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PHASE DIAGRAMS FOR THE BINARY SYSTEMS $NdCl_3$-LiCl and $PrCl_3$-LiCl

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Phase Diagrams for the Binary Systems $NdCl_3$-LiCl and $PrCl_3$-LiCl

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Equilibrium diagrams for the binary systems $NdCl_3$-LiCl and $PrCl_3$-LiCl were studied over the temperature range 200-800°C by differential thermal analysis techniques. A peritectic was observed in the $NdCl_3$-LiCl system. The eutectic occurred at 456±2°C and 30.7mol% $NdCl_3$ and the peritectic occurred at 467±1°C. A single eutectic was observed in the $PrCl_3$-LiCl system with no evidence of solid solution or compound formation. The eutectic occurred at 464±1°C and 30.6mol% $PrCl_3$ in the $PrCl_3$-LiCl system. Binary phase diagrams for the two systems were proposed from the DTA results.

Keywords: Molten Salt, Rare Earth Trichlorides, DTA, Phase Diagram, X-ray Diffraction

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$NdCl_3$-LiCl及び$PrCl_3$-LiCl2成分系状態図に関する研究

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（１９９９年３月１７日受理）

$NdCl_3$-LiCl及び$PrCl_3$-LiClの各２成分系の相状態を200～800℃の範囲における示差熱分析及び急冷したサンプルの室温Ｘ線回折によって調べた。$NdCl_3$-LiCl系では、31mol%$NdCl_3$の組成に共晶（456℃）が見られたのに加えて、包晶点（467℃）の存在が観測された。一方、$PrCl_3$-LiCl系では同じく31mol%$PrCl_3$の組成に共晶（464℃）が見いだされたのみで、包晶の存在は確認されなかった。これらの結果を基に、各２成分系の状態図を作成した。

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1. Introduction

Recently molten salt techniques have been widely investigated in the fields of nuclear fuel cycles, especially as the solvent in the pyrochemical reprocessing of spent fuel [1]. They are also being considered to be used as fluid targets in the nuclear incineration of transuranium elements with proton accelerators[2]. It is important to know the phase diagrams of the molten salts to consider their applications and to investigate their physicochemical properties.

Almost all the phase diagrams of the alkali-rare earth chlorides binary systems have been reported so far[3-5], and the phase diagrams of the $LnCl_3$-LiCl(Ln=La, Pr, Nd, and Sm) system have been reported in the literature[6-9]. However, binary systems of lithium chloride-lighter rare earth element chloride have attracted little attention because of apparently simple phase diagrams with a single eutectic point. Among the binary systems of rare earth trichlorides-LiCl, only $SmCl_3$–LiCl binary system is known to have an intermediate compound of $LiSm_2Cl_7$[10]. Both $NdCl_3$-LiCl[11] and $PrCl_3$-LiCL[12] systems were known as the simple eutectic types. The eutectic points of each system reported were at 29.7mol% $NdCl_3$ and 454°C, and 30.0mol% $PrCl_3$ and 466°C , respectively. We reinvestigated these systems and found that the results were slightly different from those in Ref.(11) for $NdCl_3$-LiClsystem. In this study, therefore, two binary phase diagrams of $NdCl_3$–LiCl and $PrCl_3$–LiCl systems were reexamined by differential thermal analysis and powder X-ray diffraction measurements.

2. Experimental

2.1 Samples

The anhydrous neodymium chloride and praseodymium chloride of 99.95% in purity and lithium chloride of 99.99% were purchased from Kojundo Chem. Co. and used to prepare the sample mixtures. The differential thermal analysis on neodymium chloride and praseodymium chloride to measure their melting points showed each a small extra peak near

the melting point. The extra peaks were thought to be ascribed to some oxychlorides. Therefore, neodymium chloride and praseodymium chloride were purified by sublimation in vacuum(10^{-5}torr) at 1000°C. Lithium chloride was dried at 300°C in vacuum(10^{-3}torr) for 2days.

The materials thus prepared were stored in a glove box under dry argon of which water and oxygen contents were below 2ppm and 5ppm, respectively. Argon was circulated through a copper-bearing alumina and a molecular sieve column to remove oxygen and water.

2.2 Differential thermal analysis

All the samples were treated and prepared in this glove box under dry inert atmosphere. The salt mixtures in desired proportions were homogenized in an agate mortar. An accurately weighed charge of about 10mg of the salt mixture to be studied was loaded into a gold crucible and hermetically encapsulated for differential thermal analysis.

The instrument used for differential thermal analysis measurements was a DTA (model DT-50A, Shimadzu Corp., Tokyo, Japan) installed in the glove box described above. Its Pt-Pt10%Rh thermocouple was calibrated against some standard substances of known melting points such as pure lead chloride. The heating rate was 10°C/min and the empty gold crucible was used as a reference. The melting points of $NdCl_3$, $PrCl_3$, and LiCl obtained were 756±2, 785±2, and 606±1°C, respectively, and they were in good agreement with those values in the literature.

For each sample, the hearting and cooling were repeated succesively to obtain two sets of DTA curves. The phase transition temperatures derived on heating were agreed very well with each other, but, due to the presence of the large degree of supercooling, the phase transition temperatures derived on cooling showed discrepancy each other. This tendency was not changed when the heating rate was lowered to 2°C/min or 5°C/min. Therefore, the DTA curves obtained during heating were used to determine the phase transition temperatures of each sample. The eutectic and peritectic reaction temperatures were determined from the extrapolated peak onsets and the liquidus temperatures were determined

from the extrapolated peak offsets.

2.3 Powder X-ray diffraction analysis

Powder samples were analyzed an X-ray diffractometer in order to characterize the chemical form of the salt samples of $NdCl_3$-LiCl system. A mixture of neodymium chloride and lithium chloride in appropriate proportions was homogenized in an agate mortar and melted in a sealed quartz tube at 800°C. After that, it was annealed at 470°C for more than 3 hours and then rapidly cooled at room temperature by air. The sample was powdered again and mounted on a standard glass sample holder. The surface of the sample was covered with Epoxy resin in order to prevent it from absorbing moisture and converting into oxides or oxychlorides. X-ray diffractometer of model RINT2000, Rigaku Corp., Japan with CuKα radiation was used.

3. Results and discussion

3.1 $NdCl_3$ –LiCl system

It was once reported that the phase diagram of this system was eutectic type[11]. However, in the present work, the phase diagram of this system was found to be peritectic type. Besides two phase transition temperatures of the eutectic and the liquidus temperatures, one or two additional phase transition temperatures were found in every thermograms of each DTA measurement as shown in Fig. 1 ~ 3. Figures 1 ~ 3 are the typical thermograms of DTA which show different aspects, that is, eutectic and liquidus in the LiCl-rich region, eutectic, peritectic and liquidus in the intermediate region, and peritectic and liquidus in the $NdCl_3$-rich region, respectively. In the range of 30~92mol% $NdCl_3$, two additional peaks other than the eutectic and the liquidus temperatures were appeared as shown in Fig. 2. Though they were small, the peaks were evident and appeared repeatedly in many different samples. The DTA curves of $NdCl_3$ sample were scrutinized in order to confirm the purity of it, and the possibility of their polymorphism was excluded.

