



# Rare earth elements recycling from waste phosphor by dual hydrochloric acid dissolution



Hu Liu<sup>a</sup>, Shengen Zhang<sup>a,\*</sup>, Dean Pan<sup>a</sup>, Jianjun Tian<sup>a</sup>, Min Yang<sup>a</sup>,  
Maolin Wu<sup>a</sup>, Alex A. Volinsky<sup>b</sup>

<sup>a</sup> School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

<sup>b</sup> Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

## HIGHLIGHTS

- The article provides a new method for recycling rare earth (RE) from waste phosphor.
- When compared with the traditional methods, leach rate was much higher.
- Y–Eu concentrate and Tb–Ce concentrate were obtained successively.
- It would reduce the burden of later extraction, separation and purification.

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## ABSTRACT

This paper is a comparative study of recycling rare earth elements from waste phosphor, which focuses on the leaching rate and the technical principle. The traditional and dual dissolution by hydrochloric acid (DHA) methods were compared. The method of dual dissolution by hydrochloric acid has been developed. The Red rare earth phosphor ( $Y_{0.95}Eu_{0.05}$ )<sub>2</sub>O<sub>3</sub> in waste phosphor is dissolved during the first step of acid leaching, while the Green phosphor ( $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$ ) and the Blue phosphor ( $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ ) mixed with caustic soda are obtained by alkali sintering. The excess caustic soda and NaAlO<sub>2</sub> are removed by washing. The insoluble matter is leached by the hydrochloric acid, followed by solvent extraction and precipitation (the DHA method). In comparison, the total leaching rate of the rare earth elements was 94.6% by DHA, which is much higher than 42.08% achieved by the traditional method. The leaching rate of Y, Eu, Ce and Tb reached 94.6%, 99.05%, 71.45%, and 76.22%, respectively. DHA can decrease the consumption of chemicals and energy. The suggested DHA method is feasible for industrial applications.

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## 1. Introduction

Rare earth elements (REEs) are becoming increasingly important in the transition to a green, low-carbon economy. Because the three-band phosphor (TBL) tubes have better color purity and higher luminous efficiency, fluorescent tubes with TBL have become a general trend in the World. Consequently, an amount of waste phosphor is huge. However, it is difficult to recycle the rare-earth phosphors from waste phosphor. The main challenges are as follows: firstly their emission intensities are sensitive to the concentrations and purities of rare earths, secondly the complicated

contents of waste phosphor, and finally degradation of phosphors depends on the kind of phosphor ( $Eu^{2+}$  in Blue phosphor tends to be oxidized to  $Eu^{3+}$ ) [1]. Waste phosphor is always mercury-contaminated, but now is landfilled or temporarily stockpiled, and recovery of rare earths from lamp phosphors could offer a total solution.

The improvement in recycling rates for REEs is a strategic necessity. It can only be realized by developing efficient, environmental-friendly and fully integrated recycling routes. In reality, commercial recycling of REEs from the waste phosphor is still extremely low. Despite the vast literature dealing mostly with lab-scale research efforts of REEs recycling from waste phosphor powders [2–8], less than 1% of the REEs was recycled in 2011 [9]. Only method for commercial recycling of REEs in China is the combination of alkali fusion [10] and the traditional extraction separation [11]. However, commercial recycling of REEs is not high.

\* Corresponding author. Tel.: +86 10 6233 3375; fax: +86 10 6233 3375.  
E-mail address: [zhangshengen@mater.ustb.edu.cn](mailto:zhangshengen@mater.ustb.edu.cn) (S. Zhang).

**Table 1**  
Chemical composition of the waste phosphor, wt.%.

Y	Eu	Tb	Ce	Al	Si	Ba	Mg	Ca	P	Zn	Others
15.51	0.95	0.43	0.70	7.73	10.27	1.51	2.80	14.61	8.98	0.11	36.4

The improvement of REEs recycling rate is a necessity. This paper presents a new method for increasing rate of recovery.

## 2. Materials and methods

### 2.1. Materials

Waste phosphor, supplied by the Baogangxinli RE Co., Ltd, used in this research was collected from Ganzhou, China. Table 1 shows the chemical composition of the waste phosphor analyzed by ICP-AES, others mainly includes O, S, Cl, Mn, Sb and organic impurity, etc., the total content of REEs is 17.59 wt.%. Prior to analysis, samples were roasted and smelted with appropriate amount of sodium carbonate and  $H_3BO_3$  at  $1200^\circ C$  for 30 min, and then dissolved using 1:1 hydrochloric acid solution.

