Recycling of waste phosphors using high gradient magnetic separation method

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Magnetic separation of a phosphor having high magnetic susceptibility from waste phosphors was tried using a high gradient magnetic separator. Since the green phosphor LAP (LaPO₄: Ce, Tb) has high magnetic susceptibility, it could be separated by this method. Repeating the separation procedure, most LAP could be recovered, and LAP purity of 87% was obtained. This method is a promising method of separating a single species of phosphor.

Key words: waste phosphor, high gradient magnetic separation, magnetic susceptibility, recycle

1. INTRODUCTION

Because of the recent shortage in the supply of rare earth elements, there is an increasing demand for recycling the waste phosphor that contains large amounts of rare earth [1]. Many researchers have reported processes for the recovery of rare earth oxides from waste phosphor by dissolving the phosphor followed by the solvent extraction [2]. Although solvent extraction is a well-established method, the reuse of rare earth phosphor is beneficial in terms of cost-effectiveness.

At present, waste phosphor is not reused because several kinds of phosphors, namely blue, green, red and white phosphors, are mixed together in waste phosphors. Therefore, a technology to extract a single species of phosphor from the waste phosphor is needed.

Here, we present a method of separating a single species of phosphor using the differences in the magnetic susceptibility of different phosphors. The magnetic force F is proportional to the magnetic field strength, H, its gradient, dH/dx and the magnetic susceptibility of the material, χ. Hence, if χ differs among materials, magnetic separation will be possible.

The magnetic attraction levitation method using a superconducting magnet is a promising way to separate phosphors [3,4]. However, the cost of this method may be a problem, since it is not suitable for mass processing. We employed a high gradient magnetic separation method and investigated its feasibility for separating different kinds of phosphors. When a magnetic metal is placed in a magnetic field, it is magnetized, and a high magnetic gradient appears around it. If a material has positive magnetic susceptibility, it will adhere on a magnetic metal when the magnetic force F is sufficiently high.

As a preliminary experiment, the separation of a small amount of mixed phosphors was confirmed, and waste phosphors recovered from the community were then tested.

2. EXPERIMENTAL

2.1 Magnetic Separator

High Gradient Magnetic Separator (HIW L4-20KI, Eries Magnetics Japan Co., Ltd.) was used for magnetic separation. It was equipped with an electromagnet with a field strength in a coreless state of up to 2T. An expanded metal made of SUS-430 was used for the matrix in the column. The internal volume of the column was 200 mL. A ball bulb was present below the column. In some cases, SUS-434 stainless wool (Nihon Glass Fiber Industrial Co., Ltd.) was used as a matrix, since the magnetic field gradient becomes stronger as the wire radius becomes smaller.

2.2 Materials

LaPO₄: Ce, Tb (LAP, LP-G1, Mitsubishi Chemical Corporation), Y₂O₃: Eu (YOX, LP-RE2, Mitsubishi Chemical Corporation), BaMgAl₁₀O₁₇:Eu (BAM, LP-B4, Mitsubishi Chemical Corporation), and two kinds of halophosphate (Warm White, WW and Cool White, CW, Nichia Corporation) were used as mixed phosphors. A waste phosphor from a used fluorescent lamp was provided by the JFE Kankyo Corporation. Since it contained a small amount of crushed glass, it was sieved, and the larger pieces of the glass were removed. The phosphors were dispersed in deionized water containing 0.15% of a polycarboxylic surfactant (Poise 520, KAO Corporation) and 0.015% of a lauramidopropyl betaine surfactant (Amphitol 20AB, KAO Corporation). This solution was also used for washing.

2.3 Separation procedure

The suspension of phosphors was passed in the column at a given magnetic strength to attract a phosphor having high magnetic susceptibility. Then the ball bulb was opened and the rest of the suspension was discharged. The column was washed with the solution twice to remove phosphors having lower magnetic susceptibility that had adhered to the target phosphor. After the magnet switch was off to demagnetize the matrix, washing solution was passed into the column to recover the adhered phosphor.
2.4 Analysis

The contents of each phosphor were estimated by fluorescence spectroscopy or X-ray fluorescence (XRF) analysis. When the amount of the mixed phosphor was small, the former method was used. A drop of mixed phosphor suspension was spread on a slide glass and dried, and then the fluorescence spectrum was measured with a fluorescence spectrophotometer (F-4500, Hitachi) at an exciting wavelength of 254 nm. The spectra of each phosphor were also measured. The ratio of each phosphor was calculated as the sum of the spectra of each phosphor.

In the case of the separation of waste phosphor, estimation of the ratio by fluorescence spectroscopy was difficult since it contains more than 7 types of phosphors. In this case, XRF was used for the estimation. Separated phosphor in an amount of 0.5 to 1 g was pressed into a pellet and measured using X-ray fluorescence equipment (XRF-1800, Simadzu). Each phosphor was also measured, and the sensitivity correction factor for each element was calculated. The LAP content was calculated from the La amount, YOX from Y, and BAM from Al. BAM (LP-B4) contained a slight amount of Sr. (Sr,Ca,Ba,Mg)10(PO4)6Cl12:Eu blue phosphor (SCA) was calculated from Sr after a corresponding amount of BAM was subtracted. Three kinds of halophosphates were calculated from the Ca amount. The glass content mixed in phosphors was calculated from Si.

