Study on the Phase Diagram of CsCl-CeCl$_3$-HCl(11%)-H$_2$O System and the Properties of the Compounds

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The equilibrium solubility of CsCl-CeCl$_3$-HCl(11%)-H$_2$O quaternary system at 25 ℃ has been determined by the physicchemical analysis method, and the phase diagram was plotted. Two new double salts 3CsCl·CeCl$_3$·3H$_2$O and CsCl·CeCl$_3$·4H$_2$O obtained from the complicated system were identified and characterized by XRD, TG-DTA, DSC, UV and fluorescence spectroscopy. Studies on the fluorescence excitation and emission show that 3CsCl·CeCl$_3$·3H$_2$O and CsCl·CeCl$_3$·4H$_2$O have upconversion luminescence of infrared-visible range, and the upconversion emission intensity increases with the increase of ratio of CeCl$_3$ in CsCl.

Keywords   phase equilibrium system, solubility diagram, 3CsCl·CeCl$_3$·3H$_2$O, CsCl·CeCl$_3$·4H$_2$O, excitation and emission spectra

Introduction

In recent year, extensive studies on quaternary systems of MX-REX$_3$-HX(13%)-H$_2$O (M = Cs; RE = La, Pr, Nd, Sm, Gd, Dy; X = Cl, Br. M = Rb; RE = Gd, X = Cl) at 25 ℃ have been done in our laboratory. Ten new compounds were obtained from the systems, they are CsRECl$_4$·nH$_2$O (RE = La, Pr, Nd), RbGdCl$_4$·4H$_2$O of 1:1 type, Cs$_4$GdCl$_7$·H$_2$O of 4:1 type, Cs$_5$RE$_2$Br$_{11}$·22H$_2$O (RE = La, Pr, Nd, Sm) of 5:2 type and Cs$_5$Dy$_3$Br$_{14}$·24H$_2$O of 5:3 type.[1-7] Optical investigation shows that some of them have upconversion fluorescence properties in the near ultraviolet and visible region excited in the near infrared region. Therefore, it seems a good way to search new compounds that have upconversion fluorescence properties by carrying out research on new quaternary systems of this kinds, the study on which is also very important for understanding the interactions between CsX and REX$_3$ in HX(10%—13%)-H$_2$O, where X = Cl, Br; RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy ···Lu. This paper reports the solubility of CsCl-CeCl$_3$-HCl(11%)-H$_2$O system at 25 ℃ and the solid state ultraviolet and fluorescence spectra of the two new double salts obtained from the system.

Experimental

Preparation of reagents and materials

CsCl and HCl (37%) are of A.R. grade. CeCl$_3$·7H$_2$O was produced from a solution of CeO$_2$ (W = 99.9%) in HCl with H$_2$O$_2$ as reducing agent. The purity of CeCl$_3$·7H$_2$O obtained is 99.99%.

Instruments

The apparatus and experimental conditions used for investigating the solubility of CsCl-CeCl$_3$-HCl(11%)-H$_2$O are the same as that reported in Refs. 4 and 5. Methods used for establishing phase equilibrium and determining the composition of solid phase are the same as that reported in Ref. 6. TG-DTG and DSC worked with heating rate 10

℃/min under Ar atmosphere of flow rate 60 mL/min. The D/Max-3C instrument of X-ray powder diffraction was used, working on Cu target, 50 kV and 80 mA.

The absorption, excitation and emission spectra of the crystal double salts were recorded on a PERKIN-ELMER LAMBDA 17 UV-vis spectrometer and on a Model F-4500 fluorescence spectrophotometer, respectively. Excitation source of the Model F-4500 fluorescence spectrophotometer is Xe lamp. Excitation and emission sources are continuously in the range of 250—900 nm and 250—700 nm, respectively. Scanning rate is 12000 nm/min and excitation and emission slits are 5.0 and 5.0 nm, respectively.