Moreover it was found that there was a peak of heat effect on each DTA curve around 446±3°C. In view of the formation of the compound in the solid state, it was observed that the unstable compound, which decomposed at 446°C, seemed to form just below the eutectic temperature in the system $NdCl_3$-LiCl. This was also reported by Zhang et al.[11] in which a metastable compound $LiNd_2Cl_7$ was forming in the solid state with temperature of decomposition at 443°C.

The transition temperatures determined are given in Table 1 and the phase diagram of the $NdCl_3$-LiCl system thus obtained is shown in Fig. 4. The diagram obtained in this work showed a good agreement with that of Zhang et al. though they could not observe the peritectic in their work. The eutectic occurred at 456±2°C and 30.7mol% $NdCl_3$ and the peritectic occurred at 467±1°C in the system.

To confirm the formation of a new phase, XRD measurements were conducted for several mixtures of LiCl and $NdCl_3$. At first, two kinds of $NdCl_3$ samples, one was without treatment(i.e. melting and annealing) and the other was with melting and annealing, was examined with XRD were taken in order to clarify whether the treatment of the sample influenced the XRD pattern or not, and the results are shown in Fig. 5. A broad peak at 2θ~20° and a peak at 2θ~36° are due to the diffraction from the epoxy resin which was used to cover the sample. The XRD patterns of both (a) and (b) in Fig.5 show almost the same patterns, so the melting and annealing of the sample could be thought not to affect the XRD pattern. Fig. 6 shows the XRD patterns of the 90mol% $NdCl_3$-LiCl mixture. The peak at 2θ~14° in Fig.6 (b) was unidentified, and we could not find out from which compound it came. Except this peak, Fig.6(a) and (b) show the same XRD patterns, and furthermore they are the same as the XRD patterns of $NdCl_3$. It might be guessed that phase transition had been occurred during quenching of the XRD sample. It might take fairly long time to cool down from 470°C of annealing temperature to room temperature because the quenching was carried out by air-cooling. Another probable reason why the new phase formation could not be detected is that the amount of LiCl in the 90mol%$NdCl_3$-LiCl mixture was too small. Because of the low density of LiCl compared with that of $NdCl_3$, the volumetric

amount ratio of LiCl to $NdCl_3$ was extremely small. Therefore, in spite of attempts made we failed to find out the new phase in the $NdCl_3$-LiCl system, and its composition and structure were still left to be studied by high temperature X-ray diffractometer.

3.2 $PrCl_3$ -LiCl system

The typical thermogram of DTA curve for this system is shown in Fig. 7. Only eutectic and liquidus reactions were observed in all the mixtures of this system. The transition temperatures obtained are summarized in Table 2 and the phase diagram determined is shown in Fig. 8. Its eutectic point is at 30.7mol% $PrCl_3$ and 464±1°C, and this agrees well with that reported previously by others[12,13]. Although the eutectic point and the general shape of the phase diagram agree well, the liquidus temperatures in this work show a little higher values than those reported by 30 to 40°C in the $PrCl_3$ rich region. This may be ascribed to the different reading method of liquidus temperatures. In Ref.(12,13), the heat effects on liquidus were determined by the cooling curves, but in our work they were determined from the extrapolated peak offsets on the heating curves due to the discrepancy of the liquidus temperatures between the consecutive two curves as described in section 2.2.

4. Conclusion

The phase diagrams of the binary system $NdCl_3$-LiCl and $PrCl_3$-LiCl were determined. A peritectic was found by the DTA measurement in the $NdCl_3$-LiCl system at 467±1°C. The eutectic occurred at 456±2°C and 30.7mol% $NdCl_3$. It was observed that an unstable compound was formed and decomposed just below the eutectic temperature of 446±3°C in the $NdCl_3$-LiCl system. A single eutectic was observed in the $PrCl_3$-LiCl system. The eutectic occurred at 464±1°C and 30.6mol% $PrCl_3$. The results fairly well agree with those of others' previously reported.

Acknowledgment

The authors gratefully acknowledge the interest and encouragement of Dr.T.Ogawa. Authors also thank Dr.K.Minato for helpful duscussions.

References

(1)McPheeters, C. C., Pierce, R. D. and Mulcahey, T. P. : "Pyroprocessing oxide spent nuclear fuels for efficient disposal", ANL/CMT/CP-8-Conf-941207(1994)

(2)Takizuka, T., Nishida, T., Sasa, T., Takada, H., Meigo, S., Mizumoto, M. and Hasegawa, K.: Proceedings of Global 1995 International Conference on Emerging Nuclear Fuel Cycle Systems, Vol.1, 207 (1995)

(3)Sato, T and Ogawa, T : J. Thermal Analysis (1998), to be published

(4)Levin, E. M., Robbins, C. R. and McMurdie, H. F. : "Phase diagrams for ceramists, 1969, supplement", compiled at the National Bureau of Standards, Edited by Reser, M. K., The American Chemical Society, Columbus, Ohio (1975)

(5)Roth, R. S., Negas, T. and Cook, L. P. : "Phase Diagrams for ceramists, Volume V", compiled at the National bureau of Standards, Edited and published by the American Ceramic Society, Columbus, Ohio (1983)

(6)Zheng, C. G., Chen, Y. P. and Zhang, L. P. : Chin. Sci. Bull. 39, 480(1994)

(7)Zhang, Y. F., Zheng, C. G. and Ye, Y. P. : Acta Metall. Sin. 24 243(1988)

(8)Zheng, C. G., Jin, J. and Ye, Y. P. : Acta Chim. Sin. 47 678(1989)

(9)Zhang, Y. F. and Meng, B. : Acta Chim. Sin. 49 839(1991)

(10)Nakamura, K. and Kurata, M. : J. Nucl. Mater. 247 309(1997)

(11)Zhang, Y. F., Zheng, C. G. and Ye, Y. P. : Acta Chim. Sin. 47 14(1989)

(12)Qiao, Z., Wang, M., Duan, S. and Zheng, C. : Acta Metall. Sin. 25 234(1989)

(13)Zheng, C. G., Qiao, Z. Y. and Ye, Y. P. : J.Chin. Rare Earth Soc. 7 81(1989)

Table 1. The transition temperatures of DTA curves in the $NdCl_3$-LiCl system.

Composition (mol% $NdCl_3$)	Transition temperature (°C)			
0				606
9.96	446	454		577
15.13	446	455		549
19.99	448	457		520
24.77	445	457		480
30.66	450	459		459
34.62	448	456		510
39.10	443	454	468	548
49.50	448	455	467	625
66.09	447	454	467	692
80.64	449	454	466	721
87.98	450	457	468	751
88.98	449		466	755
91.69	447		466	763
100.0				756

Table 2. The transition temperatures of DTA curves in the $PrCl_3$-LiCl system.

