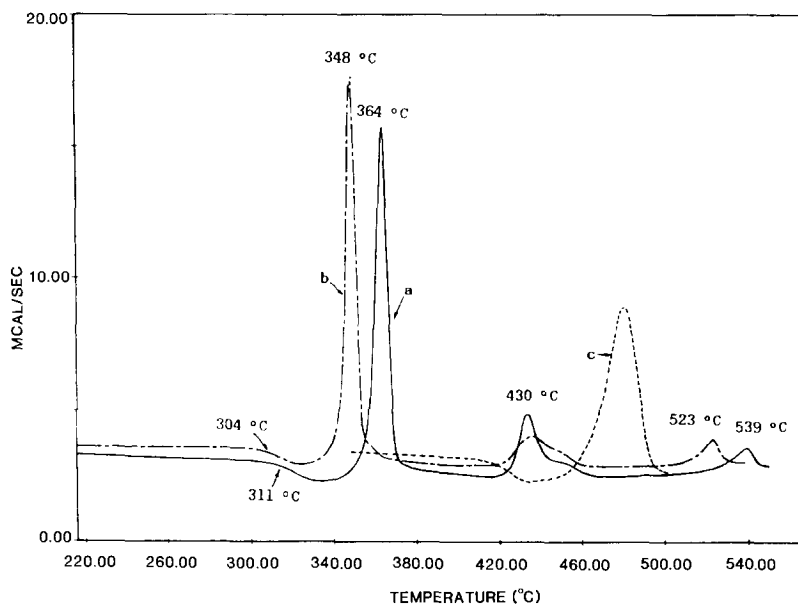


Fig. 2. DSC curves of the amorphous state of LiCdBO_3 and LiBO_2 . (a) $0.67\text{LiBO}_2:0.33\text{CdO}$; (b) $0.6\text{LiBO}_2:0.4\text{CdO}$; (c) LiBO_2 .

TABLE I
X-RAY POWDER DIFFRACTION DATA OF $\alpha\text{-LiCdBO}_3$

No.	I/I_0	H	K	L	d_{obsd} (Å)	d_{calcd} (Å)	No.	I/I_0	H	K	L	d_{obsd} (Å)	d_{calcd} (Å)
1	100	1	1	0	4.160	4.157	18	10	4	1	0	1.5695	1.5700
2	8	2	0	0	3.598	3.597	19	12	1	1	2	1.5176	1.5180
3	17	0	0	1	3.263	3.262	20	6	3	2	1	1.4725	1.4727
4	3	1	0	1	2.973	2.971	21	4	5	0	0	1.4389	1.4389
5	18	2	1	0	2.720	2.720	22	10	4	1	1	1.4141	1.4142
6	92	1	1	1	2.566	2.565	23	3	2	1	2	1.3988	1.3986
7	4	2	0	1	2.417	2.416	24	4	3	3	0	1.3844	1.3846
8	30	3	0	0	2.398	2.400	25	3	3	0	2	1.3485	1.3485
9	8	2	1	1	2.089	2.089	26	2	5	0	1	1.3169	1.3165
10	20	2	2	0	2.077	2.077	27	2	5	1	0	1.2931	1.2922
11	7	3	1	0	1.9956	1.9954	28	4	2	2	2	1.2827	1.2826
12	30	3	0	1	1.9322	1.9321	29	2	3	3	1	1.2740	1.2745
13	2	4	0	0	1.7986	1.7986	30	2	3	1	2	1.2629	1.2627
14	20	2	2	1	1.7523	1.7519	31	2	4	2	1	1.2552	1.2550
15	12	3	1	1	1.7026	1.7021	32	2	5	1	1	1.2007	1.2013
16	4	3	2	0	1.6504	1.6505	33	2	4	3	0	1.1831	1.1828
17	6	0	0	2	1.6306	1.6308	34	2	5	2	0	1.1518	1.1520

