

# Separation of Red ( $Y_2O_3: Eu^{3+}$ ), Blue (Sr, Ca, Ba)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>: Eu<sup>2+</sup> and Green (LaPO<sub>4</sub>: Tb<sup>3+</sup>, Ce<sup>3+</sup>) Rare Earth Phosphors by Liquid/Liquid Extraction

MEI Guangjun<sup>1</sup>, RAO Peng<sup>1</sup>, MITSUAKI Matsuda<sup>2</sup>, TOYOHISA Fujita<sup>2</sup>

(1.School of Resource and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China; 2. Department of Material-Process & Applied Chemistry for Environments, Akita University, Akita 010-8502, Japan)

**Abstract:** A novel process for separation of red ( $Y_2O_3: Eu^{3+}$ ), blue (Sr, Ca, Ba)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>: Eu<sup>2+</sup> and green (LaPO<sub>4</sub>: Tb<sup>3+</sup>, Ce<sup>3+</sup>) fine tricolor phosphor powders was established. First, the green phosphor was extracted and separated from three phosphor mixtures in heptane/DMF(N, N-Dimethylformamide) system using stearylamine or laurylamine (DDA) as the cationic surfactant. Then, after being treated with 99.5% ethanol, the blue and red phosphors could be separated in Heptane/DMF system in presence of 1-octanesulfonic acid sodium salt as the anionic surfactant. Satisfactory separation results have been achieved through two steps extractions with their artificial mixtures. The grades and recovery of separated products reached respectively as follows: red product was 95.3% and 90.9%, blue product was 90.0% and 95.2%, and green product was 92.2% and 91.8%.

**Key words:** rare earth phosphor; liquid-liquid extraction; separation

## 1 Introduction

It is a worldwide problem to dispose waste fluorescent lamps containing waste phosphor sludge and hazardous waste such as mercury<sup>[1-3]</sup>. However, separation and recycling of waste fluorescent lamps is a viable option<sup>[4]</sup>, which can reduce the risk of future financial liability associated with hazardous waste.

Red ( $Y_2O_3: Eu^{3+}$ ), blue (Sr, Ca, Ba)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>: Eu<sup>2+</sup> and green (LaPO<sub>4</sub>: Tb<sup>3+</sup>, Ce<sup>3+</sup>) are three color phosphors which has been widely applied in fluorescent lamps and emission display<sup>[5]</sup>, the valuable metals such as yttrium, europium, cerium, terbium, lanthanum, strontium contained in the waste phosphor complex are precious secondary rare earth resources<sup>[6,7]</sup>. In previous research regard to lamp recycling<sup>[8-10]</sup>, yttrium and europium elements could be recovered from waste phosphor sludge by means of leaching treatment and oxalate precipitation method after pneumatic classification. And then, rare earth powder of red phosphor ( $Y_2O_3: Eu^{3+}$ ) was also reproduced by coprecipitation process<sup>[11]</sup>, but the other rare earth elements can not be recovered, some disad-

vantages exist on this process due to the long treatment flow sheet and expensive cost.

However, the main problem is relying on the particle size is less than 10 μm, that it is not suitable to do this solid-solid separation by flotation and other conventional mineral processing techniques. In the present research, separation of red ( $Y_2O_3: Eu^{3+}$ ), blue (Sr, Ca, Ba)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>: Eu<sup>2+</sup> and green (LaPO<sub>4</sub>: Tb<sup>3+</sup>, Ce<sup>3+</sup>) fine tricolor phosphor powders by liquid/liquid extraction was investigated, satisfactory separation results have been achieved through two steps extractions with their artificial mixtures. This research provided a new possibility for the recycling of rare earth waste phosphor sludge in the future.

## 2 Experimental

### 2.1 Tricolor phosphor powders

Table 1 is the chemical compositions of pure three phosphor samples analyzed by ICP SPS-3000 and XRD. Before analysis by ICP, samples should be treated with 1 : 1 HClO<sub>4</sub> and HNO<sub>3</sub> at boiled temperature, and then dissolved in aqua regia (1 : 3 HNO<sub>3</sub> and HCl) solution slowly. The pure samples are commercial phosphor powders, which have been widely applied in fluorescent lights and low voltage displays, the phosphors particle size is in the range of 1-3 μm, and the average particle

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MEI Guangjun(梅光军): Assoc. Prof.; Ph D; E-mail: mgj8343@sina.com

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size is under 3  $\mu\text{m}$ . The measurement of specific gravity was conducted in specific gravity bottle, and the obtained specific gravities of the red, blue and green phosphors were 5.12, 4.27 and 5.06, respectively.