Composition (mol% $PrCl_3$)	Transition temperature (°C)	
0		606
10.60	463	577
20.23	465	530
25.20	465	499
30.62	464	464
34.84	463	548
40.95	464	591
50.44	463	648
64.90	463	713
80.48	463	765
100.0		785

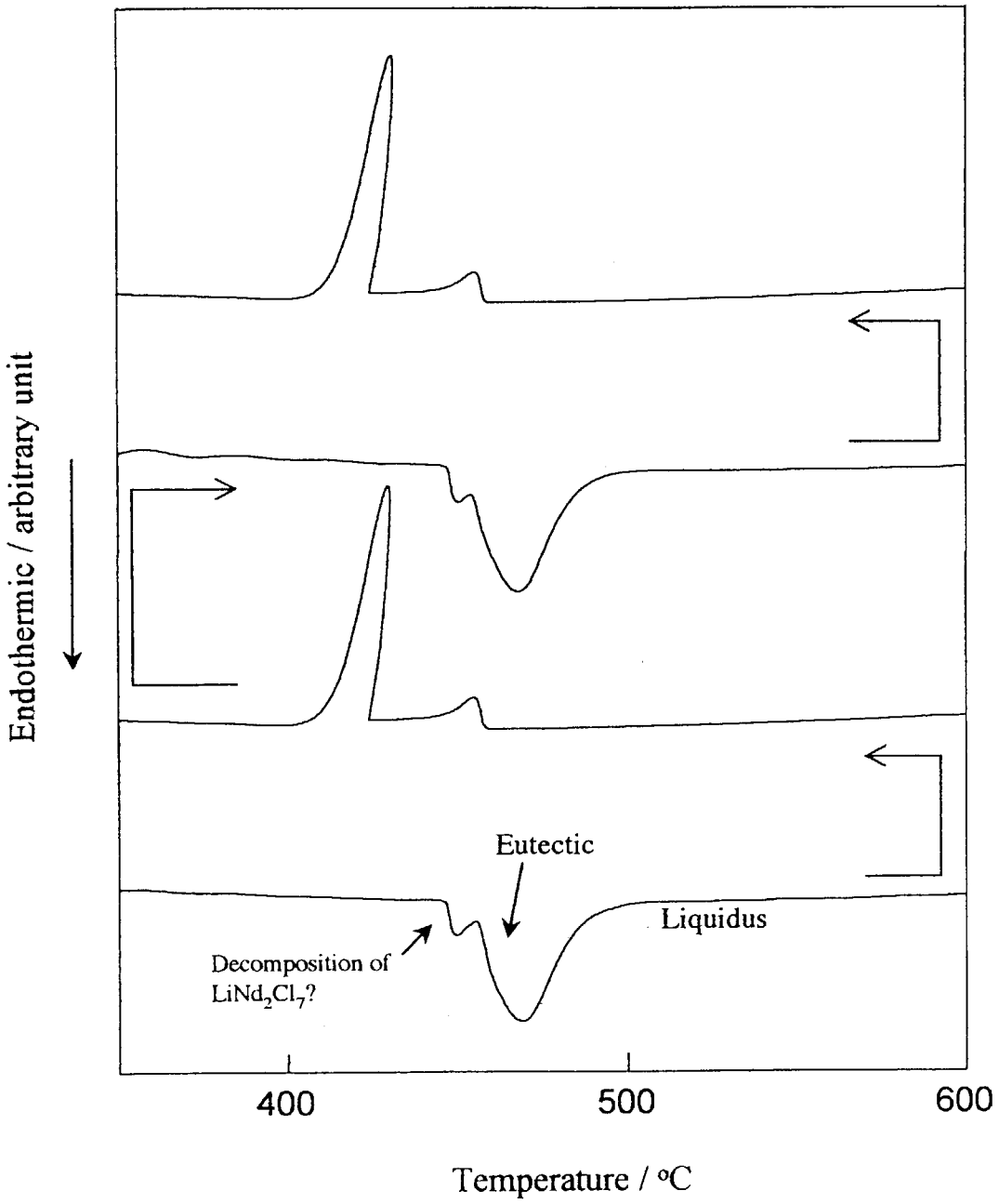


Fig.1. DTA curve for the mixture of 24.8mol% $NdCl_3$ - LiCl.