Results and discussion

CsCl-CeCl₃-HCl(11%)-H₂O *at* 25 ℃ *quaternary system*

The solubility data of CsCl-CeCl₃-HCl(11%)-H₂O

quaternary system and central projection data on CsCl-CeCl₃-H₂O triangle basal face are listed in Table 1, and shown in Fig. 1. As seen from Fig. 1, the phase diagram of the system consists of four solubility curves which correspond to four equilibrium solid phases: $CsCl$, $3CsCl \cdot CeCl_3 \cdot 3H_2O$ (3 : 1 type double salt), $CsCl \cdot CeCl_3 \cdot 4H_2O$ (1 : 1 type double salt) and $CeCl_3 \cdot 7H_2O$, respectively. The solid-phase composition of the two new double salts was determined graphically by Schreinemarkers method.[8] Chemical analysis results are $CeCl_3$ 29.85% (theory 30.60%) and CsCl 62.90% (theory 62.70%) for $3CsCl \cdot CeCl_3 \cdot 3H_2O$, $CeCl_3$ 51.05% (theory 50.63%) and CsCl 33.97% (theory 34.58%) for $CsCl \cdot CeCl_3 \cdot 4H_2O$, respectively. From Fig. 1, it can be also seen that the two new 3 : 1 type and 1 : 1 type double salts are congruently soluble in ~ 11% hydrochloric acid medium at 25 ℃. Similar phenomenon has been found in another quaternary system of $CsCl-LaCl_3-HCl-H_2O$.[2]

Table 1 Solubility data of saturated solution of the quaternary system CsCl-CeCl₃-HCl(11%)-H₂O at 25℃ and central projection data on the trigonal basal face[a]

No.	Liquid phase (% weight)						Wet solid phase (% weight)				Solid phase in equilibrium[b]
	Composition in the tetrahedra			Composition on the trigonal basal face			Composition in the tetrahedra		Composition on the trigonal basal face		
	HCl	CeCl₃	CsCl	CeCl₃	CsCl	HCl	CeCl₃	CsCl	CeCl₃	CsCl	
					Average acidity = 10.85%						
1	10.45	0.00	48.35	0.00	51.83						A
2	9.93	3.72	46.88	4.08	51.48	0.00	14.26	77.90	14.26	77.90	A + B
3	9.38	4.34	44.74	4.79	49.37	0.00	29.49	60.55	29.49	60.55	B
4	11.69	6.57	34.91	7.44	39.53	0.00	30.75	61.54	30.75	61.54	B
5	9.44	11.81	34.11	12.90	37.26	0.14	30.17	59.17	30.21	59.25	B
6	9.45	17.58	23.71	19.42	26.18	4.85	23.31	39.70	24.50	41.72	B
7	10.18	19.50	20.10	21.71	22.38	2.90	31.12	42.25	32.04	43.51	B + C
8	9.56	20.33	20.51	22.48	22.68	2.94	33.30	38.18	34.31	39.34	B + C
9	9.85	20.02	21.05	22.21	23.35	0.09	46.93	34.01	46.97	34.04	C
10	10.69	21.75	15.69	24.35	17.57	4.29	38.87	24.76	40.61	25.87	C
11	10.81	28.06	4.63	31.46	5.19	4.33	41.51	18.45	43.39	19.28	C + D
12	9.84	28.27	6.43	31.35	7.13	3.11	49.01	10.80	50.58	11.14	C + D
13	11.69	26.07	5.15	29.52	5.83	4.03	48.99	4.63	51.05	4.82	C + D
14	11.71	25.76	6.16	29.18	6.97	4.25	50.02	1.01	52.24	1.05	D
15	10.69	25.12	9.31	28.13	10.42	3.00	54.06	0.10	55.72	0.10	D
16	11.42	28.96	2.44	32.69	2.75	3.08	54.15	0.15	55.87	0.16	D
17	11.90	26.97	3.80	30.61	4.32	3.22	54.47	0.17	56.28	0.18	D
18	11.35	28.99	0.93	32.70	1.05	3.02	53.92	0.71	55.60	0.73	D

[a] Two salts-coexistence points (average): E₁ CeCl₃ 4.44%, CsCl 50.42%; E₂ CeCl₃ 22.13%, CsCl 22.80%; E₃ CeCl₃ 30.37%, CsCl 6.28%. [b] Solid phase: A, CsCl; B, 3CsCl·CeCl₃·3H₂O; C, CsCl·CeCl₃·4H₂O; D, CeCl₃·7H₂O.
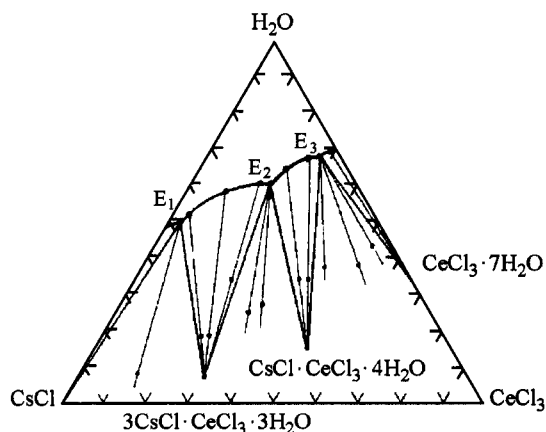
Fig. 1 Solubility diagram of the quaternary system of CsCl-Ce-Cl$_3$-HCl-H$_2$O at 25 ℃ projected on the trigonal basal face CsCl-CeCl$_3$-H$_2$O.

