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Article

Phase Equilibrium System of CsCl-YCl$_3$-(9.5%)HCl-H$_2$O at T＝298.15 K and Its Compounds

WANG, Hui*[,a,b](王惠)　　DUAN, Jin-Xia[a](段锦霞)
RAN, Xin-Quan[a](冉新权)　　GAO, Shi-Yang[b,c] (高世扬)

[a] *Department of Chemistry/Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an, Shaanxi 710069, China*
[b] *School of Chemistry and Material Science, Shaanxi Normal University, Xi'an, Shaanxi 710062, China*
[c] *Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xi'an, Shaanxi 710043, China*

The equilibrium solubility of one CsCl-YCl$_3$-H$_2$O ternary section of CsCl-YCl$_3$-9.5%HCl-H$_2$O quaternary system at T＝298.15 K was investigated by the physico-chemical analysis method and the corresponding phase diagram was plotted. The crystallization of two new double salts Cs$_4$YCl$_7$•10H$_2$O (4∶1 type) and Cs$_3$Y$_2$Cl$_9$•14H$_2$O (3∶2 type) was successful and they were obtained from the complicated system directly. Both were identified and characterized by X-ray, thermal analysis method of TG-DTG, DSC. The fluorescence experiments show that upconversion phenomenon does not exist in compounds Cs$_4$YCl$_7$•10H$_2$O and Cs$_3$Y$_2$Cl$_9$•14H$_2$O.

Keywords　solubility diagram of quaternary system, double salts, cesium chloride and yttrium chloride, compound Cs$_4$YCl$_7$•10H$_2$O and Cs$_3$Y$_2$Cl$_9$•14H$_2$O

Introduction

In a series of papers the authors reported the spectroscopy results on upconversion luminescence of the double salts between the alkali metal (Rb,Cs) halide and rare earth metal trihalide (REX$_3$).[1-4] Consequently, extensive syntheses of new double salts and studies on optical properties of such species have received much more attention.[5-12]

Although a number of these double salts have been synthesized, the formation in alkali metal halide/rare earth metal halide double salts seems to be limited to the four following types: Cs$_3$RE$_2$X$_9$ of 3∶2 type, RbRE$_2$X$_7$ of 1∶2 type, A$_2$REX$_5$ of 2∶1 type and A$_3$REX$_6$ of 3∶1 type (A＝K or Cs, RE＝La, Ce, Pr, Nd, Sm-Lu; X＝F, Cl, Br, I), respectively.[13] In contrast, many other species as 4∶1 or 5∶2 type have received much less attention, and little is known to data about the nature of optical properties in such species. In previous paper we reported the phase diagrams of CsX-REX$_3$-HX-H$_2$O (X＝Cl, Br; RE＝La, Ce, Pr, Nd, Sm, Gd, Dy) quaternary systems at 298 K, and the double salts such as 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 were found and synthesized from these equilibrium systems.[14-19] From optical investigation, it was found that some of them exhibit room temperature near infrared to visible region upconversion action.[20,21] Consequently, this new method of synthesizing such species of the double salts depending on investigating the phase relation of the systems of CsX-REX$_3$-HX-H$_2$O (X＝Cl, Br; RE＝La—Lu) has attracted our considerable interest.

The purpose of the present paper is to investigate the solubility of one CsCl-YCl$_3$-(9.5%)HCl-H$_2$O ternary section of CsCl-YCl$_3$-HCl-H$_2$O quaternary system at 298 K with a view to establishing the existence of new double salts.

Experimental

Preparation of the starting materials

For the preparation of YCl$_3$•6H$_2$O, hydrochloric acid of 0.37 HCl mass fraction (being A.R. grade) and 0.999 Y$_2$O$_3$ mass fractions, commercially available from various sources, were used as starting materials. YCl$_3$•6H$_2$O was crystallized from a solution of Y$_2$O$_3$ reacting in appropriate hydrochloric acid, and the purity is 0.999 mass fractions. It should be stored in dryer for use.