**Table 1 Chemical composition of pure tri-phosphor samples**

Samples	Content/%							
Red( $\text{Y}_2\text{O}_3$ : $\text{Eu}^{3+}$ )	$\text{Y}_2\text{O}_3$ 91.6	$\text{Eu}_2\text{O}_3$ 7.8						
Green( $\text{LaPO}_4$ : $\text{Tb}^{3+}$ , $\text{Ce}^{3+}$ )	$\text{P}_2\text{O}_5$ 29.8	$\text{La}_2\text{O}_3$ 39.7	$\text{CeO}_2$ 18.8	$\text{Tb}_4\text{O}_7$ 10.3				
Blue ( $(\text{Sr}, \text{Ca}, \text{Ba})_{10}(\text{PO}_4)_6\text{Cl}_2$ : $\text{Eu}^{2+}$ )	$\text{P}_2\text{O}_5$ 25.0	$\text{Al}_2\text{O}_3$ 1.32	Cl 1.1	CaO 1.8	$\text{Fe}_2\text{O}_3$ 0.014	SrO 41.2	BaO 27.0	$\text{Eu}_2\text{O}_3$ 1.1

The surface charge was tested using ELS-8000 zeta potential meter (manufactured by otsuka electronic co, ltd. of Japan), the results are shown in Fig.1.

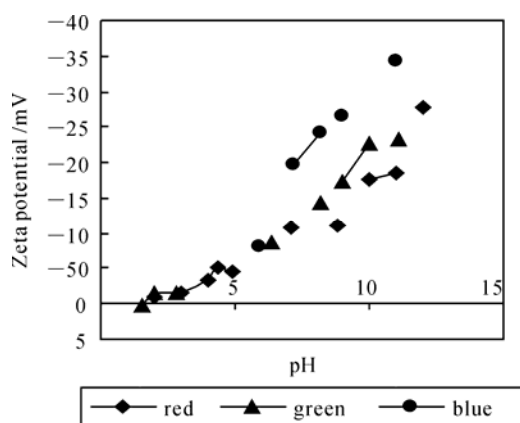


Fig.1 Zeta potentials of the phosphor powders

## 2.2 Chemical reagents

Two cationic surfactants as laurylamine (DDA:  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ ), stearylamine ( $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ ), and two anionic surfactants as laurylsulfonic acid sodium salt (SDBS:  $\text{C}_{18}\text{H}_{35}\text{SO}_3\text{Na}$ ) and 1-octanesulfonic acid sodium salt ( $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$ ) were used in these experiments. All of them were manufactured by Tokyo kasei kogyo co., ltd. in Japan, as analytical-grade reagents. Series of usual organic solvents such as N-hexane, heptane, n-decane, dodecane, and n-hexadecane were also supplied by Tokyo kasei, as guaranteed reagents or extra pure reagents. DMF (N, N-Dimethylformamide) was supplied by nakarai chemicals, LTD. as a extra pure reagent. 1-ethanol was provided by nacalai tesque, inc. with purity of 99.5%.

## 2.3 Separation procedures

The first separation is the extraction of green phosphor from three phosphor mixtures in DMF/heptane system, DDA or stearylamine were dissolved in heptane by ultrasonic wave, the mixed phosphor powders were shaken in DMF/heptane system for 2 min, at DMF/heptane volume ratio of 1 : 1, the green phosphor can be extracted into heptane (upper phase), after completely separated and filtrated, green product can be collected. The red and blue phosphors remained in DMF layer that exist in the lower phase. The filtrated red-blue mixtures were washed by 99.5% 1-ethanol, the subsequent separation of dried red-blue mixtures were con-

ducted using 1-octanesulfonic acid sodium salt which dissolved in DMF by ultrasonic wave, blue phosphor can be extracted into upper layer and separated with red phosphor which remained in DMF, the float and sink products were collected and filtrated respectively. The detail flow sheet is shown in Fig.2, and all the extraction experiments were conducted at room temperature.