Characterization of 3CsCl・CeCl$_3$・3H$_2$O *and* CsCl・CeCl$_3$・4H$_2$O

X-ray data of 3CsCl・CeCl$_3$・3H$_2$O and CsCl・CeCl$_3$・4H$_2$O double salts derived from the system are d = 0.5279(100), 0.2912(21), 0.2114(2) nm and d = 0.5640(100), 0.2996(21), 0.1886(13) nm, respectively, which are very different from those of sample salts

CsCl [d = 0.2917(100), 0.4120(45), 0.1683(25) nm] and CeCl$_3$・7H$_2$O [d = 0.6060(100), 0.4040(80), 0.3600(70) nm].

TG-DTA (A and C) and DSC (B and D) graphs of two new double salts are shown in Fig. 2. Peak temperature and weight-loss data are listed in Table 2. The curves A and B show that there is an obvious weight-loss for 3CsCl・CeCl$_3$・3H$_2$O in the temperature range of 50—105 ℃ and the peak temperature in DSC curve is at 105 ℃, the weight-loss value is 6.62% (theory 6.70%). As references to curves C and D in Fig. 2, it shows that there are three obvious weight-loss for CsCl・CeCl$_3$・4H$_2$O in the temperature range of 50—260 ℃ and the salt is dehydrated at peak temperatures 92 ℃, 161 ℃ and 257 ℃, respectively. The total weight-loss is 14.72% (theory 14.79%). Based on these thermal analysis results, it is suggested that the dehydration equations be as follows:
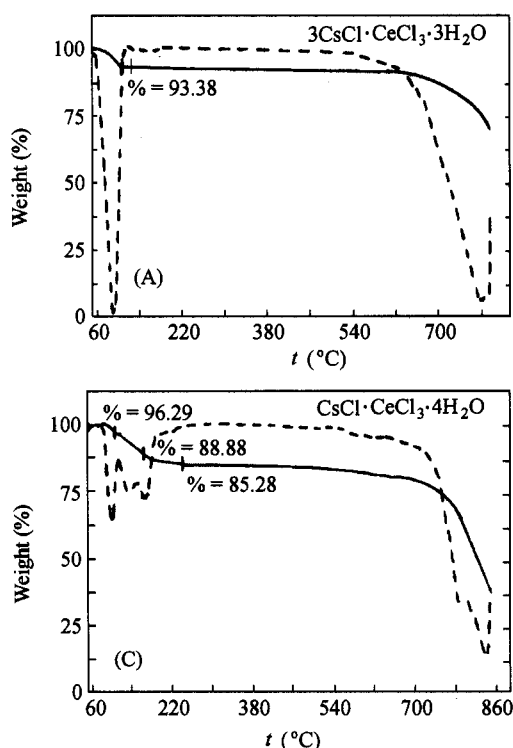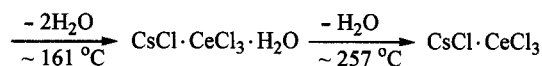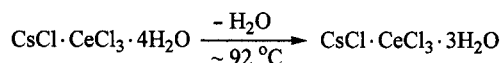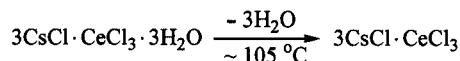
$$3CsCl・CeCl_3・3H_2O \xrightarrow[\sim 105\ ^\circ C]{-3H_2O} 3CsCl・CeCl_3$$

$$CsCl・CeCl_3・4H_2O \xrightarrow[\sim 92\ ^\circ C]{-H_2O} CsCl・CeCl_3・3H_2O$$

$$\xrightarrow[\sim 161\ ^\circ C]{-2H_2O} CsCl・CeCl_3・H_2O \xrightarrow[\sim 257\ ^\circ C]{-H_2O} CsCl・CeCl_3$$

Fig. 2 TG-DTA (A and C) and DSC (B and D) graphs of 3CsCl・CeCl$_3$・3H$_2$O and CsCl・CeCl$_3$・4H$_2$O double salts.