Investigations on the system of methods

For the investigation on the system of one ternary section (CsCl-YCl$_3$-9.5%HCl-H$_2$O) of a quaternary system (CsCl-YCl$_3$-HCl-H$_2$O) at 298 K, YCl$_3$•6H$_2$O (99.9%), CsCl (being A.R. grade) and hydrochloric acid (0.37 HCl mass fraction) were used as starting materials of the system. Different weight ratios of CsCl, YCl$_3$•

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* E-mail: huiwang@nwu.edu.cn
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$6H_2O$, hydrochloric acid of 0.37 HCl mass fraction and H_2O were used for each sample mixed according to the mass percent of the different points of the quaternary system $CsCl$-YCl_3-HCl-H_2O projected on the trigonal basal face $CsCl$-YCl_3-H_2O. Each sample was in solid-liquid phase coexistence. Thirty-six samples were prepared and sealed in a plastic container respectively. The HCl mass fraction of original liquid phase of every sample should be kept in a constant acidity (0.10 mass fraction) as possible. Then they were put in a thermostat with water of T=298 K, and agitated by an electrical stirrer. After 5—6 d, the acidity (HCl) of the liquid phase of every sample could bias from constant acidity of 0.10 mass fraction because of the system equilibrium established. Thus the liquid phase of the samples must be adjusted to constant acidity of 0.10 HCl mass fractions. The methods of adjusting acidity and analysis details were the same as those in Ref. 20.

TG-DTG, DSC, X-ray

Parkin-Elmer TGA7/4 thermal analysis apparatus (TG-DTG, DSC) was used and worked with heating rate 10℃/min under Ar atmosphere of flow rate 60 mL/min. A D/Max-3C instrument of X-ray powder diffraction was used, working on Cu target, at 50 kV and 80 mA.

Results and discussion

$CsCl$-YCl_3-9.5%HCl-H_2O system at 298 K

The solubility data of $CsCl$-YCl_3-9.5%HCl-H_2O quarternary system and central projection data on triangle basal face of $CsCl$-YCl_3-H_2O at 298 K are listed in Table 1, corresponding phase diagram is shown in Figure 1. It was established that, in addition to the sample salts CsCl and YCl_3•$6H_2O$, two double salts Cs_4YCl_7•$10H_2O$ (4∶1 type) and $Cs_3Y_2Cl_9$•$14H_2O$ (3∶2 type) also crystallizes from the saturated solutions. The solid-phase composition of the two double salts was determined graphically by Schreinemarkers method[22] and further confirmed by chemical analysis and thermal analysis method. The chemical analyses of double salts are YCl_3 18.27% (Theor. 18.62%), CsCl 63.88% (Theor. 64.22%) for 4∶1 type salt and YCl_3 34.00% (Theor. 34.03%), CsCl 44.85% (Theor. 44.01%) for 3∶2 type salt, respectively. The two new 4∶1 type and 3∶2 type

Table 1 Solubility data of saturated solution of the quaternary system $CsCl$-YCl_3-9.5%HCl-H_2O at 298 K and central projection on the trigonal basal face of $CsCl$-YCl_3-H_2O[a]