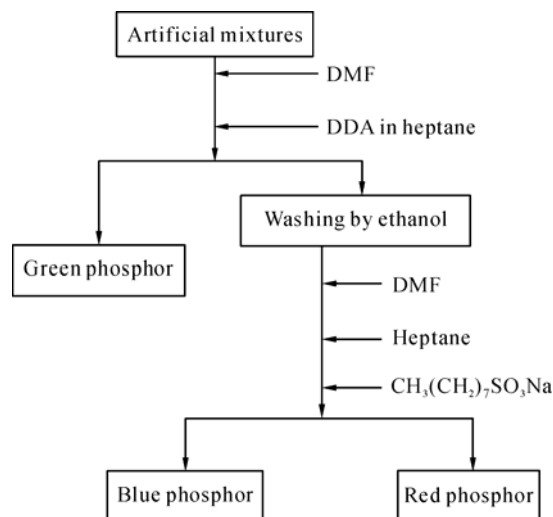


Fig.2 Flow sheet of tricolor phosphors separation

## 3 Results and Discussion

### 3.1 Separation of green phosphor from tricolor phosphors

Two cationic surfactants with different carbon chain were used in this separation, and both have the same chemical functional group  $-\text{NH}_2$ , the difference is that there are 12 carbon atoms in DDA, whereas stearylamine has a longer carbon chain with eighteen carbon atoms. Table 2 shows the extraction results of green phosphor using DDA as the surfactant that dissolved in various solvents. With the lengthening of carbon chain of solvents, the separation performance decrease slightly, the grade of separated green phosphor declined gradually when DDA concentration is kept stable, it can be concluded that low weight molecular solvents such as n-hexane and heptane are more suitable for this extraction system. In this case, heptane is chosen to be the appropriate solvent for extraction of green phosphor. The maximum grade and recovery are 90%, 95.2% respectively when DDA concentration is  $1.85 \times 10^{-4}$  mol/L.

**Table 2** Effect of different solvents on the extraction of green phosphor using DDA as the surfactant(DDA:  $1.85 \times 10^{-4}$  mol/L)

Green product	Solvents				
	n-hexane	Heptane	n-decane	Dodecane	n-hexadecane
Grade/%	89.5	90.0	86.1	86.8	83.2
Recovery/%	88.5	95.2	90.3	87.0	87.2

**Table 3** Effect of different solvents on the extraction of green phosphor in presence of stearylamine(Stearylamine:  $1.85 \times 10^{-4}$  mol/L)

Green product	Solvents				
	n-hexane	Heptane	n-decane	Dodecane	n-hexadecane
Grade/%	88.0	88.5	85.1	86.1	83.9
Recovery/%	95.8	96.4	95.0	90.7	87.6

Effect of DDA concentration on this extraction was also investigated, the results are given in Fig.3.

It can be summarized from Fig.3 that the appropriate concentration of DDA should be in the range of  $1-2 \times 10^{-4}$  mol/L. Excessive usage of DDA in heptane/DMF system results in the decreasing of the grade of separated green phosphor significantly, especially at DDA concentration is higher than  $4 \times 10^{-4}$  mol/L. When stearylamine was chosen to be the cationic surfactant in the extraction system, various solvents were also tested at constant stearylamine concentration, and the corresponding results are presented in Table 3.

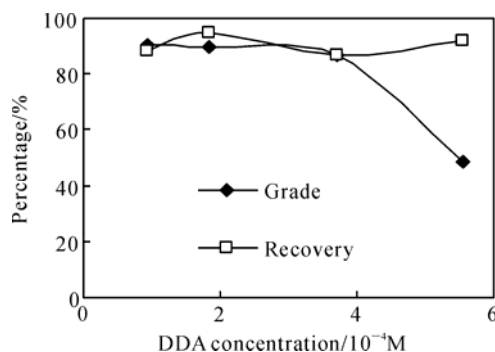


Fig.3 Effect of DDA concentrations on the green phosphor extraction

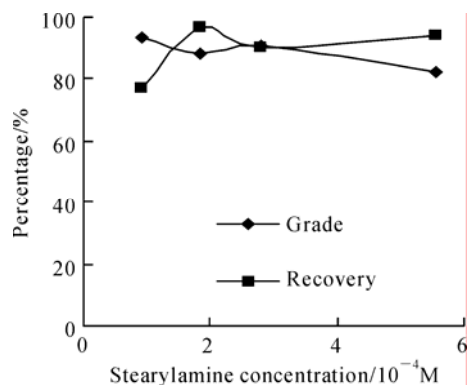


Fig.4 Effect of stearylamine concentration on the green phosphor extraction

It can be verified from Table 3 that low weight molecular solvents such as n-hexane and heptane are more suitable for this extraction system. Effects of stearylamine concentration on this extraction are shown in Fig.4.

