ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 1037–1040

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Formation and characterization of the non-crystalline lanthanoid(III) hydrate salts of lacunary heteropolytungstates, $SiW_{11}O_{39}^{8-}$ and $P_2W_{17}O_{61}^{10-}$

Akira Saito *

Chemistry Department, Tokyo Gakugei University, 4-1-1 Nukuikita-machi, Koganei, Tokyo 184-8501, Japan

Received 31 July 2004; received in revised form 11 November 2004; accepted 11 November 2004

Abstract

When aqueous solutions which contain Ln^{3+}, K^+ and lacunary heteropolytungstate ions, $SiW_{11}O_{39}^{8-}$ or $P_2W_{17}O_{61}^{10-}$, at high concentrations are cooled to nearly 0 °C, the solutions separate into two layers with a clear boundary. The lower layers are very viscous, of high densities, around 3 g cm^{-3}. The separation takes place for all the trivalent lanthanides when K^+ exists as the univalent cation. When Na^+ or Li^+ is used instead of K^+, the solutions just become very thick. When Na^+ is mixed with K^+ in certain ratios, two layer formation is observed. The oil-like materials are considered as liquid hydrate salts with average chemical compositions $Na_xK_yLn[SiW_{11}O_{39}]_2 \cdot nH_2O$, where x was varied from 0 to 5.5 and n is the molar number of water, ∼100.

Keywords: Amorphous materials; Luminescence; Chemical synthesis; Quasicrystals

---

1. Introduction

Extensive studies have been conducted on the syntheses of polyoxometalates which contain lanthanoid(III) as heteroatoms or counter cations [1]. Since polyoxometalates are oxide anions of large ionic sizes and of unique structures, counter cations in the formulation of secondary structures are taking important roles [2]. Lacunary heteropolytungstate ions, $SiW_{11}O_{39}^{8-}$ and $P_2W_{17}O_{61}^{10-}$ are known to have very large abilities to bind metal cations at their defect sites. Several authors have tried to crystallize salts with trivalent lanthanoids expecting to produce materials of useful properties. In aqueous solutions, both ions work as ligands of large basicity such that Ln(III) forms stable 1:1 and 1:2 complexes [3,4]. Peacock and Weakley [5] and Haraguchi et al. [6] described their observation about the appearance of oil-like substance at the bottom of the solution when they cooled the concentrated solution of Ln(III) and $SiW_{11}O_{39}^{8-}$ to crystallize the intended salt. Since their major objects were syntheses of crystalline products, no further investigations were made. We made sure that the separation of the concentrated solution into two layers always happens if it contains Ln(III) and K^+ or NH_4^+. We also observed that this viscous material turns to glass-like transparent film on drying. In this study, we made basic investigation to find definite conditions for the production of such non-crystalline phases and to understand the nature of the substances.

2. Experimental

2.1. Reagents

Dodecatungustosilicic acid, $H_4[SiW_{12}O_{40}] \cdot nH_2O$, potassium undecatungustosilicate hydrates, $K_8[SiW_{11}O_{39}] \cdot nH_2O$ [7], potassium octadecatungustodiphosphate hydrate, $K_8[P_2W_{18}O_{62}] \cdot nH_2O$ and potassium heptadecatungustodiphosphate hydrate $K_{10}[P_2W_{17}O_{61}] \cdot nH_2O$ [8], were synthesized according to the methods described in the reference. The products were analyzed for the W contents by ICP–AES method. Aqueous solutions of Ln(III) nitrate

---

* Tel.: +81 42 329 7507; fax: +81 42 329 7508.
E-mail address: akira@u-gakugei.ac.jp.

doi:10.1016/j.jallcom.2004.11.093

were prepared by dissolving respective oxides in nitric acid followed by removal of excess acid by evaporation. The concentrations were determined by titration with EDTA, or by ICP–AES. All the salts of alkali metals as nitrates or carbonates were of reagent grades, and used as received from Wako, Japan.