No.	Liquid phase (*w*)					Wet solid phase (*w*)					Solid phase in equilibrium
	Composition in the tetrahedron			Composition on the trigonal basal face[b]		Composition in the tetrahedron			Composition on the trigonal basal face[b]		
	HCl	YCl_3	CsCl	YCl_3	CsCl	HCl	YCl_3	CsCl	YCl_3	CsCl	
	Average acidity (*w*)=0.095										
1	0.1297	0.0322	0.4212	0.0370	0.4839	0.00					A
2	0.0896	0.0780	0.4643	0.0856	0.5099	0.0327	0.1114	0.6688	0.1151	0.6914	A+B
3	0.1044	0.0565	0.4571	0.0630	0.5104	0.0407	0.0849	0.7141	0.0885	0.7443	A+B
4	0.1131	0.0491	0.4322	0.0554	0.4873	0.0706	0.0983	0.5016	0.1058	0.5397	B
5	0.0940	0.1112	0.4060	0.1227	0.4481	0.0430	0.1618	0.5534	0.1691	0.5782	B
6	0.0811	0.1578	0.3886	0.1717	0.4229	0.0372	0.1962	0.4604	0.2038	0.4782	B+C
7	0.0785	0.1568	0.4035	0.1701	0.4379	0.0337	0.2487	0.4221	0.2574	0.4368	C
8	0.0915	0.1674	0.3040	0.1843	0.3346	0.0451	0.2509	0.3772	0.2627	0.3950	C
9	0.0809	0.2244	0.2385	0.2441	0.2595	0.0393	0.2806	0.3320	0.2921	0.3456	C
10	0.0646	0.2366	0.2757	0.2529	0.2947	0.0277	0.2839	0.3608	0.2920	0.3711	C
11	0.0728	0.2486	0.1804	0.2681	0.1946	0.0375	0.3015	0.3375	0.3132	0.3506	C
12	0.0736	0.2577	0.1787	0.2782	0.1928	0.0352	0.3240	0.2638	0.3358	0.2734	C+D
13	0.0816	0.2443	0.1889	0.2660	0.2056	0.0349	0.3518	0.2553	0.3646	0.2645	C+D
14	0.0931	0.2235	0.1907	0.2464	0.2102	0.0347	0.3721	0.2274	0.3855	0.2356	C+D
15	0.0983	0.2197	0.1970	0.2437	0.2185	0.0276	0.5149	0.0531	0.5295	0.0546	D
16	0.0942	0.2477	0.1173	0.2735	0.1295	0.0316	0.5100	0.0260	0.5266	0.0268	D
17	0.0968	0.2474	0.1229	0.2739	0.1361	0.0285	0.5237	0.0230	0.5391	0.0237	D
18	0.1070	0.2413	0.1003	0.2702	0.1123	0.0286	0.5290	0.0150	0.5446	0.0154	D
19	0.1101	0.2579	0.0399	0.2898	0.0448	0.0218	0.5623	0.0013	0.5749	0.0016	D
20	0.1170	0.2625	0.00	0.2973	0.00	0.00	0.6412	0.00	0.6412	0.00	D

[a] Two salt-coexistence points (average in percent): E_1: YCl_3 6.80%, CsCl 50.25%; E_2: YCl_3 17.09%, CsCl 43.04%; E_3: YCl_3 26.05%, CsCl 20.43%. Solid phase: A: CsCl; B: Cs_4YCl_7•$10H_2O$; C: $Cs_3Y_2Cl_9$•$14H_2O$; D: YCl_3•$6H_2O$. [b] "trigonal basal face": This is a ternary section of quaternary diagram at constant acidity (HCl).

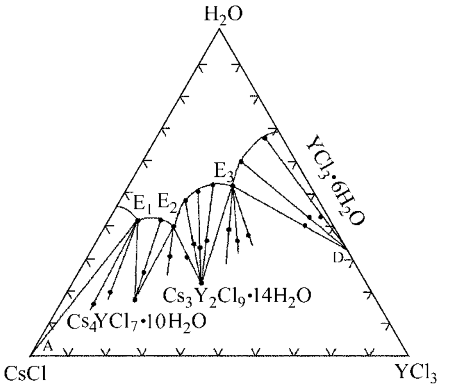

Figure 1 Solubility diagram of one ternary section $CsCl-YCl_3-H_2O$ of the quaternary system $CsCl-YCl_3-9.5\%HCl-H_2O$ at constant acidity 9.5% HCl at 298 K.

compounds are congruently soluble in 9.5% hydrochloric acid medium at 298 K (Figure 1). It was noticed that 3∶2 type compound can be synthesized directly from the equilibrium system, and this similar action has not been found in other system $CsCl-RECl_3-HCl-H_2O$ (RE=La, Pr, Nd, Sm, Gd).[16-19] Furthermore, the 4∶1 type double salt $Cs_4YCl_7\cdot10H_2O$ has not been synthesized and reported so far.

