Separation of Red (Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}), Blue (BaMgAl\textsubscript{10}O\textsubscript{17}:Eu\textsuperscript{2+}) and Green (CeMgAl\textsubscript{10}O\textsubscript{17}:Tb\textsuperscript{3}) Rare Earth Phosphors by Liquid/Liquid Extraction

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Abstract: A novel process for separation of red (Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}), blue (BaMgAl\textsubscript{10}O\textsubscript{17}:Eu\textsuperscript{2+}) and green (CeMgAl\textsubscript{10}O\textsubscript{17}:Tb\textsuperscript{3}) rare earth fluorescent powders was proposed. At first, the blue powder can be extracted selectively from an aqueous solution using a chelating collector 2-thienyltrifluoroacetone (TTA) dissolved in heptane at alkaline pH condition, then, chloroform was used for extracting the green powder into organic phase. The red phosphor remains in aqueous phase with potassium sodium tartrate depressant (PST). Therefore, three phosphors can be separated successfully from their artificial mixtures by liquid/liquid extraction, and grades and recovery of separated products reach respectively as follows: red is 96.9% and 95.2%, blue is 82.7% and 98.8%, green is 94.6% and 82.6%.

Key words: rare earth phosphor; solid-solid separation; liquid/liquid extraction

1 Introduction

Proper handling and disposal of used fluorescent light tubes containing mercury is becoming an increasingly expensive and problematic chore for big users of these lights\textsuperscript{[1]}. Recycling is a viable option that can reduce the risk of future financial liability associated with hazardous waste\textsuperscript{[2,3]}. After crushed under closed system, the lamp materials are separated into four waste streams\textsuperscript{[4]}: aluminum and brass end caps, glass, mercury, and phosphor powders. The metals, glass and mercury can be classified and purified by magnetic separation and tripel distillation for recycling. Up to now, the collected phosphor complex can not be further separated and reused to make new lamps. At previous research work\textsuperscript{[5-7]}, 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\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}) was also reproduced by coprecipitation process\textsuperscript{[8]}. But some disadvantages exist on this process due to the long treatment flow sheet and expensive cost. Furthermore, the feasibility of an efficient recovery of rare earth-activated phosphors from waste fluorescent lamps through dense-medium centrifugation or froth flotation also has been studied\textsuperscript{[9,10]}. Our research purpose is looking for a new method to separate rare earth phosphor powders, aimed at recycling these valuable secondary rare earth resources conveniently in the future. As we known, it is not suitable to do this solid-solid separation by floatation and other conventional mineral processing techniques due to the fine particle size (the average grain size is under 5 µm). In the present work, the separation of red (Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}), blue (BaMgAl\textsubscript{10}O\textsubscript{17}:Eu\textsuperscript{2+}) and green (CeMgAl\textsubscript{10}O\textsubscript{17}:Tb\textsuperscript{3}) rare earth fluorescent powders by liquid/liquid extraction was achieved with their artificial mixtures. This result provides 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 tri-phosphor samples tested by ICP SPS-3000 and XRD. Before analysis by ICP, samples were roasted and smelted with appropriate sodium carbonate and H\textsubscript{3}BO\textsubscript{3} at 1100-1200 °C for 20-30 minutes, and then dissolved in distilled water slowly using 1 : 1 HCl solution. Three of pure samples were commercial phosphor products, which are widely applied in fluorescent lights and low voltage
displayed[11]. The phosphors particle size was in the range of 1 to 10 µm, the average particle size was less than 5 µm. The measurement of specific gravity was conducted in specific-gravity bottle, and the obtained specific gravities of the red, blue and green phosphors were 4.295, 3.506 and 4.062, respectively.

The zeta potentials of phosphor powders were investigated using an ELS-8000 zeta potential meter (manufactured by Otsuka Electronic Co., Ltd. of Japan). The results are shown in Fig. 1.

2.2 Chemical reagents
Potassium sodium tartrate (PST, KNaC₄H₄O₆·4H₂O) was supplied by Nakarai Chemicals. Ltd, as analytical grade reagent 2-thenoyltrifluoroacetone(TTA, CF₃COCH₂COCH₃) was synthesized by Tokyo Kasei Kogyo Co., Ltd (the purity was over 98%). 1-pentanol, chloroform, and heptane were the products of Nacalai Tesque, Inc. Deionized water was purified by simple distillation prior. HCl, NaOH, and Na₂CO₃ were adopted to adjust the pH value of aqueous solution.

2.3 Extraction and separation of rare earth phosphors
In the first liquid/liquid extraction, TTA was dissolved in heptane, as the organic upper phase. The aqueous solutions consisted of appropriate amount of potassium sodium tartrate and Na₂CO₃ regulator. The phosphor mixtures were shaken with the aqueous solution for 1 or 2 minutes, after that, the mixed organic and aqueous solutions, at an organic /aqueous (O/A) volume ratio of 2 : 3, were shaken at room temperature for 5 minutes. The blue phosphor could be extracted into the upper layer and separated with the others. In the second separation, chloroform was effective to extract the green phosphor into organic phase selectively, at organic/aqueous (O/A) volume ratio from 1 : 5 to 1 : 1. A little amount of 1-pentanol was necessary to improve the separation performance. The detail process flow sheet is shown in Fig. 2.

### Table 1 The Chemical compositions of pure tri-phosphor samples

<table>
<thead>
<tr>
<th>Phosphor (Formula)</th>
<th>O</th>
<th>Y</th>
<th>Eu</th>
<th>Al</th>
<th>Mg</th>
<th>Ba</th>
<th>Ce</th>
<th>Tb</th>
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</thead>
<tbody>
<tr>
<td>Red (Y₂O₃:Eu³⁺)</td>
<td>17.5</td>
<td>67.2</td>
<td>6.5</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Green(CeMgAl₁₀O₁₇:Tb³⁺)</td>
<td>42.6</td>
<td></td>
<td>31.3</td>
<td>5.7</td>
<td></td>
<td>9.5</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Blue (BaMgAl₁₀O₁₇:Eu²⁺)</td>
<td>42.3</td>
<td>1.9</td>
<td>32.4</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
<td>12.4</td>
</tr>
</tbody>
</table>

3 Results and Discussion

3.1 Extraction with single phosphor samples
Fig.3 shows the extraction results using TTA as the surfactant at different pH ranges. The blue phosphor could be extracted into organic phase selectively in the pH range from 7 to 11. Red and green powders almost can not be extracted during this pH range. The extraction recovery of blue phosphor is up to 100% when the solution pH value is about 10.34. It is also seen from Fig.1 that there is a significant difference between the zeta potentials of the three samples at this point, and the zeta potential of blue powder is higher than the others. It can be assumed that there is a relationship between the extraction performance and particle surface charge. Hence, it is possible to separate the blue powder from three mixtures with TTA surfactant.