2.2. Procedures for the preparation of the Ln(III) salt hydrates

Solutions of Ln(III) salts with K^+ were prepared by use of $K_8[SiW_{11}O_{39}]\cdot 13H_2O$ and Ln(III) nitrate in a molar ratio of 2:1. In a typical preparation, 10 g of $K_8[SiW_{11}O_{39}]\cdot 13H_2O$ (3.0×10^{-3} moles) was added to 60 mL of distilled water and heated to about 75 °C. To the clear solution, 1.5×10^{-3} moles of $Ln(NO_3)_3$ was added. The volume of the solution was then reduced by evaporation on a water bath to about 20 mL. The solution was cooled in an ice bath. At about 30 °C, the solution first started to become cloudy, and as the temperature decreased the cloudiness prevailed in the whole part of the solution. At around 10 °C, the solution turned completely cloudy, and in a few tens of seconds the solution became bilayer. The upper layer was transparent, and the bottom one was slightly cloudy at first, then it turned completely transparent when the solution warmed to about 3 °C. Two layers were separated for further characterization. Dodecatungustosilicic acid hydrate was also used as a starting material with use of the alkali carbonates to neutralize the acid. Degradation of the heteropolytungstates was effected by the adjustment of the pH to 4.5. The other procedures were essentially the same as described above.

2.3. Analysis of the composition

The density was obtained by weighing a known volume of the liquid. Weighed amounts of the bottom layers were dissolved in dilute nitric acid, and made up to definite volumes. Ln(III) and W were determined by ICP–AES, and K^+ and NH_4^+ ions were determined by gravimetry as tetraphenylborate.

2.4. Luminescence spectroscopy of Eu(III) compounds

Emission spectra were measured by excitation with a dye laser beam of 394 nm and the decay of the excited state was detected by measuring intensity of the emission at 615 nm. The samples were placed between quartz plates. All the measurements were made at room temperature.

3. Results

3.1. Formation of oil-like layers

3.1.1. M^+/Ln(III)/$SiW_{11}O_{39}^{8-}$ systems

The separation of the solutions into two layers was observed for all the trivalent lanthanoids when K^+ exists as the univalent counter cation. The volumes of the lower phases were about 20% of the totals. These ratios showed only slight decreases for the heavy lanthanoids. When Na^+ or Li^+ is used instead of K^+, the solutions just became very thick. On the other hand, Na^+ is mixed with K^+ in the ratios up to 50%, two layers formation is also observed. The oil-like layers showed the color of the respective Ln(III).

Parts of clear, oil-like layers were taken into shallow petri dishes and heated on a water bath. In a few minutes, the viscous solutions turned transparent glass-like films. Once they are transformed, they stayed as stable transparent materials. No clear diffraction lines were observed in the X-ray diffraction measurement, suggesting that they are non-crystalline materials.

The boundary of the two layers gradually became unrecognizable if the solution was warmed to room temperature. The oil-like bottom layers, once separated, were not stable, since the precipitation took place in a few hours. Powder X-ray diffraction measurements indicated that the precipitated substances were crystalline compound, though poorly grown. The composition was confirmed as the formula $K_{13}Ln[SiW_{11}O_{39}]_2\cdot nH_2O$, by the analysis.

3.1.2. K^+/Ln(III)/$P_2W_{17}O_{61}^{10-}$ system

The concentrated solutions of Eu(III) or Nd(III) nitrates and $K_{10}[P_2W_{17}O_{61}]\cdot nH_2O$ of pH ∼ 5 were prepared initially as a hot solution. On cooling to 30 °C, separation of viscous oil-like layer was also observed. For this system, however, the crystallization proceeded more quickly even at room temperature.

3.2. Characterization

3.2.1. K^+/Ln(III) system

The analytical data of the composition of the oil-like substances for the selected Ln(III) are given in Table 1. If the substances are hydrate salts obtained as liquid state of the formula $K_{13}Ln[SiW_{11}O_{39}]_2\cdot nH_2O$, theoretical molar ratios of K and W to Ln should be 13 and 22, respectively. In every case, the analytical data are smaller than these values by various degrees. It suggests the substances are mixtures of the compound given above and Ln(III) nitrates added as starting

Table 1
Analytical data of the oil-like substances for the selected Ln(III) with K^+ and $SiW_{11}O_{39}^{8-}$