For the preparation of $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$, CsCl and $YCl_3\cdot6H_2O$ were used as starting materials according to the molar ratio CsCl/ $YCl_3\cdot6H_2O$ of the 4∶1 type and the 3∶2 type existing in phase region (Figure 1), respectively. Both were derived from the equilibrium system of the solid-liquid phase coexistence by following equations:

$$4CsCl+YCl_3\cdot6H_2O+4H_2O\ (9.5\%HCl) \longrightarrow Cs_4YCl_7\cdot10H_2O \qquad (1)$$

$$3CsCl+2YCl_3\cdot6H_2O+2H_2O\ (9.5\%HCl) \longrightarrow Cs_3Y_2Cl_9\cdot14H_2O \qquad (2)$$

Characterization of $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$

X-ray powder diffraction data of two compounds $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$ are d=0.4913 (100), 0.4772 (88), 0.3435 (76), 0.2904 (66) nm and d=0.4823 (100), 0.2424 (40), 0.3435 (28) nm, respectively, which are obviously much different from the literature data of X-ray powder diffraction of two sample salts CsCl d=0.2917(100), 0.4120(45), 0.1683(25) nm[23a] and $YCl_3\cdot6H_2O$ d=0.6000 (100), 0.2750 (80), 0.3400 (50), 0.1986(50) nm.[23b]

TG-DTG and DSC data for compounds $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$ are presented in Table 2 and Figure 2 (A, B, C and D). The curves A (DTG) and B (DSC) show that, for $Cs_4YCl_7\cdot10H_2O$, there are two obvious mass-loss steps at T=334 to 420 K (DTG) and at T=330 to 407 K (DSC). For example, from the curves A (DTG), the salt is dehydrated on 2 stages releasing five water molecules at T=334 K and releasing another five water molecules at T=420 K, respectively, with the anhydrous salt being followed [Eq. (3)]. The total mass-loss value is 17.36% (Theor. 17.16%). The same investigation was for the second salt $Cs_3Y_2Cl_9\cdot14H_2O$. There are three obvious mass-loss steps in the temperature range 350—482 K (DTG), and the salt is dehydrated on 3 stages releasing eight, five and one water molecules, respectively, with the anhydrous salt being followed [Eq. (4)].

$$Cs_4YCl_7\cdot10H_2O \xrightarrow[334.7\ K]{-5H_2O}$$

$$Cs_4YCl_7\cdot5H_2O \xrightarrow[420.2\ K]{-5H_2O} Cs_4YCl_7 \qquad (3)$$

$$Cs_3Y_2Cl_9\cdot14H_2O \xrightarrow[350.1\ K]{-8H_2O} Cs_3Y_2Cl_9\cdot6H_2O \xrightarrow[394.7\ K]{-5H_2O}$$

$$Cs_3Y_2Cl_9\cdot H_2O \xrightarrow[481.7\ K]{-H_2O} Cs_3Y_2Cl_9 \qquad (4)$$

The total value of the mass-loss is 21.82% (Theor. 21.98%). The curves A and curves C also show that pyrolysis peak temperatures of compounds $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$ are at 1071.5 K and at 1119.6 K, respectively. The results of TG-DTG and DSC further confirm that there are really ten crystal-water molecules for 4∶1 type and fourteen crystal-water molecules for 3∶2 type salts, respectively. It means that the formation of the solid phase compounds determined by Schreinemarkers method is believable.

Table 2 TG-DTG and DSC date for $Cs_4YCl_7\cdot10H_2O$ and $Cs_3Y_2Cl_9\cdot14H_2O$

Compound	Peak temp./K		Loss ratio weight/%		Product
	DTG	DSC	Experimental	Theoretical	
$Cs_4YCl_7\cdot10H_2O$					
Lost $5H_2O$	334.7	330.8	8.69	8.58	$Cs_4YCl_7\cdot5H_2O$
Lost $5H_2O$	415.2	407.1	8.67	8.58	Cs_4YCl_7
Lost total $10H_2O$			17.36	17.16	Cs_4YCl_7
$Cs_3Y_2Cl_9\cdot14H_2O$					
Lost $8H_2O$	350.1	346.1	12.23	12.56	$Cs_3Y_2Cl_9\cdot6H_2O$
Lost $5H_2O$	404.7	411.2	8.07	7.85	$Cs_3Y_2Cl_9\cdot H_2O$
Lost $1H_2O$	491.7	494.8	1.52	1.57	$Cs_3Y_2Cl_9$
Lost total $14H_2O$			21.82	21.98	$Cs_3Y_2Cl_9$

