

Recovery of Rare Earth Oxide from Phosphor Powder of Spent Fluorescent Lamp

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Phosphor powder contained inside fluorescent tubes is a rich source of rare earths. Phosphor used in fluorescent lamps is of tricolour type that emits visible light of three different colours, *i.e.*, red, green and blue. Among three phosphors, europium-doped Y_2O_3 is a typical red phosphor that is used predominantly in tri-band phosphor for displays and fluorescent lamps. In view of above, the present work was focussed on optimising conditions to recover yttrium and europium selectively and synthesizing highly pure $Y_2O_3:Eu^{3+}$ (red phosphor) from the liquor arising from leaching of a phosphor powder of spent fluorescent lamps in chloride medium and using oxalic acid as precipitant. The typical composition of the leach liquor obtained at optimum leaching conditions was (g/L): 26.9 Y, 1.6 Eu, with slight impurities of Al and Ca. Process parameters, including acidity, concentration of oxalic acid and temperature, were optimized to produce yttrium oxalate. Under the optimum conditions, the recovery of yttrium and europium as oxalates was quantitative. The synthesised yttrium-europium oxalate was calcined at $600^\circ C$ to convert it into $Y_2O_3:Eu^{3+}$. The yttrium-europium oxalate/oxide powder so formed was characterized by thermogravimetric differential thermal analysis, X-ray diffraction, scanning electron microscopy and chemical analysis, all of which confirmed the presence of pure Y-oxalate and oxide. The microscopy image of the synthesised $Y_2O_3:Eu^{3+}$ exhibited flaky particles of $5\ \mu m$ size; the purity of synthesized red phosphor was $>99\%$, as determined by chemical analysis and energy-dispersive spectroscopy.

INTRODUCTION

Based on their optical, electrical and magnetic characteristics, rare earth (RE) elements have been widely used in high-technology applications, such as phosphors, magnets, batteries, lasers, high-temperature superconductors and transport of hydrogen in the post-hydrocarbon economy (Croat et al., 1984; Alonso et al., 2012). As a consequence, large amounts of wastes containing RE are generated as end-of-life products discarded in the environment without any treatment. Among RE-containing wastes, lamp phosphors that have high concentration of yttrium, europium, terbium, lanthanum and cerium may be considered as potential secondary resources for RE elements.

As per 2014 estimates, about 5000 t of rare earth oxides (REOs) were consumed for the manufacture of different kinds of phosphor, and the demand for RE phosphor is expected to grow by 3.3% per year (Roskill, 2015). A typical fluorescent lamp contains 4 g tricolour phosphors (Tunsu et al., 2015). The average service life of a fluorescent lamp accounts for 7000 to 24 000 h. In 2011, China produced 7024 billion units of fluorescent lamps using 8000 t phosphor (Tan et al., 2015). It is also reported that about 4800 million fluorescent lamps (FL) were scrapped in 2011. With reference to the domestic market price of RE at the end of 2011, the value of RE contained in waste fluorescent lamps was more than 1600 million dollars (Wu et al., 2014).

In the Indian context, about 486 million units of FLs/CFLs (compact fluorescent lamps) were produced in 2010, containing 2000 t of REOs, which is more than four times of the total Indian RE demand (Indian Ministry of Mines, 2012). If these waste phosphor powders can be efficiently recycled and reused, this will not only reduce the exploitation of primary RE resources and will also be helpful in turning this waste into significant value.

The separation and purification of RE metals is still a matter of utmost concern because of their similar chemical properties. The recovery of RE content from lamp phosphors generally includes chemical leaching with HCl, HNO₃ or H₂SO₄ solutions at elevated temperatures. After leaching, the RE are recovered from the leach liquor either by solvent extraction or by precipitation from the purified/mixed strip solution with oxalic acid or ammonium carbonate as precipitant, forming RE oxalates or carbonates (Rabah, 2008; Mei et al., 2009; Yang et al., 2013; Wu et al., 2014).