TABLE II
X-RAY POWDER DIFFRACTION DATA OF β -LiCdBO₃

No.	I/I_0	H	K	L	d_{obsd} (Å)	d_{calcd} (Å)	No.	I/I_0	H	K	L	d_{obsd} (Å)	d_{calcd} (Å)
1	57	-2	1	0	4.548	4.543	30	7	4	0	4	1.8396	1.8385
2	10	-2	1	1	4.263	4.259	31	10	0	4	4	1.7399	1.7401
3	90	1	1	2	4.190	4.187	32	7	-6	1	0	1.7178	1.7175
4	100	2	1	1	4.131	4.124	33	21	-6	1	1	1.7095	1.7098
5	62	-2	1	2	3.564	3.562	34	21	4	2	4	1.7034	1.7039
6	36	2	1	2	3.411	3.408	35	6	2	5	1	1.6896	1.6898
7	55	-2	1	3	2.892	2.893	36	2	6	1	1	1.6831	1.6831
8	30	0	2	3	2.829	2.828	37	15	-4	4	2	1.6524	1.6523
9	57	0	0	4	2.714	2.712	38	<1	4	4	2	1.6200	1.6204
10	59	-2	3	0	2.622	2.621	39	16	4	1	5	1.6047	1.6051
11	3	-2	2	3	2.534	2.533	40	3	-6	1	3	1.5828	1.5829
12	16	-4	0	2	2.411	2.411	41	6	0	4	5	1.5675	1.5679
13	42	-2	3	2	2.384	2.384	42	6	-2	5	3	1.5599	1.5600
14	28	2	3	2	2.336	2.336	43	13	4	4	3	1.5301	1.5303
15	9	0	2	4	2.328	2.328	44	10	6	1	3	1.5218	1.5216
16	14	4	0	2	2.317	2.315	45	40	-6	3	0	1.5139	1.5142
17	18	0	4	0	2.269	2.269	46	12	-2	3	6	1.5066	1.5065
18	52	-3	2	3	2.244	2.244	47	13	-6	1	4	1.4848	1.4855
19	31	0	4	1	2.220	2.221	48	13	2	3	6	1.4705	1.4704
20	13	4	2	1	2.204	2.203	49	<1	-6	1	5	1.3814	1.3812
21	7	-4	2	2	2.129	2.129	50	<1	6	2	4	1.3691	1.3693
22	<1	4	2	2	2.063	2.062	51	30	-2	5	5	1.3573	1.3567
23	<1	-2	1	5	1.9936	1.9927	52	30	-6	3	4	1.3482	1.3481
24	30	-2	4	2	1.9577	1.9576	53	40	2	5	5	1.3347	1.3345
25	13	-4	0	4	1.9366	1.9364	54	40	0	6	4	1.3206	1.3209
26	42	2	1	5	1.9255	1.9243	55	40	6	3	4	1.2976	1.2975
27	9	-2	3	4	1.9094	1.9094	56	20	-2	6	4	1.2891	1.2887
28	17	-4	3	2	1.8863	1.8856	57	25	0	5	6	1.2803	1.2808
29	11	5	2	1	1.8613	1.8614	58	25	-5	1	7	1.2661	1.2662

Discussion

Reference (10) reported that two intermediate compounds, Li₃Cd₂B₃O₈ and LiCdBO₃, exist in the Li₂B₂O₄-CdO system, and that LiCdBO₃ exhibits a reversible phase transition at 760°C and melts congruently at 835°C. In the present work, however, only LiCdBO₃ was found in this system and observed to melt incongruently: $L + \text{CdO} \xrightarrow{867^\circ\text{C}} \text{LiCdBO}_3$. According to the experimental conditions of Ref. (10), four samples with compositions of 15, 25, 45, and 50 mol% CdO were treated. But their results cannot be repeated. In the present study a dark red solid was formed in the

sample having a composition containing more than 45 mol% CdO when heat treated above 867°C. X-ray diffraction analysis