Ln	K, found (%)	Ln, found (%)	W, found (%)	H_2O, calculated[a]	
				%	*n*
La	5.17	1.98	49.1	27.9	109
Nd	7.23	2.19	53.9	19.3	70.6
Gd	5.20	2.12	50.8	25.6	105
Dy	5.57	2.20	52.1	23.3	95.5
Tm	5.09	2.13	48.5	28.6	126
Lu	5.40	2.23	50.7	25.4	111

[a] Water contents were calculated on the supposition that the substances are $K_{13}Ln[SiW_{11}O_{39}]_2\cdot nH_2O$.

materials. The discrepancies must be partly due to systematic errors because of the large difference in mass percentages between K, Ln and W. Densities of the oil-like layers for all lanthanoids were within the average of 2.94(±0.10) g/mL. No trends along the series were observed. Number of moles of water in the oil-like phases were estimated based on the W determination of the samples and on the supposition that the phases are hydrates of $K_{13}Ln[SiW_{11}O_{39}]_2 \cdot nH_2O$. Widely scattering values for n from 60 to 130 were obtained. No apparent trends along the Ln(III) series were recognized, that is, the number of water molecules is not affected by the properties of Ln(III) such as ionic radii. The glass-like products obtained by drying the oil-like substances were found to have the same compositions as those reported for the crystalline compounds. Numbers of water of hydration of the glass-like substances were 27(±2) for La–Lu, while those of the crystalline compounds were 28(±3), which were determined by thermal analysis.

3.2.2. $Na^+/K^+/Nd(III)$ systems

The compositions of the oil-like substances obtained from the solutions of Na^+ and K^+ mixed systems were determined similarly. The contents of K^+ were determined by gravimetry as tetraphenylborate. The results suggest that the substances are liquid hydrates of the formula $Na_xK_yNd[SiW_{11}O_{39}]_2 \cdot nH_2O$, in which $x + y = 13$. In Fig. 1, the estimated values of x and n are plotted against the molar ratio of Na^+ added to the initial solution. The water content decreases with a decrease in x.

3.2.3. $K^+/Ln(III)/P_2W_{17}O_{61}{}^{10-}$ system

The analytical data of the compositions of the oil-like substances obtained for Nd(III) and Eu(III) with $P_2W_{17}O_{61}{}^{10-}$ are listed in Table 2. The number of water, n, was calculated based on the analytical data for W, providing that the substances are represented as $K_{17}Ln[P_2W_{17}O_{61}]_2 \cdot nH_2O$. The analytical data of the glass-like and crystalline substances indicated that they are $K_{17}Ln[P_2W_{17}O_{61}]_2 \cdot nH_2O$.

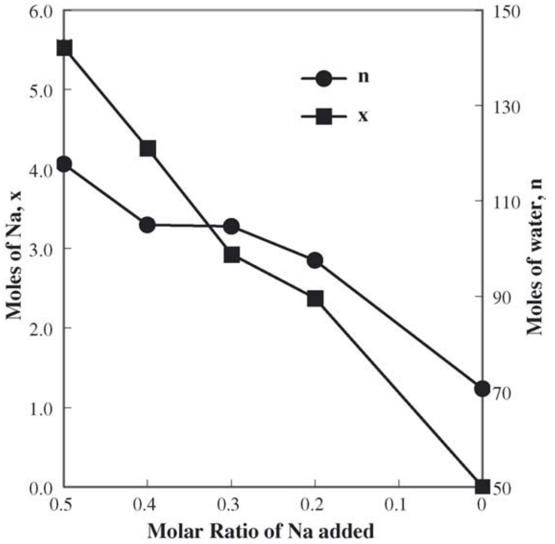

Fig. 1. Composition of the oil-like substance formed in the Na^+ and K^+ mixed system as $Na_xK_yLn[SiW_{11}O_{39}]_2 \cdot nH_2O$.