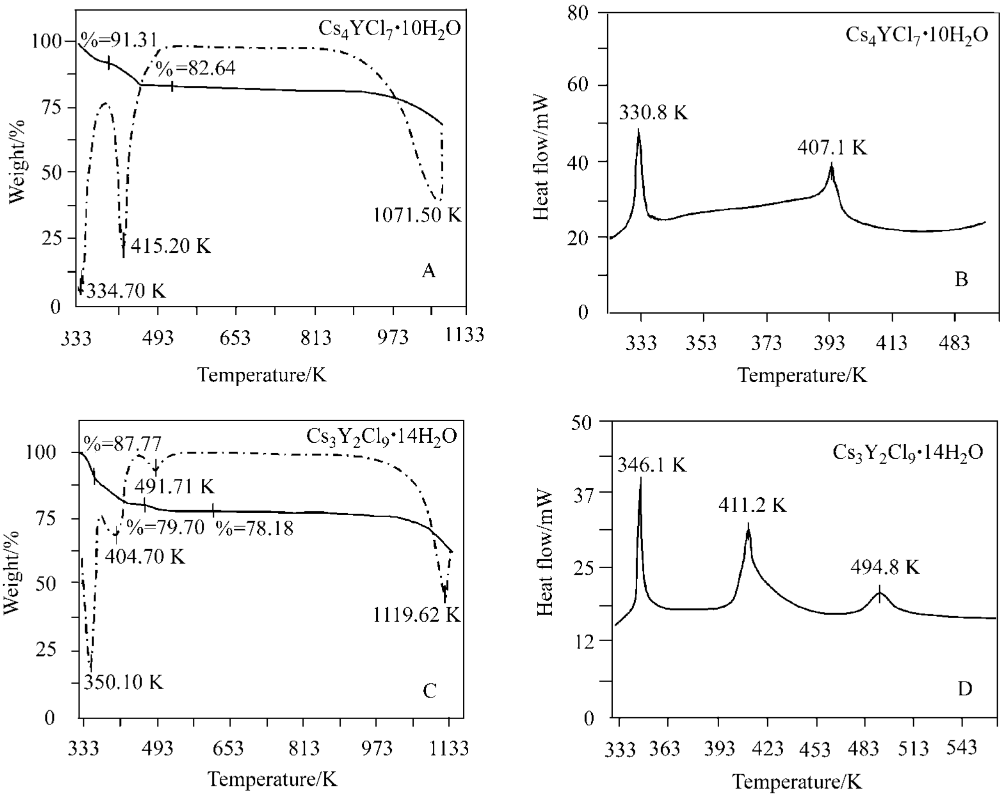

Figure 2 TG-DTG (A and C) and DSC (B and D) graph of $Cs_4YCl_7•10H_2O$ and $Cs_3Y_2Cl_9•14H_2O$ double salts.

Fluorescence excitation and emission spectra of compounds $Cs_4YCl_7•10H_2O$ and $Cs_3Y_2Cl_9•14H_2O$

The ternary rare-earth halides $Cs_3CeCl_6•3H_2O$ (3 : 1 type) and $CsCeCl_4•4H_2O$ (1 : 1 type) show intense upconversion luminescence when excited in the near infrared or visible region, and the upconversion intensity becomes stronger with the increasing of $CeCl_3$ ratio in CsCl.[21] Then, how are the fluorescence excitation and emission spectra of $Cs_4YCl_7•10H_2O$ (4 : 1 type) or $Cs_3Y_2Cl_9•14H_2O$ (3 : 2 type)?

In order to know the optical properties of $Cs_4YCl_7•10H_2O$ and $Cs_3Y_2Cl_9•14H_2O$, scanned fluorescence excitation and emission 3-D spectra of them were measured at 200—900 nm wavelength range. The result shows that, for $Cs_4YCl_7•10H_2O$, there are not obviously excitation spectra monitored at 200—900 nm and emission spectra excited at 200—900 nm, respectively. But for $Cs_3Y_2Cl_9•14H_2O$ scanned, a series of excitation spectra monitored at 250—650 nm range were observed with their peaks being at 200 nm (λ_{EM}=480, 620 nm), 220 nm (λ_{EM}=280, 350, 370 nm) and 255 nm (λ_{EM}=350 nm), respectively, and the intensity of excitation spectrum at 255 nm (λ_{EM}=350 nm) is the strongest. Emission luminescence spectra of $Cs_3Y_2Cl_9•14H_2O$ were observed at 480, 620 nm (λ_{Ex}=200 nm), 280, 350, 370 nm (λ_{Ex}=220 nm) and 350 nm (λ_{Ex}=255 nm) respectively. The intensity of emission spectrum at 350 nm (λ_{EX}=255 nm) is the strongest. The emission spectra of $Cs_3Y_2Cl_9•14H_2O$ originate from "Stokes" luminescence of Y^{+3} ion in CsCl. While compound $Cs_4YCl_7•10H_2O$ (4 : 1 type) dose not exhibit emission luminescence, due to the decreasing of YCl_3 ratio in CsCl.