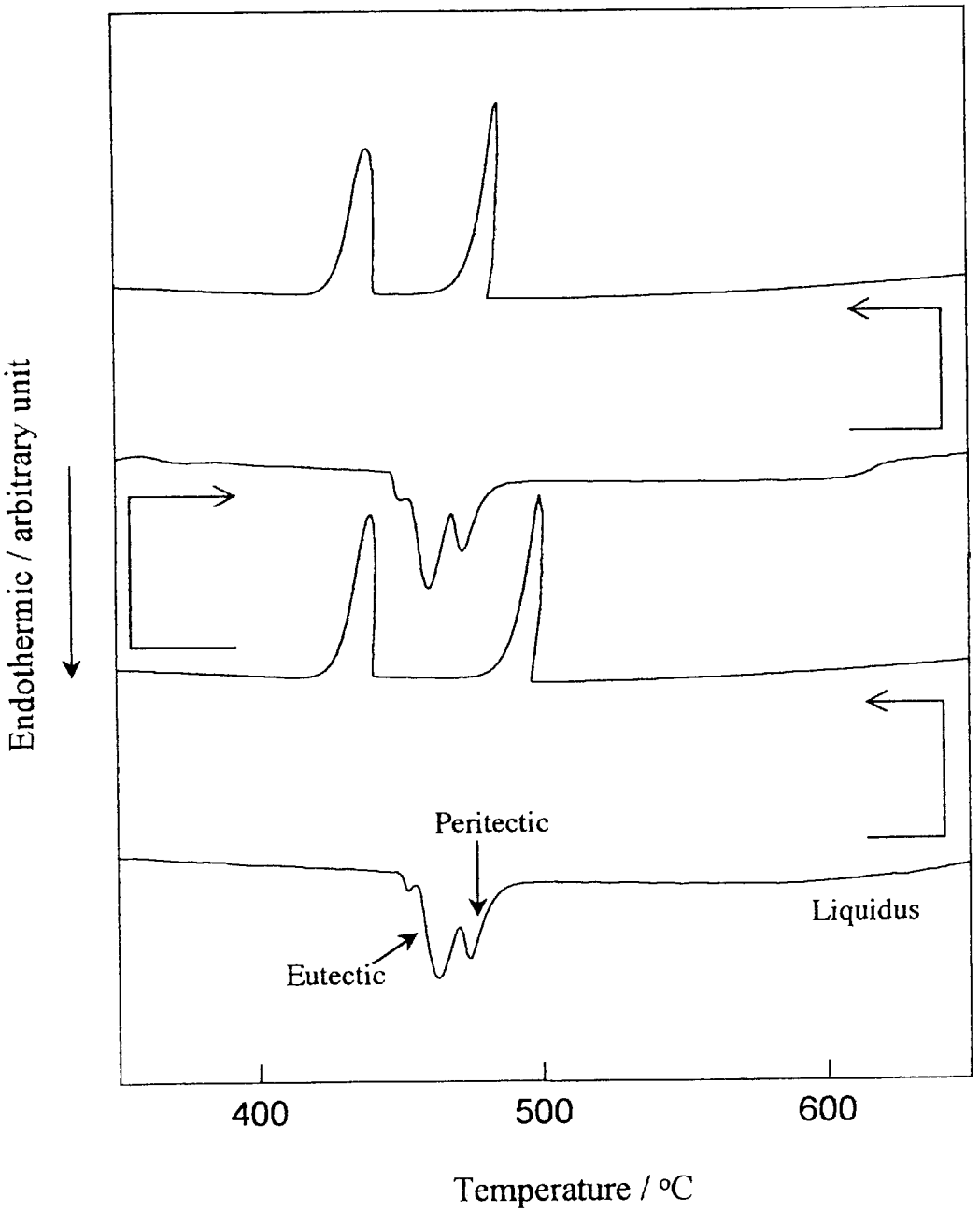


Fig.2. DTA curve for the mixture of 49.5mol% $NdCl_3$-LiCl.

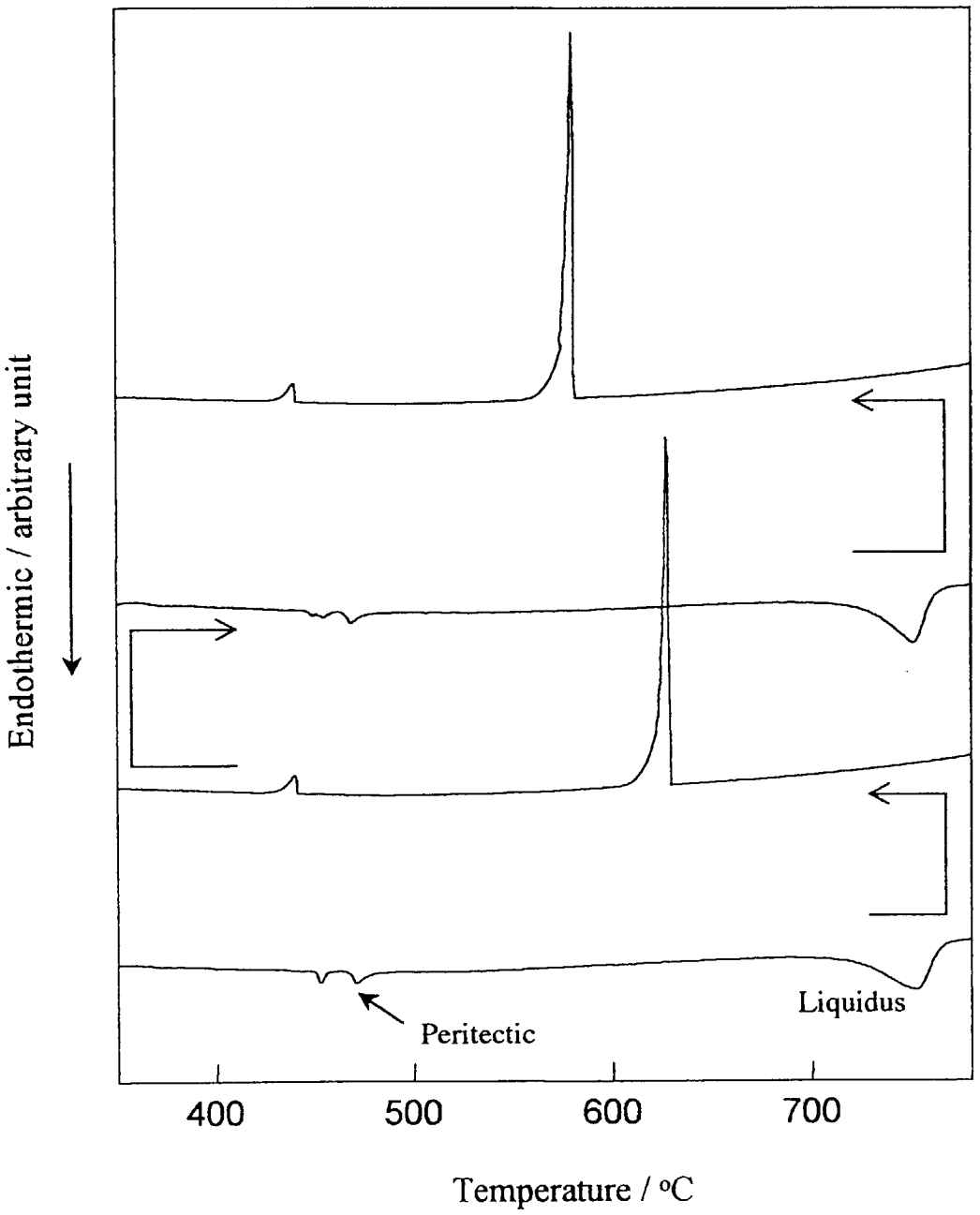


Fig.3. DTA curve for the mixture of 91.7mol% $NdCl_3$-LiCl.