3. RESULTS AND DISCUSSION

3.1 Separation of mixed phosphors

Table 1 shows the magnetic susceptibility of phosphors [3] typically used in fluorescent lamps. As seen in the table, each phosphor shows a different value of magnetic susceptibility. It should be noted that the magnetic susceptibility of LAP (No. 1) is higher than that of other phosphors for one order of magnitude.

To examine whether separation based on the difference in magnetic susceptibility is possible, five kinds of phosphors (Nos. 1-5) having different magnetic susceptibilities were separated in a suspension by using a high gradient magnetic separator operating at 2T. It was found that LAP was easily extracted from the suspension, and the concentration of LAP was increased nearly 70% with a single series of separation procedures as shown in Fig. 1.

By repeating the process three times, LAP with 99% purity was obtained.

As shown in Fig. 2, it was also revealed that the separation of phosphors having much closer magnetic susceptibilities, such as Nos. 3 and 5 or Nos. 3 and 7, was also possible if the absorber used was stainless wool, which is supposed to induce higher magnetic force in the separation column.

3.2 Separation of waste phosphors

A total of 60 g of the sieved waste phosphor was used for separation. It contained a large amount of halophosphate as shown in Table II. It was suspended in 80 mL of washing solution and poured into the column at 1T. We have found that the separation efficiency becomes higher if the magnet is repeatedly turned on and off during washing. The mechanism for this is believed to be as follows: When the magnet is off, adhered phosphors having lower magnetic susceptibility will leave from the matrix preferentially. When the magnet is turned on, detached phosphor having higher susceptibility will adhere again onto the matrix.

The results of separation are shown in Table II. Calculating from the table, about 90% of LAP could be

### Table I. Magnetic susceptibility values of phosphors [3].

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Color</th>
<th>Magnetic Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LaPO4:Ce,Tb (LAP)</td>
<td>green</td>
<td>1.64x10^3</td>
</tr>
<tr>
<td>2</td>
<td>Ca5(PO4)3(F,Cl):Sb,Mn (Warm White)</td>
<td>white</td>
<td>1.89x10^4</td>
</tr>
<tr>
<td>3</td>
<td>BaMgAl10O17:Eu2+ (BAM)</td>
<td>blue</td>
<td>1.78x10^4</td>
</tr>
<tr>
<td>4</td>
<td>Ca5(PO4)3(F,Cl):Sb,Mn (Cool White)</td>
<td>white</td>
<td>9.55x10^3</td>
</tr>
<tr>
<td>5</td>
<td>Y2O3:Eu3+ (YOX)</td>
<td>red</td>
<td>8.56x10^3</td>
</tr>
<tr>
<td>6</td>
<td>(Sr,Ca,Ba,Mg)10(PO4)6Cl2:Eu2+ (SCA)</td>
<td>blue</td>
<td>6.59x10^3</td>
</tr>
<tr>
<td>7</td>
<td>Ca5(PO4)3(F,Cl):Sb,Mn (Daylight White, DL)</td>
<td>white</td>
<td>4.09x10^5</td>
</tr>
</tbody>
</table>
(Sr,Ca,Ba,Mg)\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{12}:Eu blue phosphor (SCA) was BAM (LP -B4) contained a slight amount of Sr. from the La amount, YOX from Y, and BAM from Al. element was calculated. The LAP content was calculated measured, and the sensitivity correction factor for each In this case, XRF was used for the estimation. S eparated calculated as the sum of the spectra of each phosphor. spectrum was measured with a fluorescence spectrophotometer (F-4500, Hitachi) at an exciting susceptibilities, such as No s. 3 and 5 or No s. 3 and 7, susceptibilities were separated in a suspension by using difference in magnetic susceptibility is possible, five magnetic susceptibility of LAP (No. 1) is higher than of magnetic susceptibility. It should be noted that the seen in the table, each phosphor shows a different value recovered after the second operation. LAP purity after the second operation was about 86%. Newton’s separation efficiency ranged from 75 to 78%, which is a fairly good value for a physical separation method. Most of the glass contained as an impurity moved to the outflow at the beginning.

After repeating the operation again, the LAP purity grew to more than 90%. The luminance of LAP was found to be related to the impurity content. An LAP of 96% purity showed almost the same luminance as a new one. Hence the recovered LAP with high purity could be reused in a new fluorescent lamp.

4. CONCLUSION
A high gradient magnetic separation method was applied to mixed phosphor and waste phosphors. Since LAP has high magnetic susceptibility, it could be separated easily with this method. LAP purity became 86% when the separation was performed twice. Newton’s separation efficiency was nearly 80%. When thin stainless wire was used as a matrix, phosphors having closer magnetic susceptibility could be separated to some extent. These results indicate that the high gradient magnetic separation method is a promising method to separate a single species of phosphor.

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References

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