Table 2
Analytical data of the oil-like substances obtained for Nd(III) and Eu(III) with K^+ and $P_2W_{17}O_{61}{}^{10-}$

Ln	K, found (%)	Ln, found (%)	W, found (%)	H_2O, calculated[a]	
				%	n
Nd	5.40	1.07	49.5	27.6	207
Eu	5.27	1.16	48.9	28.4	207

[a] The number of water, n, was calculated based on the analytical data for W, providing that the substance in each state is represented as $K_{17}Ln[P_2W_{17}O_{61}]_2 \cdot nH_2O$.

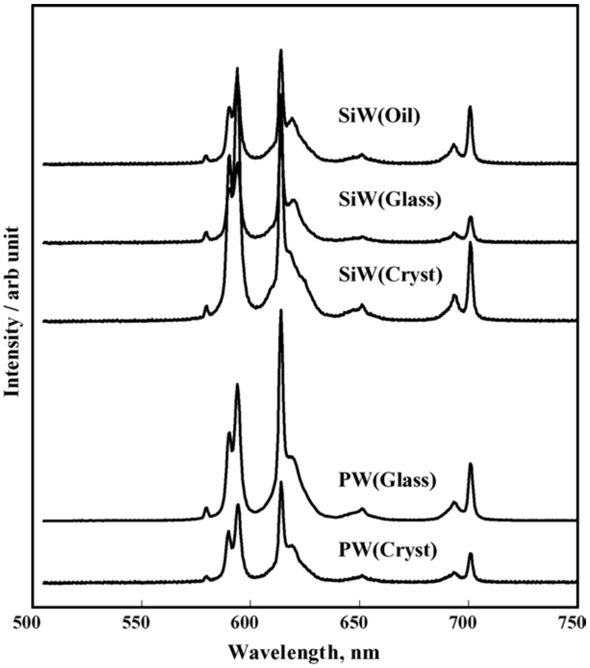

Fig. 2. Emission spectra of Eu(III) compounds due to the transition $^5D_0 \rightarrow {}^7F_J$ ($\lambda_{ex} = 394$ nm). SiW and PW refer to the compounds given in Table 3.

3.3. Luminescence spectroscopy of Eu(III) compounds

In Fig. 2 emission spectra of the substances of Eu(III) are reproduced. All spectra are very similar to each other and are indicating that the coordination environments of Eu(III) are the same [9]. Inner-sphere hydration number, N_{H_2O}, was obtained from the decay constants of the excited state of Eu(III) as given in Table 3 [10]. No water coordinates to Eu(III) in any of the samples.

4. Discussion

From the density and the analytical data of the oil-like substance, the "concentration" of $K_{13}Ln[SiW_{11}O_{39}]_2$ can be calculated. For the samples with Ln from La to Lu, they were

Table 3
Inner-sphere hydration numbers, N_{H_2O}, of Eu(III) heteropolytungstates

Compounds	State	k_{obs} (ms^{-1})[a]	N_{H_2O}[b]
$K_{13}Eu[SiW_{11}O_{39}]_2 \cdot nH_2O$ (SiW)	Oil-like	0.802	0.40
	Glass-like film	0.742	0.34
	Crystalline	0.420	0.00
$K_{17}Eu[P_2W_{17}O_{61}]_2 \cdot nH_2O$ (PW)	Glass-like film	0.558	0.15
	Crystalline	0.572	0.16

[a] Measurements at λ_{em} = 615 nm, λ_{ex} = 394 nm, HV = 600 V, slit = 0.1 mm.

[b] $N_{H_2O} = 1.05 \times k_{obs} - 0.44$ [10].

averaged to 0.354(±0.025) mol/L. From the mass balance, the material distribution between two phases is estimated as 85% in the oil-like phase and 15% in the supernatant. Therefore, the upper layer is a solution of the salt, the concentration of which is around 0.06 mol/L. However, the lower layer cannot be a solution of the same salt as that of the upper layer because it is improbable that solutions of one chemical species with different concentrations coexist as two contacting layers. Therefore, the oil-like phase must be a single chemical species that has separated out as intermediate metastable state.