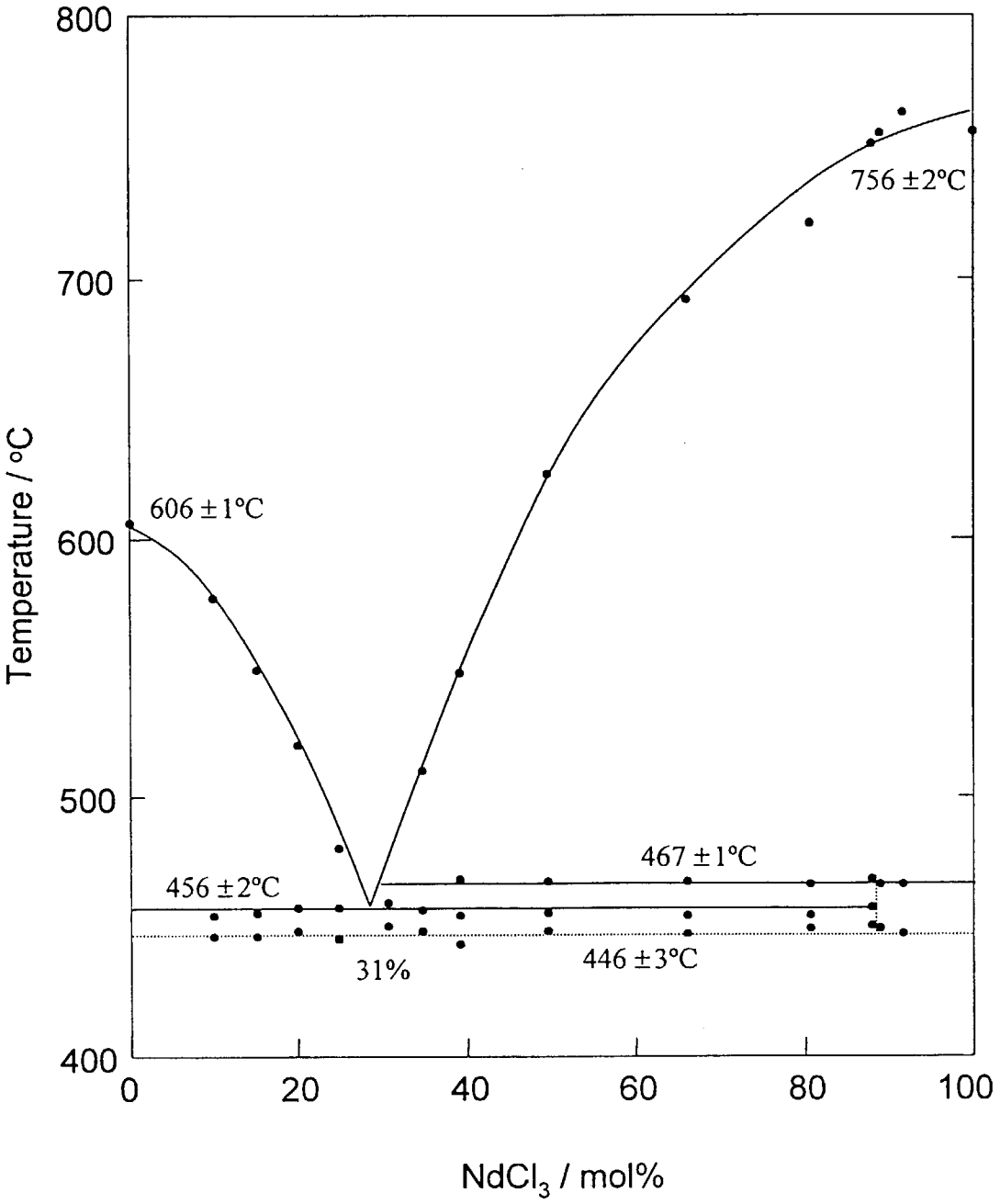
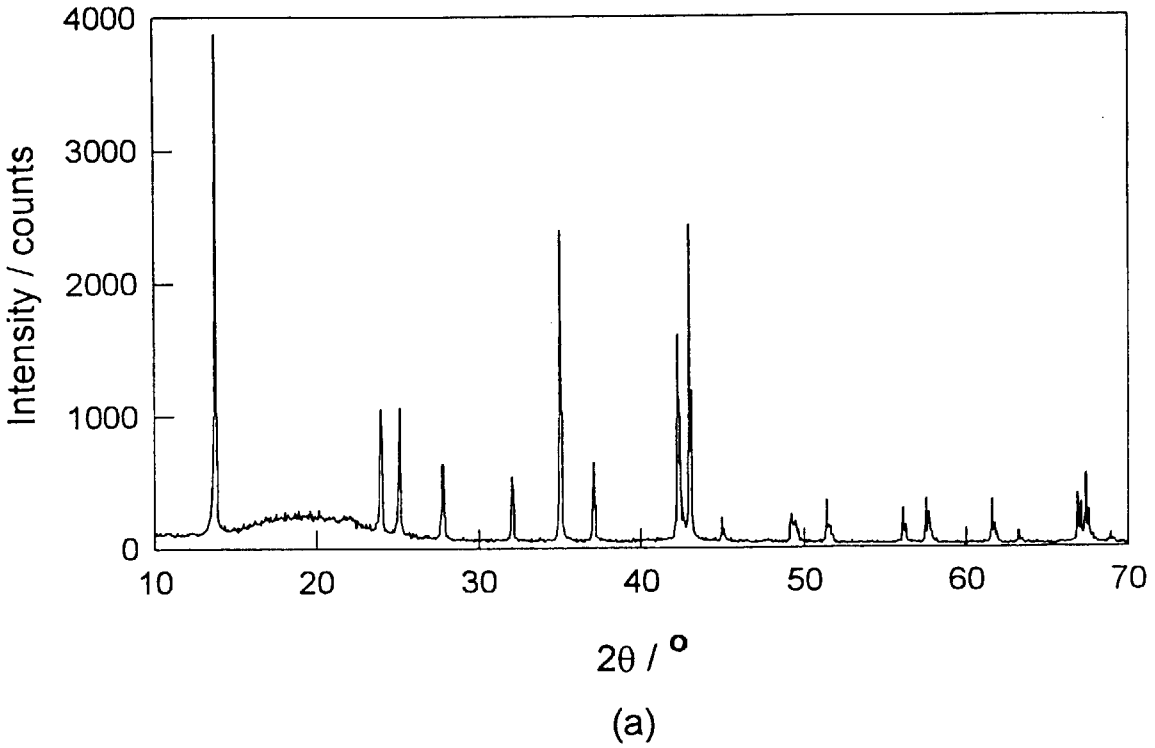
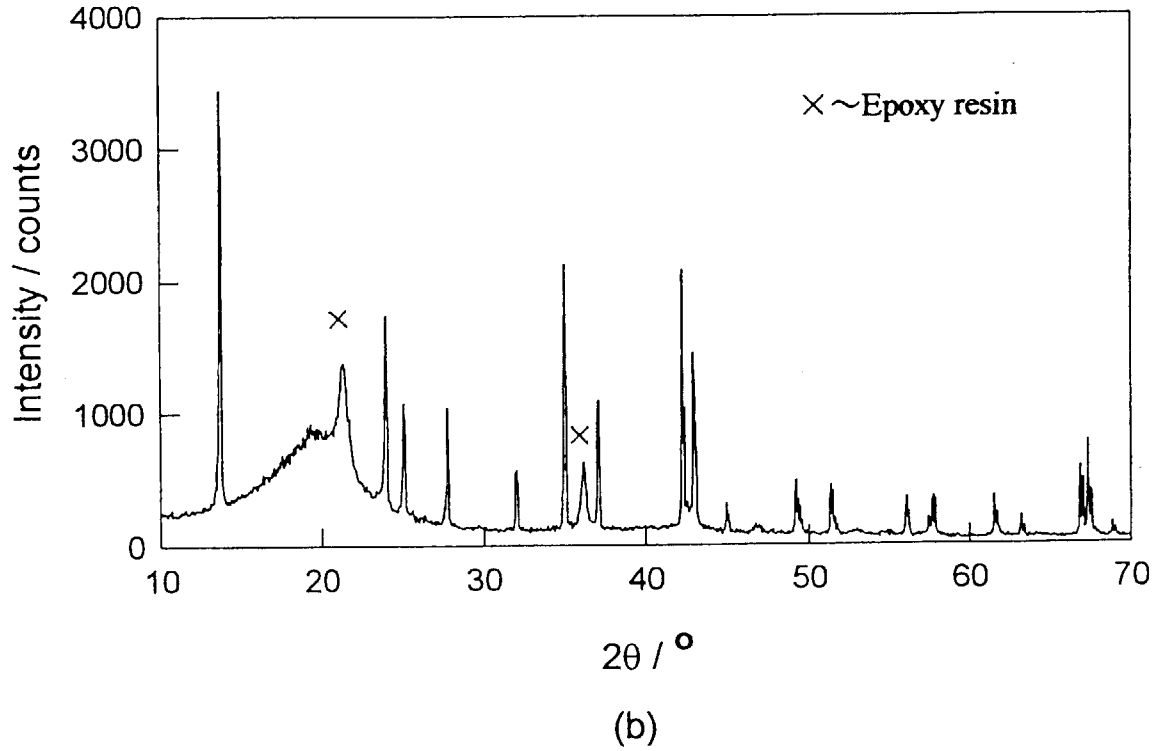