TABLE III
THE CRYSTALLOGRAPHIC PARAMETERS OF α - AND β -LiCdBO₃

α -LiCdBO ₃	β -LiCdBO ₃ (powder)	β -LiCdBO ₃ (crystal)
Space group: $P6$	Monoclinic	Monoclinic
$a = b = 8.307 \text{ \AA}$	$a = 10.509 \text{ \AA}$	$a = 10.479 \text{ \AA}$
$c = 3.262 \text{ \AA}$	$b = 9.075 \text{ \AA}$	$b = 9.049 \text{ \AA}$
$Z = 3$	$c = 10.862 \text{ \AA}$	$c = 10.845 \text{ \AA}$
$D_x = 4.551 \text{ g/cm}^3$	$\beta = 92.97^\circ$	$\beta = 92.91^\circ$
$D_0 = 4.550 \text{ g/cm}^3$	$Z = 16$	$Z = 16$
	$D_x = 4.574 \text{ g/cm}^3$	$D_x = 4.607 \text{ g/cm}^3$
	$D_0 = 4.570 \text{ g/cm}^3$	

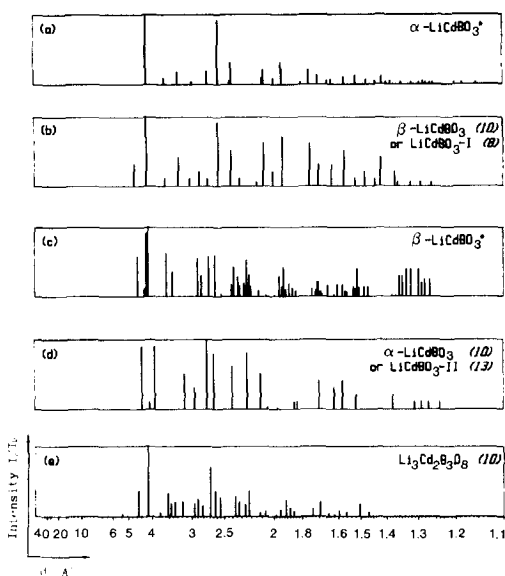


FIG. 3. Guinier X-ray powder diffraction patterns of compounds in the $\text{LiBO}_2\text{-CdO}$ system. *, in the present work.

showed that this red solid was CdO . That gives full proof that CdO and liquid coexist in the system when the temperature is above 867°C : $\text{L} + \text{CdO} \rightarrow \text{LiCdBO}_3$. In order to investigate these results further, a colorless single crystal of $\beta\text{-LiCdBO}_3$ with a dimen-

sion of $2 \times 3 \times 5$ mm was grown by cooling a melt with the composition of 43 mol% CdO slowly from 850 to 840°C . DTA shows that the crystal melts incongruently at $867 \pm 3^\circ\text{C}$. Chemical analysis by flame atomic absorption spectrometry shows that 3.90 wt% Li and 64.10 wt% Cd are contained in the $\beta\text{-LiCdBO}_3$ single crystal, which is in good agreement with its theoretical values of 3.896% Li and 63.093% Cd . By adding LiCl as flux into LiCdBO_3 , $\beta\text{-LiCdBO}_3$ single crystals were grown from melt by cooling slowly in a temperature range of $750\text{--}730^\circ\text{C}$, and transparent crystals of $\alpha\text{-LiCdBO}_3$ with dimensions $2 \times 2 \times 3$ mm were also grown below 650°C . The cell parameters of $\beta\text{-LiCdBO}_3$ obtained from the single crystal structure analysis are in good agreement with that from powder (shown in Table III).