There are many investigations reported on the recovery of yttrium as yttrium oxide from the leach liquors of various RE resources (Deshpande et al., 1992; Vijayalakshmi et al., 2001; Singh et al., 2012). Naitou et al. (1987) studied the recovery of mixed REO from waste phosphors containing Fe and Ca as impurities. They proposed efficient leaching of phosphors either with HCl using H₂O₂ at 70°C or leaching with HNO₃ only, followed by precipitation using oxalic acid. Tooru et al. (2001) studied a process for separation and recovery of REs from fluorescent lamp waste. In this process, 98% pure yttrium-europium oxides were produced by sulphuric acid leaching followed by oxalate precipitation. De Michelis et al. (2011) studied the recovery of yttrium from phosphor powders using different acids. Thereafter, recovery of yttrium by precipitation using oxalic acid was presented using a model solution. Leaching of REEs from fluorescent lamps using various acids was also investigated by Innocenzi et al. (2013a). After leaching, calcium and other impurities were removed from the leach liquor using sodium sulphide. RE in the residual solution were precipitated as oxalates using oxalic acid, which was then calcined to obtain yttrium oxides. In another work, Innocenzi et al. (2013b) developed a process for recovery of yttrium from phosphor powders of cathode ray tubes (CRT). The treatment included leaching with H₂SO₄ in presence of H₂O₂, removal of impurity metals like zinc and precipitation by oxalic acid.

The presence of impurity ions in the synthesised RE oxides makes the product purity low and requires and extra step of purification. The objective of the present work was therefore to identify the most favourable and selective leaching conditions for yttrium and europium from phosphors of spent fluorescent lamps and to synthesize high-purity Y₂O₃:Eu³⁺ from the chloride leach liquor of phosphor powder using oxalic acid as the precipitating agent.

EXPERIMENTAL

Materials

Waste FL were collected in large numbers from an industrial compound. They were first washed and then the ends were cut by a diamond cutter to remove the aluminium cap. After releasing the vacuum, mercury was collected and the inner walls of the tubes were gently brushed to remove the dry phosphor powder. The chemical analysis of the phosphor powder is given in Table I. The X-ray diffraction (XRD) pattern showed that the major mineral phases in the phosphor powder was red phosphor ((Y₂O₃:Eu³⁺), followed by blue (BaMgAl₁₀O₁₇:Eu²⁺) and green (CeMgAl₁₀O₁₇:Tb³⁺) phosphor. Leaching studies were carried out with the desired concentration of hydrochloric acid. A saturated solution of oxalic acid was prepared by dissolving H₂C₂O₄.2H₂O in distilled water. All other chemicals used in the experiments were of analytical-reagent grade.

Leaching and Preparation of Y, Eu Oxide Particles

The leaching experiments were carried out in a -necked glass reactor kept on a hot plate equipped with a magnetic stirrer and auto-regulated heating system. After heating of the leaching solution to desired temperature, the required amount of phosphor powder was introduced into the reactor. At specific time intervals, 2 mL sample was withdrawn, diluted appropriately and analysed for metal

content using inductively coupled plasma optical emission spectroscopy (ICP-OES). For RE oxalate precipitation, stoichiometric amounts of oxalic acid were added drop-wise into the leach solution at 50°C and left for a period of 1 h under constant stirring using a magnetic stirrer. All experiments were performed in triplicate. After complete reaction, the oxalate precipitate was filtered through filter paper and washed with distilled water four to five times and dried in an oven overnight at 80°C. Finally, the washed oxalate was calcined at 600°C in a ceramic crucible for 2 h, producing the REO as a white powder.

Table I. Chemical composition of phosphor powder obtained from waste fluorescent lamps

Element	Y	Eu	La	Ce	Tb	Al	Ca	P	Ba
Wt%	27.2	1.6	7.8	4.8	2.2	12.3	1.7	2.8	1.3

Characterization

Concentrations of RE and other metal ions present in the leach liquor and filtrate obtained after each experiment were determined by ICP-OES (Varian VISTA-MPX). The thermal behaviour of the oxalate powders was investigated in air atmospheres employing thermogravimetric (TG) and differential thermal analysis (DTA) (LINSIES GmbH, Germany). Characterization of phase purity was carried out using XRD (Bruker D8 Discover) in the 2θ range from 10° to 90°. Particle morphology of oxalate and oxide powders was analyzed by scanning electron microscopy (SEM) (FEI NOVA Nano SEM-430).