Fig.4. The phase diagram of the $NdCl_3$-LiCl binary system.

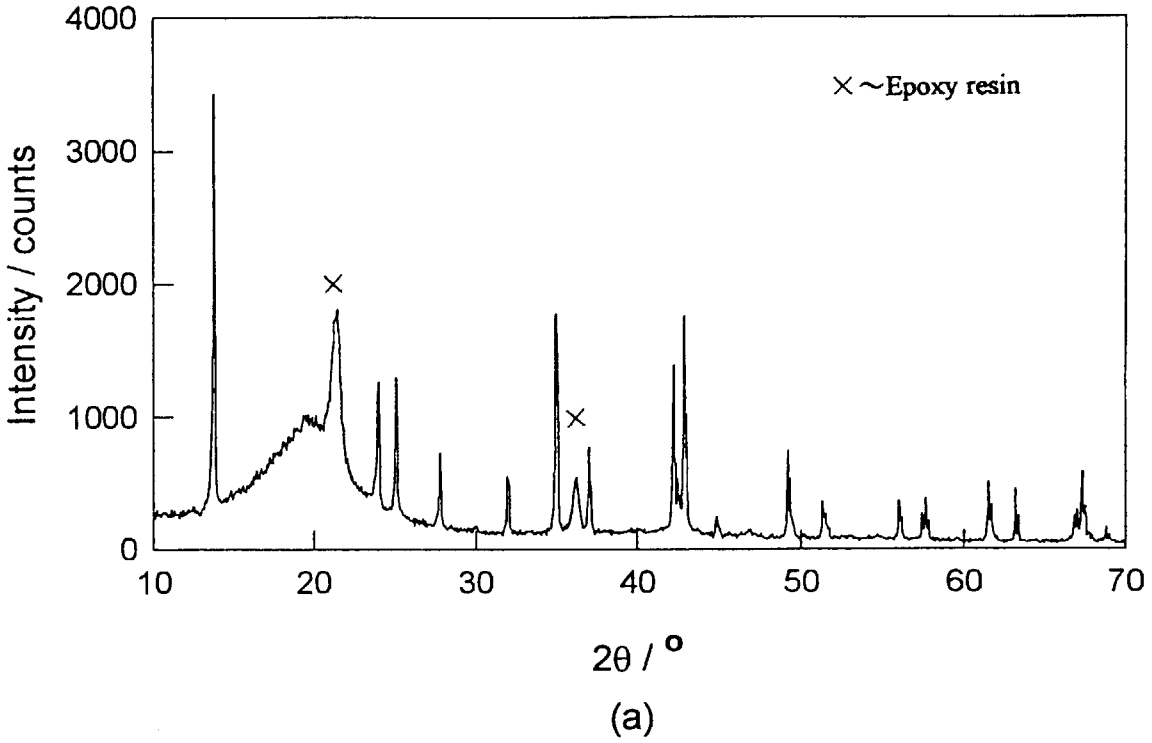


(a)

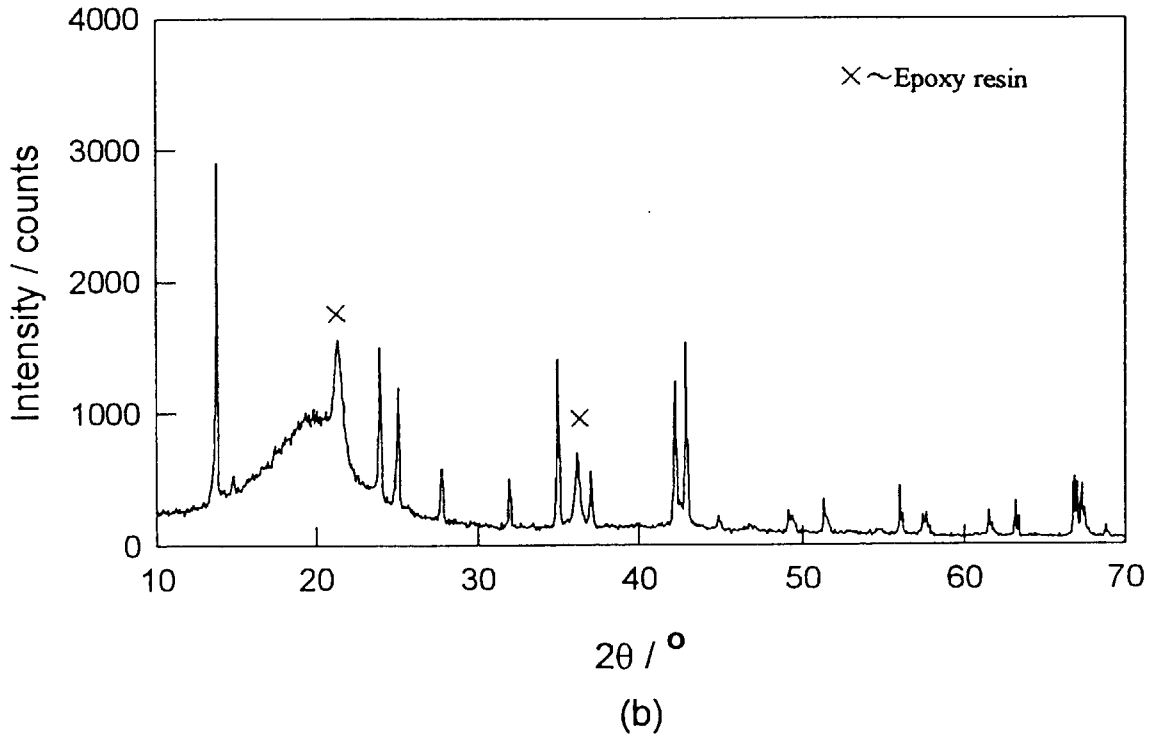


(b)

Fig.5 XRD pattern of $NdCl_3$; (a)before melting, (b)after melting and annealing.