As mentioned above it indicates that upconversion phenomenon dose not exist in compounds $Cs_4YCl_7•10H_2O$ and $Cs_3Y_2Cl_9•14H_2O$.

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References

1 Toni, R.; Karl, K.; Hans, U. G. *Inorg. Chem.* **1995**, *34*, 2745.
2 Dorenbos, P.; Kramer, K.; Gudel, H. U. *Methods Phys. Res. Sect, B.* **1997**, *132*, 278.
3 Hans, U. G.; Albert, F.; Herma, B. *Inorg. Chem.* **1990**, *29*, 4081.
4 Markus, P. H.; Hans, U. G. *J. Chem. Phys.* **1994**, *101*, 10303.
5 Gert, R.; Gerlinde, F. *J. Solid State Chem.* **1995**, *116*, 329.
6 Karbowiak, M.; Hanuza, J.; Drozdzynski, J.; Hermanowiez, K. *J. Solid State Chem.* **1996**, *121*, 312.
7 Schilling, G.; Meyer, G. *Z. Anorg. Allg. Chem.* **1996,** *622*, 759.
8 Markus, P. H.; Karl, K.; Hans, U. G. *Phys. Rev. B* **1994**, *49*, 12475.
9 Aebersold, M. A.; Gudel, H. U.; Furrer, A.; Blank, H. *Inorg.*

Chem. **1994**, *33*, 1133.

10 Markus, P. H.; Gabrieb, F.; Hans, U. G. *Phys. Rev. B* **1994**, *50*, 16264.

11 John, R.; Quag, L.; Nigel, J. C. *J. Chem. Phys.* **1996**, *150*, 9812.

12 Van't, S. J. C. *Radiat. Meas*. **1995**, *24*, 378.

13 Meyer, G. *Inorg. Synth*. **1983**, *22*, 1.

14 Wang, H.; Ran, X. Q.; Chen, P. H. *Chem. J. Chin. Univ.* **1997**, *18*, 1420 (in Chinese).

15 Wang, H.; Ran, X. Q.; Chen, P. H. *Chin. Sci. Bull.* **1996**, *41*, 910.

16 Jao, H.; Wang, H.; Ran, X.; Chen, P. *Acta Chim. Sinica* **1998**, *56*, 854 (in Chinese).

17 Li, Y.; Ran, X.; Chen, P.; Gao, S. Y. *Chem. Papers-Chem. Zvesti*. **1998**, *52*, 211.

18 Li, Y.; Ran, X.; Chen, P. *J. Rare Earth.* **1997**, *15*, 113.

19 Li, Y.; Ran, X.; Chen, P.; Gao, S. Y. *J. Inorg. Chem.* **1999,** *44*, 1207.

20 Wang, H.; Duan, J. X.; Ran, X. Q.; Gao, S. Y. *J. Chem. Thermodyn.* **2002**, *34*, 1495.

21 Wang, H.; Duan, J. X.; Ran, X. Q.; Gao, S. Y. *Chin. J. Chem*. **2002**, *20*, 904.

22 Cheng, Y. S. *Analysis of Physical Chemistry*, Higher Education Press, Beijing, **1988**, p. 505 (in Chinese).

23 Powder Diffraction File, *Alphabetical Index Inorganic Phases*, Sets 21 to 22, Inorganic volume, No. PDIS-22iRB. Published by the JCPDS International Centre for Diffraction Data, Pennsylvania, USA, **1989**, a: p. 146, b: p. 156.

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