



Recycling of rare earths from lamp phosphor waste: Enhanced dissolution of $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$ by mechanical activation



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ABSTRACT

With the promoted use of compact fluorescent lamps and the increasing amount of stockpiled compact fluorescent lamp waste, lamp phosphors are becoming an interesting secondary source for critical metals (yttrium, europium and terbium). This paper explores on the mechanism of a new potential hydro-metallurgical route to improve the recovery efficiency of rare-earth elements from the green phosphor $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$ using mechanical activation as a pretreatment step prior to leaching. By applying an intense frictional action, the leaching yields of rare-earth elements were enhanced from 0.9% to 81% at room temperature, as a consequence of the change in activation energy. The shrinking core model was employed for modelling the leaching kinetics of the rare-earth elements and to calculate the decreasing apparent activation energy of the unmilled and milled samples (from 68 kJ mol^{-1} to 1.4 kJ mol^{-1}). This difference can be explained by the physicochemical changes, including structural decomposition, specific surface area increase and particle size reduction, which were related to the corresponding leaching pattern. The optimized mechanical activation procedure was successfully applied to lamp phosphor waste, containing a mix of different phosphors. After sequential removal of the halophosphate phosphor and the red YOX phosphor, 99.0%, 87.3% and 86.3% of La, Ce and Tb present in the $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$ phosphor could be dissolved. These observations provide more insight in the mechanical activation process and may contribute to a more sustainable alternative route to the rare-earth element recycling industry.

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1. Introduction

The use of compact fluorescent lamps (CFLs) has been widely adopted over the last decades, as CFLs are 70% more energy-efficient and have 10 times longer lifetimes than incandescent lamps, despite the expected rapidly growing market share (15% p.a.) of light emitting diodes (LEDs) (Bonneville Power Administration, 2015; Lim et al., 2013; McKinsey and Company, 2012; NorthWestern Energy, 2015). Phosphors for fluorescent lamps and CFLs are an important application of rare-earth elements (REEs). Regardless of the decreasing demand of REEs (Eu and Tb) for phosphors by two third since 2011, the general demand for REEs is expected to grow by 6% (Roskill, 2015). Since REEs account for more than 20 wt% within lamp phosphor waste (Table 1), including three of the most critical REEs (yttrium, europium and terbium),

recycling of these metals from end-of-life products has several advantages over primary supply. Besides the presence of REEs in concentrated form in comparison to the minimum industrial grade of rare-earth ores (0.06–2.0 wt%), recycling reduces the environmental impact, landfilling problems and co-production of the unwanted REEs, resolving the so-called balance problem (Binnemans and Jones, 2014; Machacek et al., 2015; Tan et al., 2016a).

Lamp phosphors consist of a mix of a red (YOX), green (LAP or CAT), and blue (BAM) phosphor (Table 2). Besides the REE-bearing phosphors, lamp phosphor waste can consist of up to 50% halophosphate phosphor (HALO) which has low intrinsic value and contains no REEs (Binnemans et al., 2013; Dupont and Binnemans, 2015). A lot of research has been conducted both by industry and academic research groups to efficiently recycle the rare earths from lamp phosphor waste (Binnemans and Jones, 2014; Binnemans et al., 2013; Tunsu et al., 2015; Wu et al., 2014). Most studies focus on the recovery of yttrium (Y) and europium (Eu) from the red phosphor YOX, because these are the elements that are the easiest to recover and they represent the highest value in the

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Abbreviations

BPR	ball-to-powder ratio
CFL	compact fluorescent lamp
<i>D</i>	crystallite size
ϵ	lattice strain
LED	light emitting diode
MA	mechanical activation
PS	particle size
S:L	solid-to-liquid (ratio)
SSA	specific surface area
wt%	percentage weight total

Table 1
Composition of lamp phosphor waste, analyzed by XRF.

Element	wt%	Element	wt%
Al	11.05	Mn	0.54
Ba	2.10	Na	7.14
Ca	21.42	P _x	10.64
Ce	3.05	Sb	0.36
Cl	0.50	Si	10.89
Eu	1.30	Sr	2.47
La	3.94	Tb	1.28
Mg	0.88	Y	19.62

phosphor waste. Recycling of the green phosphors (LAP or CAT) is also very interesting due to the high concentration of the critical and expensive terbium (Tb). However, the green phosphors are much more difficult to dissolve than YOX, and often high concentrations of mineral acids in combination with high temperatures (e.g. 18 M H₂SO₄, 120–230 °C) or cracking with molten sodium hydroxide or sodium carbonate is required (Porob et al., 2012; Wu et al., 2014). These methods are not attractive due to the waste generation, the use of corrosive chemicals and the high energy consumption. Therefore, effective methods for the recovery of REEs from the green phosphors, with a low energy consumption and high recovery rates are highly desirable.