Table 2   TG-DTA data of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ and $CsCl \cdot CeCl_3 \cdot 4H_2O$ double salts

Compound	Lost water number	Peak temp. (℃)	Weight-loss (%)		Product
			Experimental	Theoretical	
$3CsCl \cdot CeCl_3 \cdot 3H_2O$	lost $3H_2O$	105	6.62	6.70	$3CsCl \cdot CeCl_3$
$CsCl \cdot CeCl_3 \cdot 4H_2O$	lost $1H_2O$	92	3.71	3.70	$CsCl \cdot CeCl_3 \cdot 3H_2O$
	lost $2H_2O$	161	7.41	7.39	$CsCl \cdot CeCl_3 \cdot H_2O$
	lost $1H_2O$	257	3.60	3.70	$CsCl \cdot CeCl_3$
	lost total $4H_2O$		14.72	14.79	

UV-vis *absorption spectra*, *fluorescence excitation and emission spectra*

Because of the special electron structure of Ce^{3+} $(4f^1)$, only 5d→4f energy level transition is permitted, and Ce^{3+} has good photoactivation and good energy transfer effect.[9-12] In order to understand the spectroscopy of Ce^{3+} ion in CsCl well, the UV-vis absorption spectrum, fluorescence excitation and emission spectra of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ and $CsCl \cdot CeCl_3 \cdot 4H_2O$ were investigated.

The UV-vis absorption spectra of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ show that absorption peaks are at 388 nm and 263 nm, respectively, and the strongest photoabsorption occurres at 388 nm. Fluorescence excitation and emission 3-D (three-dimension) spectrum of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ is presented in Fig. 3 by the contour plot. A series of excitation spectra monitored at 263 nm to 388 nm were observed in the range of 400—900 nm. Their peaks are at 590 nm, 750 nm, 780 nm and 860 nm, respectively, in which the strongest intensity of the excitation is at 590 nm (Fig. 4). The intensity decreased from 860 nm, to 780 nm and 750 nm. Excited by the lights of 860 nm, 780 nm, 750 nm and 590 nm, respectively, the compound emission is within 300 nm to 400 nm and the emission
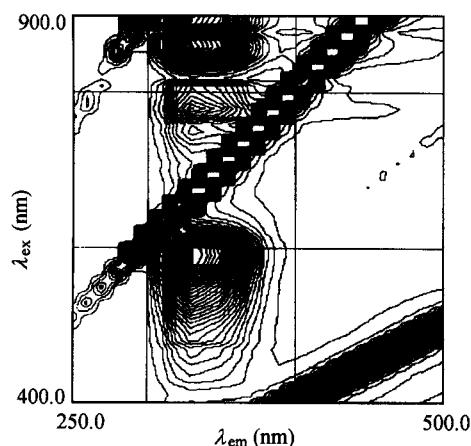
maximum is at 330 nm. Fig. 5 is the upconversion luminescence spectra of the 3 : 1 type salt, excited by 860 nm. It is believed that the emission at 330 nm is the upconversion fluorescence which is attributed to the 5d→4f $(^2F_{5/2})$ energy level transition of Ce^{3+} ion in CsCl, the luminous energy of emission fluorescence is about $\Delta E = 30302 \ cm^{-1}$.
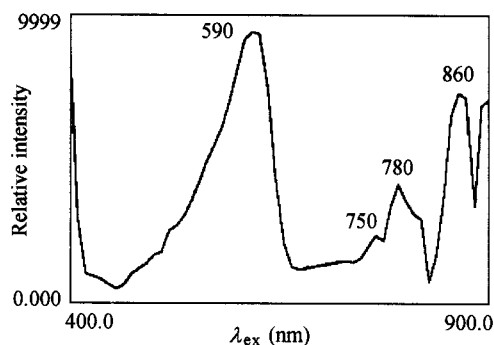

Fig. 4   Excitation spectra of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ ($\lambda_{em} = 330$ nm).
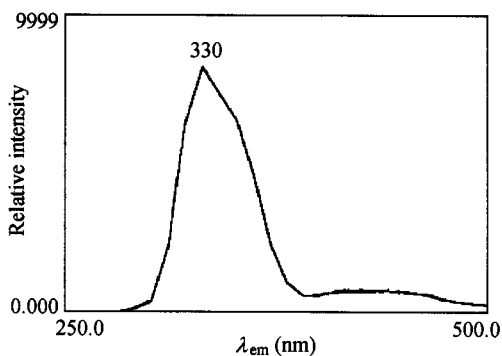
Fig. 5   Upconversion luminesence spectra of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ ($\lambda_{ex} = 860$ nm).