From the luminescence spectral measurements, the existence of the complex anions $Ln[SiW_{11}O_{39}]_2{}^{13-}$ and $Ln[P_2W_{17}O_{61}]_2{}^{17-}$ in the oil-like substance is obvious. Since no water is in the inner-sphere of Ln(III), the anions have the same configurations as those found in the crystals by X-ray diffraction study [3,11]. It is also established that the coordination geometry around Ln(III) is a skewed square antiprism formed by eight oxygen atoms, four from each lacunary anion. Therefore, conformation, which would be one of the reasons why crystallization is retarded. The characteristic features of these units are that they have far more larger ionic sizes and formal negative charges, and that they have unique conformations with two anions tied by Ln(III) with angles. This might be one of the reasons why such a novel phase appears.

The inclusion of larger number of water molecules must be the important factor that brings the oil-like substance to metastable phase. There are three types of water: (a) water of hydration of the counter cations, M^+ (M: K, Na, or NH_4), (b) water of hydration of the complex anions, probably interacting through hydrogen bonding to surface oxygen atoms of $Ln[SiW_{11}O_{39}]_2{}^{13-}$ and $Ln[P_2W_{17}O_{61}]_2{}^{17-}$ and (c) those which are not interacting with any of these ions.

The existence of K^+ seems to be essential to the formation of the oil-like substances. The effective ionic radii of Li^+, Na^+ and K^+ increase in this order, while the hydration numbers decrease rapidly in the same order. When larger cations such as Rb^+ or Cs^+ were added to the solutions, very insoluble, white precipitates formed instantly. An X-ray structural study of α-$K_8[SiW_{11}O_{39}] \cdot 13H_2O$ found that K^+ is linking two anion units through four oxygen atoms from each [12]. Very large water contents of the oil-like substances may indicate that counter cations mostly exist as hydrated ions filling the gaps between the large complex anions, but some part of the K^+ ions must be taking another role to give the oil-like substance somewhat structured state. As seen in Fig. 1, the oil-like substances formed from the mixtures of Na^+ and K^+ contain more water as the ratio of Na^+ increases. This is consistent with the idea that larger number of water molecules is necessary to hydrate Na^+. Even in the most concentrated solutions, the interaction between the Na^+ or Li^+ and the complex anions would not be direct, but through coordinated water, so that it is not enough strong to produce metastable hydrates.

Acknowledgements

The author is deeply indebted to Dr. T. Kimura and Y. Kato of Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Japan, for providing the TRLSP system, for their assistance in measurements and discussion about the results. Part of the study has been presented as the master's dissertation (Tokyo Gakugei University, 2000) by K. Ibaraki, whom the author would like to acknowledge.

References

[1] A. Müller, F. Peters, Chem. Rev. 98 (1998) 239–271.
[2] M. Misono, Chem. Commun. (2001) 1141–1152.
[3] J. Bartis, S. Sukal, M. Dankova, E. Kraft, R. Kronzon, M. Blumenstein, L.C. Francesconi, J. Chem. Soc., Dalton Trans. (1997) 1937–1944.
[4] C.E. VanPelt, W.J. Crooks III, G.R. Choppin, Inorg. Chim. Acta 340 (2002) 1–7.
[5] R.D. Peacock, T.J.R. Weakley, J. Chem. Soc. (1971) 1836–1840.
[6] N. Haraguchi, Y. Okaue, T. Isobe, Y. Matsuda, Inorg. Chem. 33 (1994) 1015–1020.
[7] A. Teze, G. Herve, Inorganic Syntheses, vol. 27, Wiley Interscience, 1990, p. 85 (Chapter 3, Section 16).
[8] R. Contant, Inorganic Syntheses, vol. 27, Wiley Interscience, 1990, p. 104 (Chapter 3, Section 18).
[9] G. Blasse, G.J. Dirksen, F. Zonnevijlle, J. Inorg. Nucl. Chem. 43 (1981) 2847–2853.
[10] V.N. Molchanov, L.P. Kazanskii, E.A. Torchenkova, V.I. Simonov, Sov. Phys. Crystallogr. 24 (1979) 96–97.
[11] T. Kimura, Y. Kato, J. Alloys Compd. 275–277 (1998) 806.
[12] K.Y. Matsumoto, Y. Sasaki, Bull. Chem. Soc. Jpn. 49 (1976) 156–158.