RESULTS AND DISCUSSION

Selective Leaching of Y and Eu

Preliminary leaching studies were carried out by varying the HCl concentration (0.1–2 M) at 95°C using 100 g/L pulp density and 500 rpm stirring speed (Figure 1). Leaching of yttrium and europium increased with increase in HCl concentration. At 1 M HCl, almost quantitative and selective leaching of both yttrium and europium was achieved in 30 min. Under these conditions, the leaching of other REs (viz., La, Ce and Tb) and other impurities was found to be in the range of 0.2–5%. Table II reports the leach liquor composition obtained at optimized leaching conditions. The leach residue was analyzed by XRD and found to consist of only blue and green phosphor phases. A few leaching experiments were also carried out in presence of an oxidizing agent. The results obtained showed that the oxidizing agent had no significant effect on the leaching of yttrium and europium. The high leaching rate of yttrium and europium relative to that of other metal ions is attributed to their oxide nature in the triband phosphor powder. The leaching of yttrium and europium can be expressed by following reaction:

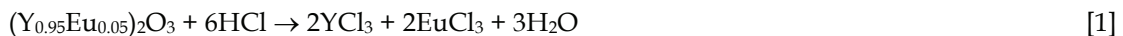
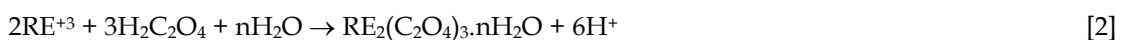


Table II. Composition of leach liquor obtained at optimized leaching condition

Elements	Y	Eu	La	Al	Ca	P	Acidity
g/L	26.9	1.6	0.05	0.07	0.02	0.04	0.9 M

Precipitation with Oxalic Acid

The leach liquor thus obtained was subjected to recovery of yttrium and europium as oxalate by precipitation with a stoichiometric amount of oxalic acid. Precipitation of rare earth elements by oxalic acid can be expressed as:



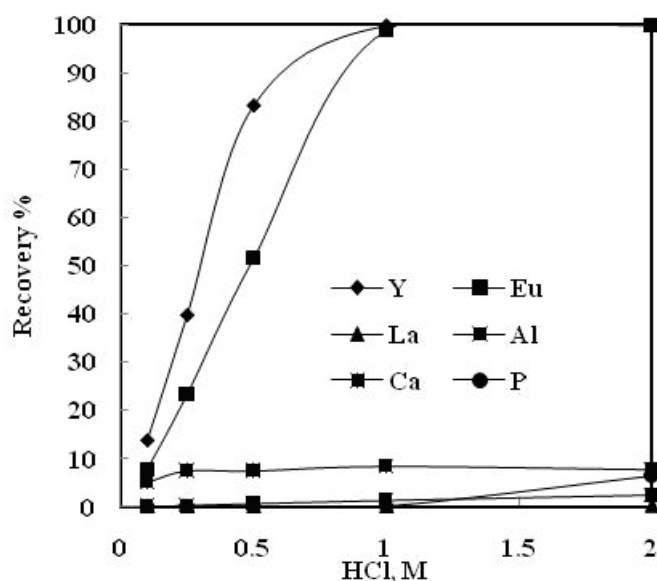


Figure 1. Effect of HCl concentration on leaching of phosphor.
Pulp density: 100 g/L; temperature: 95°C; stirring speed: 500 rpm; time: 30 min.

While studying the effect of leach liquor acidity by varying the H^+ concentration of the leach liquor from $0.9-10^{-4}$ M by addition of the required amount of dilute NaOH solution, it was observed that complete precipitation of RE as oxalate occurred under highly acidic conditions. Precipitation of Al and Ca was only around 7–10% (Figure 2). However, when the acidity of leach solution was decreased, RE and the non-RE species present in the leach liquor were precipitated. The contamination of oxalate precipitate with phosphorus was negligible under all acidities. The precipitation of Ca and Al increased with an increase in pH and reached maxima of 77% and 38%, respectively, at pH 3. From these results, it can be inferred that pH does not affect the efficiency of precipitation of RE, but rather it causes precipitation of other impurity metals present in the leach liquor. Further optimizations were carried out using the leach liquor without any pH regulation. The acidity of the filtrate obtained after oxalate precipitation under the optimized conditions was 0.7 M.

