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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Introduction

With the promoted use of compact fluorescent lamps (CFLs) and the increasing amount of stockpiled CFL waste, lamp phosphors have become an interesting secondary source for critical metals (Y, Eu and Tb). Phosphors for fluorescent lamps and compact fluorescent lamps are an important application of rare-earth elements (REEs), accounting for more than 30% of the total REE market by value. These phosphors consist of a mix of a red $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (YOX), green $\text{LaPO}_4\text{:Ce}^{3+},\text{Tb}^{3+}$ (LAP) or $\text{CeMgAl}_{11}\text{O}_{19}\text{:Tb}^{3+}$ (CAT), and blue $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}^{2+}$ (BAM) phosphor. Besides the rare-earth bearing phosphors, lamp phosphor waste consists up to 50% of $\text{Ca}_{4.86}\text{Mn}_{0.10}\text{Sb}_{0.04}\text{Sr}_{0.004}(\text{PO}_4)_3\text{Cl}_{0.10}\text{F}_{0.90}$ halophosphate phosphor (HALO) which has low intrinsic value and contains no REEs¹.

Most studies focus on the recovery of yttrium and europium from the red phosphor YOX, because these are the elements that are easiest to recover and they represent the highest value in the phosphor waste^{1,2}. Recycling of the green phosphors (LAP, CAT) is also very interesting due to the high concentration of the critical and expensive terbium. However, the green phosphors are much more difficult to dissolve than YOX or

HALO, and often high concentrations of mineral acids in combination with high temperatures (e.g. 18 M H_2SO_4 , 120 - 230 °C) or cracking in molten sodium hydroxide or sodium carbonate is required³. Therefore the use of an efficient and environmental friendly method for the recovery of LAP is necessary.

To improve this recovery efficiency of rare-earth elements (REEs) from the green phosphor $\text{LaPO}_4:\text{Ce}_{3+},\text{Tb}_{3+}$ by a hydrometallurgical process, mechanical activation (MA) was used as a pretreatment step prior to leaching. Valuable information on the mechanism of MA of lamp phosphors can be obtained from the characterization of the leaching process of LAP after milling. Emphasis is put on two aspects: the effect of the mechanical activation parameters on the leaching process of LAP and the characterization of the physicochemical changes during the milling process.

Results

MA applies an intense frictional action which enhances the leaching yield of REEs, improving the leaching yield by 80% at room temperature, compared to unactivated sample where the leaching yield was below 1% (Fig 1). Kinetic modeling was employed for the calculation of the apparent activation energy of the unmilled and milled samples. The physicochemical changes, including structural decomposition, specific surface area increase and particle size reduction were related to the corresponding leaching pattern. The structural decomposition causing amorphization and changes in the crystal lattice was shown to be the main driving force of the improved reactivity (Fig 2). 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.

Figure 1: Changes in the leaching yield (%) of REEs (by 4N HNO_3) from unmilled and milled (600 rpm, 60 min) LAP phosphor as a function of leaching time. Note the break in the Y-axis.

Figure 2: Changes in the XRD pattern of the LAP phosphor for different activation times ($\varnothing = 1$ mm grinding balls, rotational speed 600 rpm).

References

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