(a)



(b)

Fig.6 XRD pattern of $PrCl_3$; (a)before melting, (b)after melting and annealing.

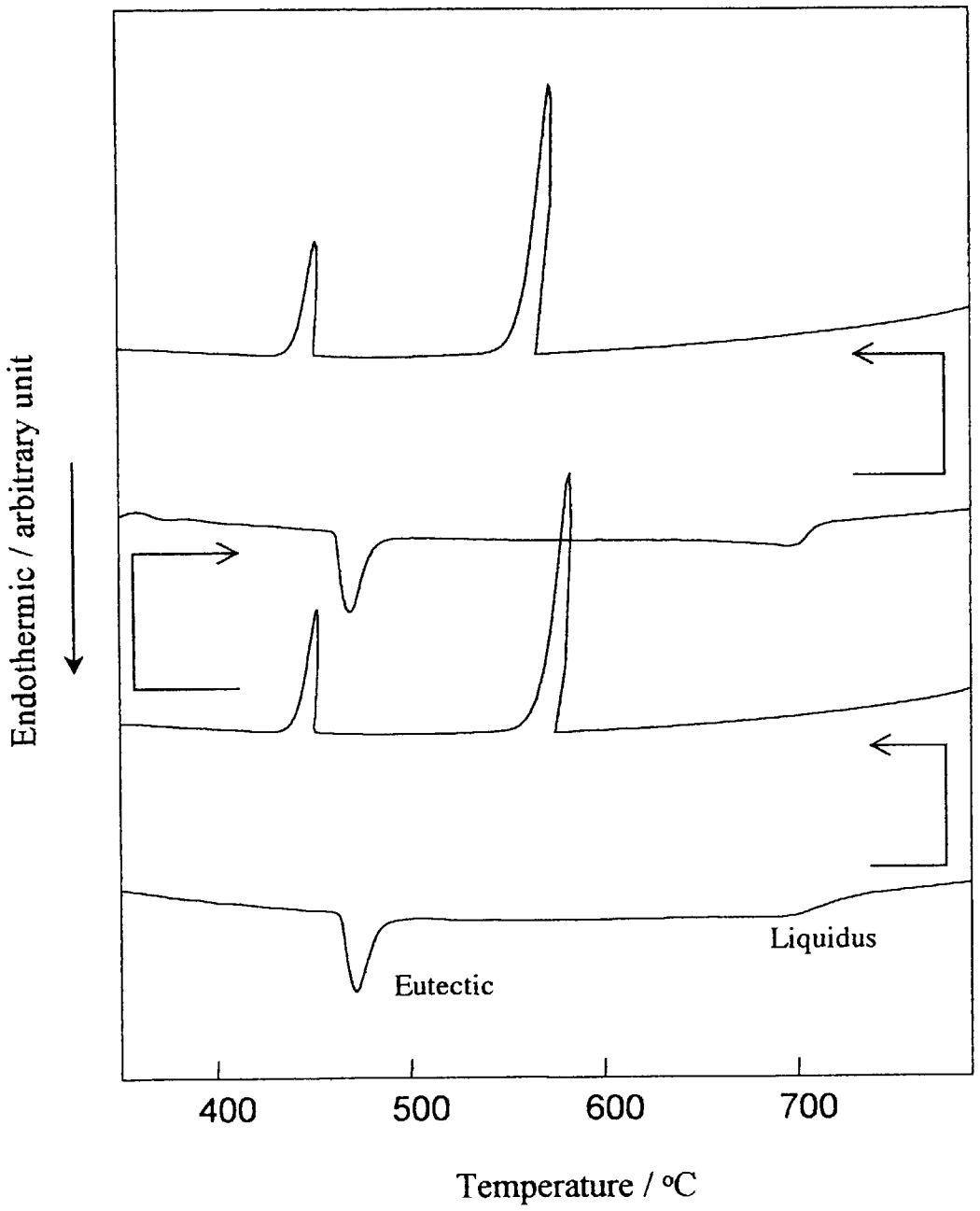


Fig.7. DTA curve for the mixture of 25.2mol% $PrCl_3$-LiCl.