Figure 3 shows the X-ray powder diffraction patterns of the compounds so far reported in the $\text{LiBO}_2\text{-CdO}$ system. Two intermediate compounds are formed in this system. Three polymorphic forms of LiCdBO_3 were observed. Figures 3a and 3b show the XRD patterns of the interesting polymorphic form of LiCdBO_3 (named as $\beta\text{-LiCdBO}_3$ (10), $\text{LiCdBO}_3\text{-I}$ (8), and

TABLE IV
THERMAL AND CRYSTALLOGRAPHIC DATA OF LiCdBO_3

	$\text{LiCdBO}_3\text{-II}$ (13) or $\alpha\text{-LiCdBO}_3$ (10)	$\text{LiCdBO}_3\text{-I}$ (8) or $\beta\text{-LiCdBO}_3$ (10)	$\alpha\text{-LiCdBO}_3$ (in the present work)	$\beta\text{-LiCdBO}_3$
Melting point	835°C, congruently (10)		867°C, incongruently	
Stable temperature range	Below 760°C (10)	Above 760°C (10)	Below 690°C	Above 690°C
Crystallographic data	S.G. $P\bar{1}$ (13) $a = 6.118 \text{ \AA}$ $b = 8.486 \text{ \AA}$ $c = 5.257 \text{ \AA}$ $\alpha = 91.46^\circ$ $\beta = 89.64^\circ$ $\gamma = 124.85^\circ$ $Z = 4$ $D_0 = 4.50 \text{ g/cm}^3$	S.G. $P\bar{6}$ (8) $a = 8.324 \text{ \AA}$ $c = 3.246 \text{ \AA}$ $Z = 3$ $D_0 = 4.46 \text{ g/cm}^3$	S.G. $P\bar{6}$ $a = 8.307 \text{ \AA}$ $c = 3.262 \text{ \AA}$ $Z = 3$ $D_0 = 4.550 \text{ g/cm}^3$	Monoclinic $a = 10.479 \text{ \AA}$ $b = 9.049 \text{ \AA}$ $c = 10.845 \text{ \AA}$ $\beta = 92.97^\circ$ $Z = 16$ $D_0 = 4.570 \text{ g/cm}^3$

α -LiCdBO₃ in the present study) which belongs to the hexagonal system with cell parameters $a = 8.307$, $c = 3.262$ Å, and promises to become an excellent new NLO material because of its large SHG effect ($d_{\text{eff}} = 3$ relative to d_{eff} for powder KH₂PO₄). The new polymorphic form shown in Fig. 3c found in the present study belongs to the monoclinic system, $a = 10.479$, $b = 9.049$, $c = 10.845$ Å, $\beta = 92.97^\circ$ (named as β -LiCdBO₃ in the present work). Another polymorphic form (with the S.G. $P\bar{1}$, $a = 6.118$, $b = 8.486$, $c = 5.257$ Å, $\alpha = 91.46^\circ$, $\beta = 89.64^\circ$, and $\gamma = 124.85^\circ$, named LiCdBO₃-II and α -LiCdBO₃ in the Refs. (13) and (10), respectively) cannot be repeated in the present work. Their thermal and crystallographic data are listed in Table 4, respectively.

The single crystal structure analysis indicates that the present β -LiCdBO₃ belongs to the monoclinic system. But the systematic absence of $0kl$, $k = 2n$; $h0l$, $l = 2n$; $0k0$, $k = 2n$; and $00l$, $l = 2n$ causes the structure analysis to be difficult. In comparison with the cell parameters of LiMBO₃ ($M = \text{Zn}$, S.G. $C2/c$, $a = 5.094$, $b = 8.806$, $c = 10.374$ Å, $\beta = 91.09^\circ$, and $Z = 8$; $M = \text{Mn}$, S.G. $C2/c$, $a = 5.118$, $b = 8.952$, $c = 10.367$ Å, $\beta = 91.75^\circ$, $Z = 8$) (14), the a -axis is doubled for $M = \text{Cd}$. Further structure analysis of β -LiCdBO₃ and the crystal growth of α -LiCdBO₃ are in progress.

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