To improve the product purity and removal of non-RE species from the RE oxalate, the effect of temperature was investigated in the range of 30–80°C (Figure 3). It was found that the precipitation of RE was quantitative across the entire temperature range, whereas the impurity metals Al and Ca were not recovered in the precipitate. The reason may be the stability of the solubility product of the RE oxalate in the given temperature range while the solubility products of Al and Ca slightly increase with temperature. Finally, the oxalate product obtained under optimized precipitation conditions was filtered, dried and characterized to determine the phase purity and morphology.

Characterization of Oxalate Precursor and Y,Eu-Oxide Synthesised at Optimum Conditions

The RE oxalate powder so produced was characterized by XRD. All diffraction peaks were indexed to monoclinic structured $Y_2(C_2O_4)_3 \cdot 10H_2O$ (JCPDS card no.033-1460). TG-DTA curves recorded on heating the synthesised oxalate from room temperature to 800°C at 10°C/min in air is given in Figure 4. The total weight loss for this oxalate product in the temperature range 25–600°C was found to be 58.7%, which is very close to the value obtained by Muresan et al. (2009) for the synthesis of europium-activated yttrium oxide via oxalate precipitation. The decomposition of oxalate was signified by two characteristics endothermic peaks in the DTA curve. The TG-DTA analysis therefore confirmed the formation of decahydrate oxalate and agreed well with the XRD result.

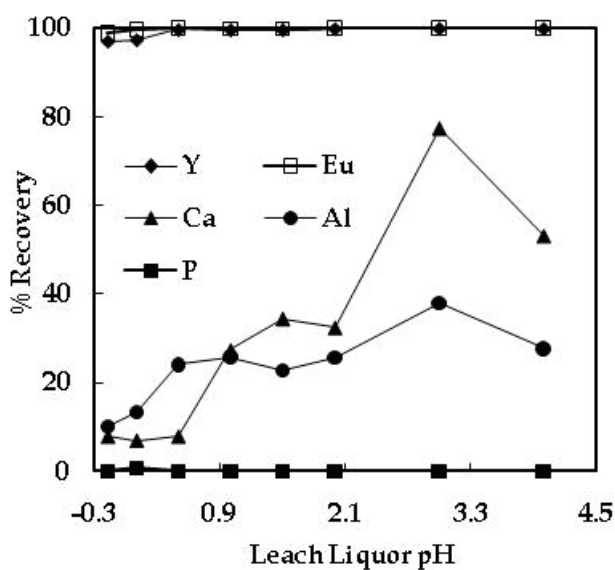


Figure 2. Effect of leach liquor acidity on precipitation of rare earths.

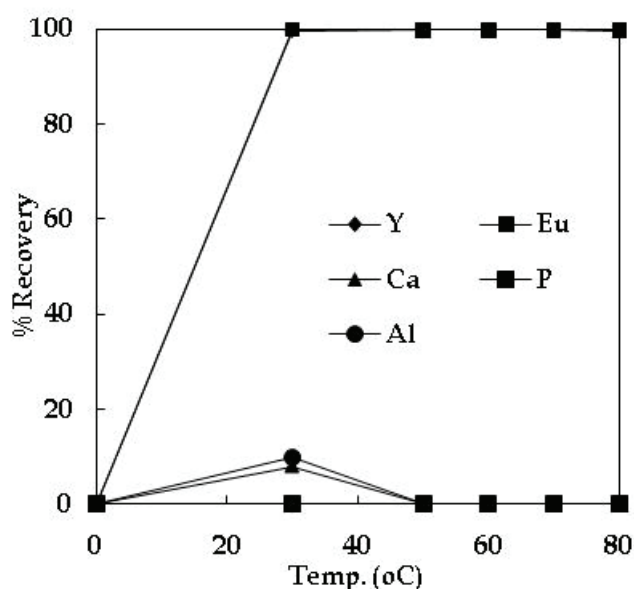


Figure 3. Effect of temperature on precipitation of rare earths.