According to Fig.4, the curves of grade and recovery using stearylamine are almost the same as that of using DDA surfactant. The grade of green product is very high at low stearylamine concentration, while its recovery is not satisfactory. However, when excessive stearylamine was used, the grade of green product decreases gradually. Therefore, the stearylamine concentration should be strictly controlled between  $1-3 \times 10^{-4}$  mol/L.

Comparison of DDA and stearylamine at the same conditions, implies that the extracting ability of

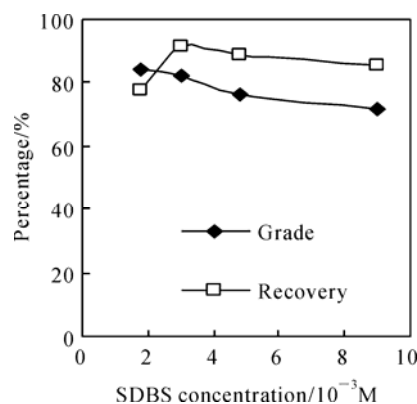


Fig.5 Effect of SDBS concentration on the separated red phosphor

stearylamine is very close to that of DDA, but stearylamine is more suitable for this process system because of its better selectivity in a wide concentration range.

### 3.2 Extraction and separation of blue and red phosphor mixtures

Two species of anionic surfactants SDBS and 1-octanesulfonic acid sodium salt were used in the second separation respectively. SDBS has a long chain with twelve carbon atoms and one benzene cycle, while 1-octanesulfonic acid sodium salt is of eight carbon atoms, and both of them have the same chemical functional group  $-SO_3Na$ , when SDBS was used in this separation. The corresponding results are given in Figs.5 and 6.

Figs.5 and 6 indicate that the best results were achieved when SDBS concentration is about  $3 \times 10^{-3}$  mol/L,

continuing to increase the amount of SDBS, both the grades and recovery of separated blue and red phosphor products decrease gradually.

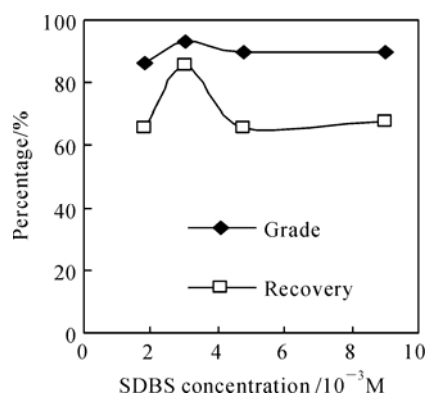


Fig.6 Effect of SDBS concentration on the separated blue phosphor

1-octanesulfonic acid sodium salt was adopted in this extraction system, and effect of its concentration and various solvents on the blue-red separation was investigated in detail. Table 4 shows the effect of various solvents on the extraction.

**Table 4 Effect of various solvents on the blue-red separation using  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  as the surfactant**

Solvents	Red product		Blue product	
	Grade/%	Recovery/%	Grade/%	Recovery/%
Heptane	99.1	97.4	97.5	99.1
n-decane	92.2	99.3	99.1	90.5
n-dodecane	98.7	72.6	76.9	98.9
n-hexadecane	99.2	90.6	90.8	99.2

According to Table 4, except for n-dodecane, there is no significant difference among the other three solvents, over 90% grade and recovery have been obtained, heptane was chosen because the best results can be achieved, and the grade and recovery of separated red and blue products are over 95%. Effect of 1-octanesulfonic acid sodium salt concentration on this separation is given in Figs.7 and 8.