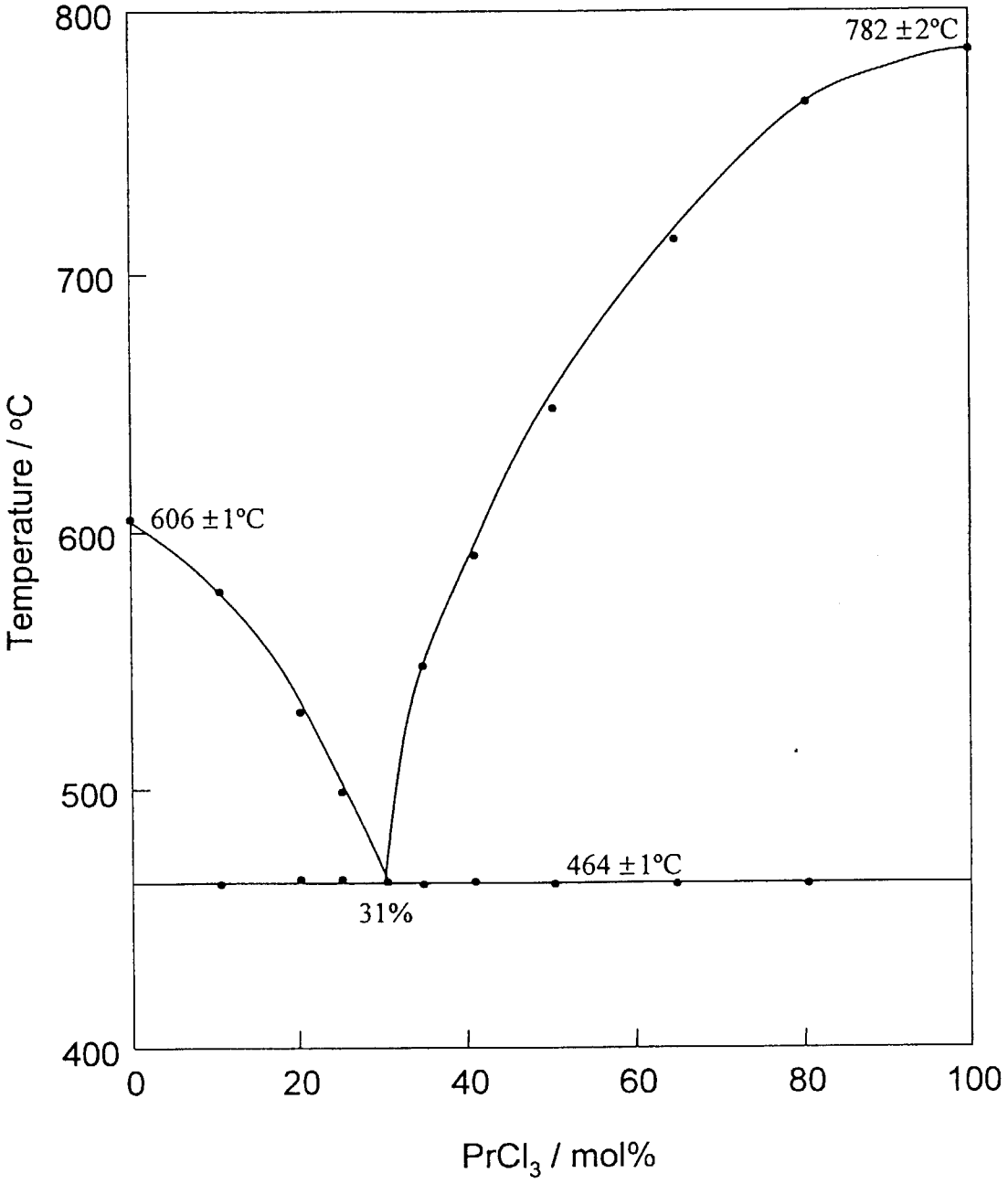


Fig.8 The phase diagram of the $PrCl_3$-LiCl binary system

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国際単位系 (SI) と換算表

表1　SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質量	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表2　SIと併用される単位

名称	記号
分，時，日	min，h，d
度，分，秒	°，′，″
リットル	l，L
トン	t
電子ボルト	eV
原子質量単位	u

1 eV = 1.60218 × 10^{-19} J

1 u = 1.66054 × 10^{-27} kg

表5　SI接頭語

倍数	接頭語	記号
10^{18}	エクサ	E
10^{15}	ペタ	P
10^{12}	テラ	T
10^{9}	ギガ	G
10^{6}	メガ	M
10^{3}	キロ	k
10^{2}	ヘクト	h
10^{1}	デカ	da
10^{-1}	デシ	d
10^{-2}	センチ	c
10^{-3}	ミリ	m
10^{-6}	マイクロ	μ
10^{-9}	ナノ	n
10^{-12}	ピコ	p
10^{-15}	フェムト	f
10^{-18}	アト	a

表3　固有の名称をもつSI組立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	s^{-1}
力	ニュートン	N	m·kg/s^2
圧力，応力	パスカル	Pa	N/m^2
エネルギー，仕事，熱量	ジュール	J	N·m
工率，放射束	ワット	W	J/s
電気量，電荷	クーロン	C	A·s
電位，電圧，起電力	ボルト	V	W/A
静電容量	ファラド	F	C/V
電気抵抗	オーム	Ω	V/A
コンダクタンス	ジーメンス	S	A/V
磁束	ウェーバ	Wb	V·s
磁束密度	テスラ	T	Wb/m^2
インダクタンス	ヘンリー	H	Wb/A
セルシウス温度	セルシウス度	℃	
光束	ルーメン	lm	cd·sr
照度	ルクス	lx	lm/m^2
放射能	ベクレル	Bq	s^{-1}
吸収線量	グレイ	Gy	J/kg
線量当量	シーベルト	Sv	J/kg

表4　SIと共に暫定的に維持される単位

名称	記号
オングストローム	Å
バーン	b
バール	bar
ガル	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

1 Å = 0.1 nm = 10^{-10} m

1 b = 100 fm^2 = 10^{-28} m^2

1 bar = 0.1 MPa = 10^5 Pa

1 Gal = 1 cm/s^2 = 10^{-2} m/s^2

1 Ci = 3.7 × 10^{10} Bq

1 R = 2.58 × 10^{-4} C/kg

1 rad = 1 cGy = 10^{-2} Gy

1 rem = 1 cSv = 10^{-2} Sv

（注）

1. 表1－5は「国際単位系」第5版，国際度量衡局 1985年刊行による。ただし，1 eVおよび1 uの値はCODATAの1986年推奨値によった。
2. 表4には海里，ノット，アール，ヘクタールも含まれているが日常の単位なのでここでは省略した。
3. barは，JISでは流体の圧力を表わす場合に限り表2のカテゴリーに分類されている。
4. EC閣僚理事会指令ではbar，barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れている。

換算表

力

N(=10^5 dyn)	kgf	lbf
1	0.101972	0.224809
9.80665	1	2.20462
4.44822	0.453592	1

粘度　1 Pa·s(N·s/m^2) = 10 P(ポアズ)(g/(cm·s))

動粘度　1 m^2/s = 10^4 St(ストークス)(cm^2/s)

圧力

MPa(=10 bar)	kgf/cm^2	atm	mmHg(Torr)	lbf/in^2(psi)
1	10.1972	9.86923	7.50062 × 10^3	145.038
0.0980665	1	0.967841	735.559	14.2233
0.101325	1.03323	1	760	14.6959
1.33322 × 10^{-4}	1.35951 × 10^{-3}	1.31579 × 10^{-3}	1	1.93368 × 10^{-2}
6.89476 × 10^{-3}	7.03070 × 10^{-2}	6.80460 × 10^{-2}	51.7149	1

エネルギー・仕事・熱量

J(=10^7 erg)	kgf·m	kW·h	cal(計量法)	Btu	ft·lbf	eV
1	0.101972	2.77778 × 10^{-7}	0.238889	9.47813 × 10^{-4}	0.737562	6.24150 × 10^{18}
9.80665	1	2.72407 × 10^{-6}	2.34270	9.29487 × 10^{-3}	7.23301	6.12082 × 10^{19}
3.6 × 10^6	3.67098 × 10^5	1	8.59999 × 10^5	3412.13	2.65522 × 10^6	2.24694 × 10^{25}
4.18605	0.426858	1.16279 × 10^{-6}	1	3.96759 × 10^{-3}	3.08747	2.61272 × 10^{19}
1055.06	107.586	2.93072 × 10^{-4}	252.042	1	778.172	6.58515 × 10^{21}
1.35582	0.138255	3.76616 × 10^{-7}	0.323890	1.28506 × 10^{-3}	1	8.46233 × 10^{18}
1.60218 × 10^{-19}	1.63377 × 10^{-20}	4.45050 × 10^{-26}	3.82743 × 10^{-20}	1.51857 × 10^{-22}	1.18171 × 10^{-19}	1

1 cal = 4.18605 J(計量法)

= 4.184 J　(熱化学)

= 4.1855 J　(15 °C)

= 4.1868 J(国際蒸気表)

仕事率　1 PS(仏馬力)

= 75 kgf·m/s

= 735.499 W

放射能

Bq	Ci
1	2.70270 × 10^{-11}
3.7 × 10^{10}	1

吸収線量

Gy	rad
1	100
0.01	1

照射線量

C/kg	R
1	3876
2.58 × 10^{-4}	1

線量当量

Sv	rem
1	100
0.01	1

(86年12月26日現在)

PHASE DIAGRAMS FOR THE BINARY SYSTEMS $NdCl_3$-LiCl and $PrCl_3$-LiCl