Fig. 3   Excitation and emission 3-D spectra of $3CsCl \cdot CeCl_3 \cdot 3H_2O$ (three-dimension).

Similar spectroscopy investigations were also carried out for $CsCl \cdot CeCl_3 \cdot 4H_2O$ (1:1 type). UV-vis absorption peaks were found at 389 nm and 262 nm, respectively, which is almost the same as the 3:1 type. Fig. 6 shows that the excitation spectra of the 1:1 type double salt,

emitted by 263—400 nm light, were found in 400—900 nm range and the peaks are at 550 nm, 860 nm, 780 nm and 750 nm, respectively. The excitation intensity of 550 nm peak is the strongest one (Fig. 7). Excited by 550 nm, 860 nm, 780 nm and 750 nm, respectively, the e-mission spectra of the compound were observed in the range from 330 nm to 400 nm. What different from the 3 :1 type double salt is that the emission peak is at 360 nm, not at 330 nm. It is shown that the 1:1 type double salt has upconversion luminescence phenomenon at 360 nm (Fig. 8). When excited at the same wave-length, e-mission intensity of the 1:1 type double salt is stronger than that of the 3:1 type double salt, which demonstrates that when the ratio of Ce^{3+} in CsCl increases, the emis-sion intensity of the upconversion luminescence of the double salt also increases. The upconversion fluorescence may be attributed to the $5d \rightarrow 4f$ $(^2F_{7/2})$ energy level transition of Ce^{3+} ion, and the luminous energy of emis-sion fluorescence is about $\Delta E = 27778$ cm^{-1}.
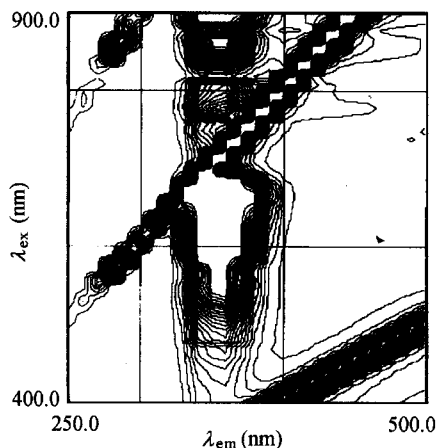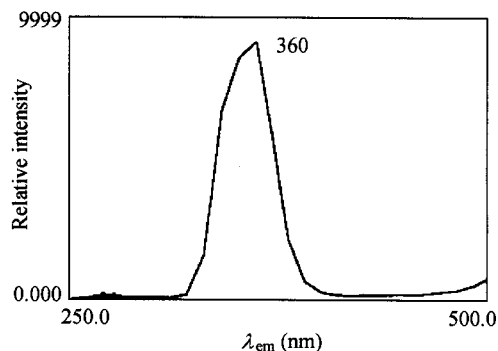
Fig. 8   Upconversion luminesence spectra of CsCl · CeCl$_3$ · 4H$_2$O ($\lambda_{ex} = 860$ nm).

The luminescence mechanism of the two compounds and the effect of crystal field and structure on the lumi-nescence property will be discussed elsewhere.

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Fig. 6   Excitation and emission 3-D spectra of CsCl · CeCl$_3$ · 4H$_2$O (three-dimension).
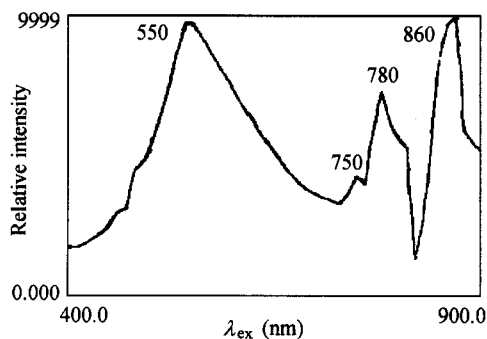
Fig. 7   Excitation spectra of CsCl · CeCl$_3$ · 4H$_2$O ($\lambda_{em} = 330$ nm).