Mechanical activation (MA) by ball-milling has been used to enhance the acid digestion of various minerals that are hardly soluble, including monazite, which has a similar structure to that of LAP (Abdel-Rehim, 2002; Achimovičová and Baláz, 2005; Kim et al., 2009). This technique has also been applied for the recovery of various metals from secondary waste streams (Ou et al., 2015; Tan and Li, 2015). Typically MA refers to the application of shear, impact and compression forces that induce a modification in the physicochemical properties of the solids, enhancing their reactivity

Table 2
Overview of the approximate lamp phosphor waste composition found in lamp phosphor waste (Binnemans et al., 2013).

Type phosphor	Name	Content (wt%) ^a	Economic value
White	Ca _{4.86} Mn _{0.10} Sb _{0.04} Sr _{0.004} (PO ₄) ₃ Cl _{0.10} F _{0.90} (HALO)	40–50	Low
Red	Y ₂ O ₃ :Eu ³⁺ (YOX)	20	High
Green	LaPO ₄ :Ce ³⁺ , Tb ³⁺ (LAP)	6–7	High
	CeMgAl ₁₁ O ₁₉ :Tb ³⁺ (CAT)	6–7	High
Blue	BaMgAl ₁₀ O ₁₇ :Eu ²⁺ (BAM)	5	Low

^a Besides the presence of phosphors, the lamp waste consists of fine glass particles (up to 20 wt%), and Al₂O₃.

(Baláz, 2008; Boldyrev, 2006). Recent studies have applied mechanical activation for recycling of REEs from the YOX and LAP lamp phosphors (Tan et al., 2016a; Zhang and Saito, 1998; Zhang et al., 2000). The mechanical activation method investigated by Tan et al. (2016b) in combination with a leaching process has succeeded in increasing the dissolution of REEs (Y, Eu and Tb) from fluorescent lamp waste.

Despite the number of publications on the recovery of REEs from lamp phosphors, studies using MA are scarce and lacking information on the effect of MA on individual phosphors. By milling the complete lamp phosphor waste (including HALO and YOX), no definite conclusions can be drawn on the effect of MA for the phosphors which are difficult to leach (such as LAP). The scope of this paper is to conduct a systematic study of the effect of MA on the reactivity of LAP phosphor, with emphasis on the physicochemical changes and the milling parameters, to reveal the activation mechanism. In the present study, the potential use of the determined optimal MA parameters for recycling rare-earth metals from lamp phosphor waste was discussed.

2. Experimental

2.1. Materials

The lamp phosphor LAP (La_{0.57}Ce_{0.27}Tb_{0.16}PO₄, 99%) was purchased from Nichia (Japan). Lamp phosphor waste was kindly provided by OSRAM (Munich, Germany). Nitric and hydrochloric acid solutions were prepared using ultrapure water (Milli-Q, Millipore; 18.2 MΩ cm⁻¹ at 25 °C), concentrated nitric acid (65 wt%, Chem-Lab) and concentrated hydrochloric acid (37 wt%, Merck). The ICP standards (Fluka, 1000 µg mL⁻¹) and lithium metaborate (99.9%) were purchased from Sigma-Aldrich (Diegem, Belgium).

2.2. Equipment and characterization

Quantitative analysis of the leachates was performed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Optima 8300, Perkin Elmer) for concentrations higher than 10 ppb and by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, 7700X, Agilent) for concentrations lower than 10 ppb. The concentrations of REEs in the LAP lamp phosphor were determined by quantitative analysis of the solutions (in triplicate) after LAP was fully dissolved in a 37% HCl solution via microwave-assisted digestion (Monowave 300, Anton Paar). For the analysis of the waste phosphor, a sample of 100 mg (in triplicate) was dissolved by fusion (1000 °C) with lithium metaborate (500 mg). The melt was dissolved in 50 mL of diluted nitric acid (3% HNO₃). XRF analysis was performed using an X-ray fluorescence spectrometer (PW 2400, Philips, Netherlands). The particle size distribution of the activated samples was characterized by laser particle size analyzer (Mastersizer 3000, Malvern, UK) using the laser diffraction method in liquid mode. The specific surface area was determined by a surface area analyzer (NOVA 2200e, Quantachrome, USA) at -196 °C. XRD data was recorded using an X-ray powder diffractometer (D2 phaser, Bruker, Germany). Amorphous content, crystal size and strain of the material was calculated by total Rietveld refinement analysis with the TOPAS software (Bruker, Germany). The powder morphology was investigated by scanning electron microscopy (XL30, Philips, Netherlands).

2.3. Mechanical activation of lamp phosphors

The mechanical activation of the phosphors was conducted using a planetary ball-mill (P-7 premium, Fritsch, Germany) in air. Phosphor samples were mixed with zirconia balls (Ø = 1, 3 or

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