The oxalate precipitates thus obtained were calcined at 600°C for 2 h to convert it into REO and characterized. The XRD peaks of calcined product (Figure 5(a)) show an identical pattern to the reported data in JCPDS cards No. 025-1011 for red phosphor without any other impurity phases. The presence of sharp peaks indicated that the oxide particles were crystalline in nature. The morphology and size of the oxide particles were determined from SEM studies. Figure 5(b) shows that the oxide particles size ranged from 5–10 μm and exhibited flake-like morphology with some cracks and curls on the surface arising from the release of gas during calcination. The EDS spectra revealed that the oxide particles consisted of Y, O and Eu only, with no other impurities. The oxide particle purity by EDS and chemical analysis was found to be >99%.

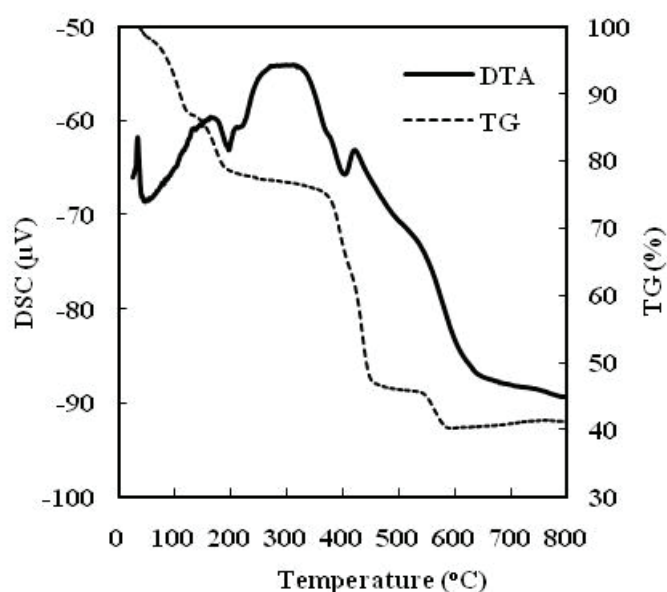


Figure 4. TG-DTA plot of prepared yttrium-europium oxalate.

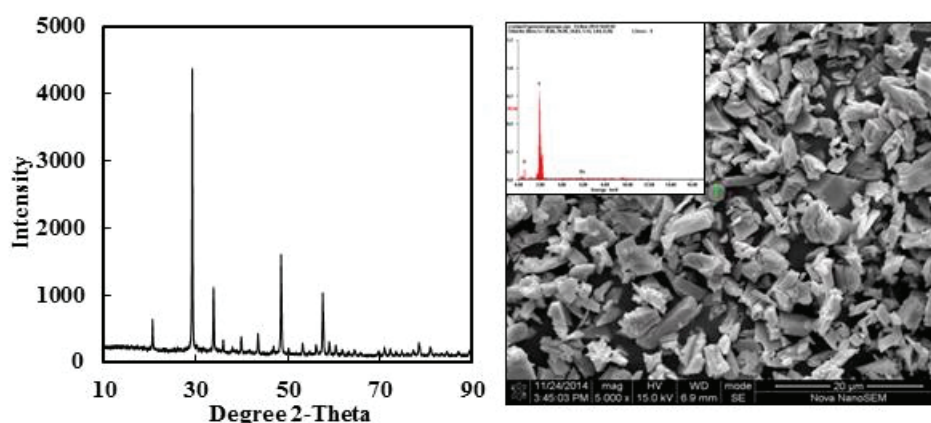


Figure 5. (a) XRD and (b) SEM-EDS of as-prepared yttrium-europium oxide.

CONCLUSIONS

Waste fluorescent lamp phosphor was utilized to recover yttrium and europium as a value-added product, viz., yttrium-europium oxide, via a selective leaching and oxalate precipitation route. The optimized leaching conditions for yttrium and europium were found to be 1 M HCl, 95°C temperature, 100 g/L pulp density and 500 rpm stirring speed. Various parameters were investigated to improve the product purity. The stoichiometric requirement of oxalic acid, at higher acidity with increased temperature, were found to be the best conditions to obtain impurity-free RE oxalate. The oxalate was calcined to yttrium oxide. The morphology and purity were characterized by SEM, XRD and chemical analysis.

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