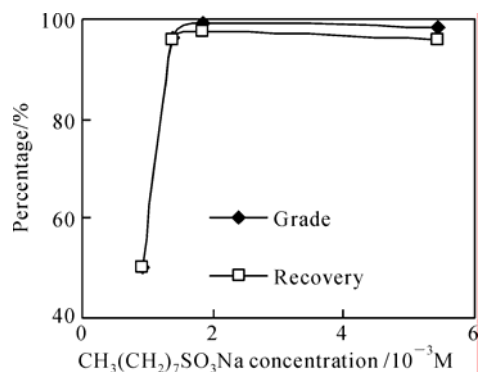


Fig.7 Effect of  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration on the separated red phosphor

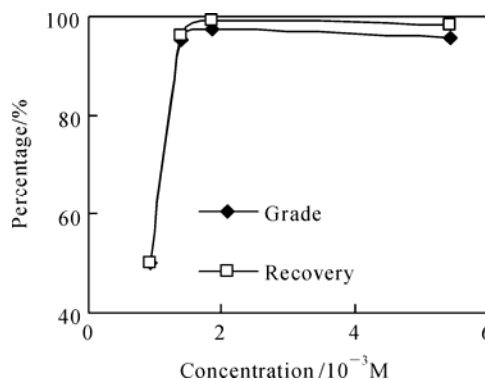


Fig.8 Effect of  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration on the separated blue phosphor

It is easily seen from Figs.7 and 8 that the blue and red phosphors can not be separated at low  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration, *e.g.* when  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration is less than  $1 \times 10^{-3}$  mol/L, the grade and recovery of both separated products are about 50%, indicating no selectivity under this conditions. In this case, the blue phosphor cannot be extracted into heptane layer from DMF. But with increasing of  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration, both the grade and recovery of blue and red products increase rapidly, the best results can be achieved when  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration is around  $1.85 \times 10^{-3}$  mol/L.

Compared with SDBS surfactant,  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  is a better surfactant for this extraction, because higher grade and recovery of separated blue and red phosphors are obtained at suitable  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration., the optimized blue-red separation conditions can be concluded as follows: the ratio of heptane/DMF is 1 : 1,  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration is  $1.85 \times 10^{-3}$  mol/L.

### 3.3 Separation of green, blue and red phosphor mixtures

#### 3.3.1 Effect of the solid concentration

Solid concentration always affects the separation efficiency because of the interaction between particles. The effect of solid concentration on the extraction should be taken into consideration. Relationships between the ratios of solid/ liquid and separation results are presented in Tables 5 and 6.

**Table 5 Effects of the solid/ liquid ratio on the first separation**

Solid/liquid(g/L)	Green product/%	
	Grade	Recovery
24	88.0	95.8
30	87.5	98.0
58	77.5	97.6

**Table 6 Effects of the solid/ liquid ratio on the second separation**

Solid/liquid(g/L)	Red product/%		Blue product/%	
	Grade	Recovery	Grade	Recovery
15	99.1	97.4	97.5	99.1
35	95.3	93.0	93.2	95.4
59	94.6	89.3	88.6	94.3

**Table 7 Effect of the feed compositions on the separation (stearylamine: 1.85 × 10<sup>-4</sup> mol/L)**

Feed Red: blue: green	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> SO <sub>3</sub> Na (g/L)	Red product/%		Blue product/%		Green product/%	
		Grade	Recovery	Grade	Recovery	Grade	Recovery
1 : 1 : 1	0.2	90.0	89.4	92.2	85.5	88.5	96.4
1 : 0.5 : 1	0.2	75.8	77.8	62.0	30.0	80.5	97.3
1 : 0.5 : 1	0.35	85.9	84.6	73.8	47.8	78.6	95.8
1 : 0.5 : 1	0.7	98.4	88.3	91.6	85.6	84.6	99.9

It is revealed from Tables 5 and 6 that the suitable solid concentration of the first separation is about 30 g/L, and that of the second separation is about 15-35 g/L.

### 3.3.2 Effect of the feed compositions

With the variables of the feed compositions, the separation conditions need be adjusted, otherwise, the separation performance decrease to some extent, if we change the feed ratio of red, blue and green phosphors from 1 : 1 : 1 to 1 : 0.5 : 1, the corresponding separation results are compared in Table 7.

The first separation was conducted under this stable condition: stearylamine concentration was 1.85 × 10<sup>-4</sup> mol/L, the solid concentration was 24 g/L, and the ratio of heptane/ DMF by volume was 1 : 1. As in Table 7, the grades and recovery of obtained green phosphor have no evident decline. But for the second separation, with the varying of the feed compositions from 1 : 1 : 1 to 1 : 0.5 : 1, the blue and red separation is affected significantly, where the concentration of CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SO<sub>3</sub>Na need be increased from 0.2 g/L to 0.7 g/L in order to achieve the blue-red separation sufficiently. It should be noted that at different feed compositions, the amount of anionic surfactant CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SO<sub>3</sub>Na need be adjusted correspondingly.

### 3.3.3 Separation results by a two- steps flow sheet

According to the flow sheet of Fig.2, the first extraction was conducted under this conditions: stearylamine 1.85 × 10<sup>-4</sup> mol/L, feed composition of red, blue and green phosphor was 1 : 1 : 1, the solid concentration was 24 g/L, the ratio of heptane/ DMF by volume was 1 : 1. After washing by 99.5% ethanol, the second extraction was carried out on the following conditions: the ratio of heptane/DMF is 1 : 1, CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SO<sub>3</sub>Na concentration is 1.85 × 10<sup>-3</sup> mol/L. The corresponding separation results are presented in Table 8.

**Table 8 Separation results through two-steps flow sheet**

	Red product	Blue product	Green product
Grade/%	95.3	90.0	92.2
Recovery/%	90.9	95.2	91.8

It can be seen in Table 8 that satisfactory results have been achieved by liquid/liquid extraction with two immiscible organic solvents, three phosphors were separated with high grade and recovery through a two-steps flow sheet.

## 3.4 Separation mechanism

Interfacial partitioning is a novel technology for the separation of physically near-identical particles, which are particles with similar densities and similar sizes but different chemical compositions. Different crystals partition differently to the interface of a biphasic system, forming a substantial interfacial layer (the interphase) as well as sediment, just like the well-known organic solvent/water two-phase system. The top phase is more hydrophobic, and the bottom phase more hydrophilic. The partition of dispersed particles is dependent on the interfacial interaction between the particles and the conjugate aqueous biphasic solutions. In particular, the hydrophilic/hydrophobic properties of the surface determine the transfer of the dispersed particles into either the top (more hydrophilic) phase or the bottom (more hydrophobic) phase. Accordingly, differences in the surface chemistry of particles can be exploited to achieve selective separations. In this case, collector adsorption may be exploited to facilitate particle transfer, and in the first extraction, cationic surfactant DDA was used as a selective collector of the green phosphors, and render the hydrophilic surface to be hydrophobic and float into top phase. However, in the second extraction, anionic surfactant CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SO<sub>3</sub>Na was adsorbed on the blue phosphors surface with selectivity, render the hydrophilic surface to be hydrophobic and transfer into top phase, while the red phosphors remains in bottom phase. Therefore, a higher degree separation of three rare earth phosphors mixtures was achieved.

## 4 Conclusions

a) Liquid/liquid extraction is effective to separate red (Y<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup>), blue ((Sr, Ca, Ba)<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>Cl<sub>2</sub>: Eu<sup>2+</sup>) and green (LaPO<sub>4</sub>: Tb<sup>3+</sup>, Ce<sup>3+</sup>) fine tricolor fluorescent powders with their artificial mixtures.

b) Two-steps flow sheet was recommended in this paper. First, the extraction and separation of green phosphor with others under following conditions: stearylamine was 1.85 × 10<sup>-4</sup> mol/L, feed composition of red, blue and green phosphor was 1 : 1 : 1, the solid concentration was 24 g/L, the ratio of heptane/ DMF by

volume was 1 : 1. Then, the separation of red and blue phosphors in the optimized conditions: the ratio of heptane/DMF is 1 : 1, while  $\text{CH}_3(\text{CH}_2)_7\text{SO}_3\text{Na}$  concentration is  $1.85 \times 10^{-3}$  M. Before the second separation, washing process with 99.5% ethanol is necessary.

c) The grades and recovery of separated products reached respectively as follows: red was 95.3% and 90.9%, blue was 90.0% and 95.2%, green was 92.2% and 91.8%. The colors and emissions of separated products are very close to that of pure phosphors under ultraviolet ray radiation.

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