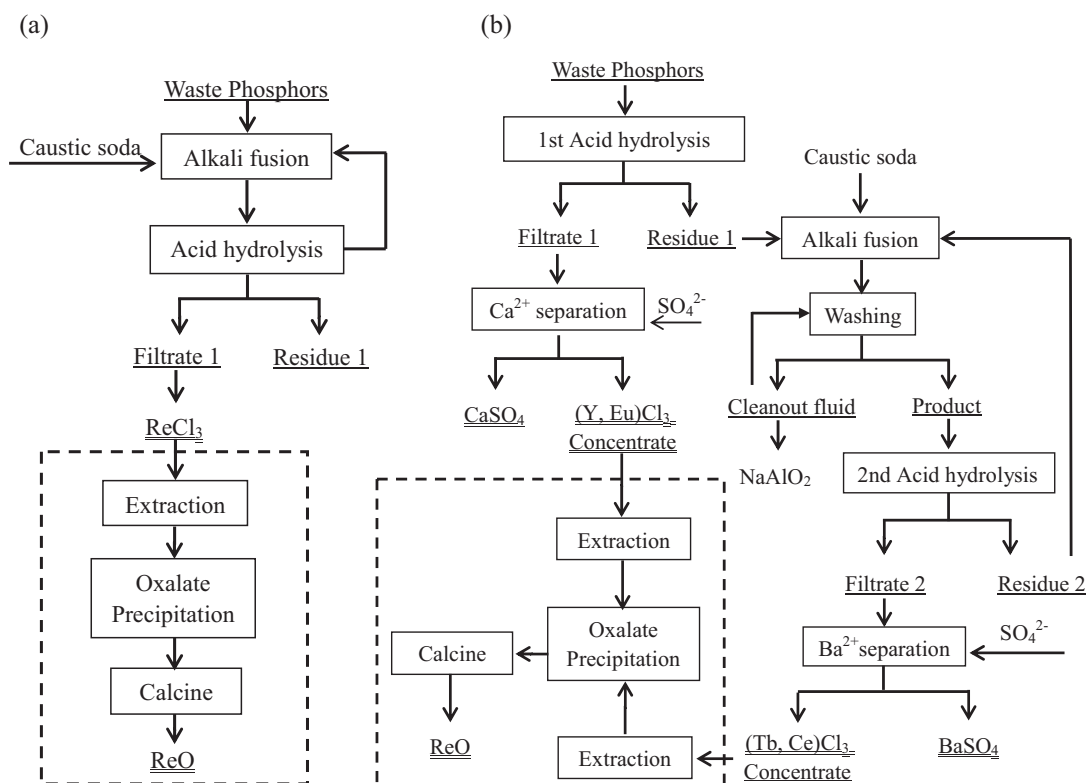
### 2.2. Proposed process flow

Fig. 1 shows the flow chart of the traditional and the new methods for recycling REEs from the waste phosphor. (a) Traditional method: 100 g of waste phosphor and sodium hydroxide were mixed as 1:1.5 waste phosphor/NaOH mass ratio. The mixture was placed into 100 ml iron crucible. Sintering was performed in a furnace at  $800^\circ C \pm 10^\circ C$  for 120 min. The fusion product was cleaned several times under stirring at 200 rpm for 20 min, with 500 ml of water at  $60^\circ C$ . The insoluble matter was filtered and dried. 30 g of insoluble residue were employed. It was leached with 300 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at

$60^\circ C$ . The acidic leachate, called Filtrate 1, was obtained. Finally after oxalate precipitation and calcination, rare earth oxides (REOs) were obtained, and the Residue 2 was returned to the alkali fusion process. (b) The DHA method is a two steps acid hydrolysis method, where first 100 g of waste phosphor were leached with 300–500 ml hydrochloric acid (3–6 mol/L) for 4 h with stirring (250 rpm) at  $60^\circ C$ , thus calcium in Filtrate 1 was removed by adding  $Na_2SO_4$ . Y–Eu chloride concentrate was obtained. Residue 1 and sodium hydroxide were mixed as 1:0.5–2 Residue 1/NaOH mass ratio. The mixture was placed into 100 ml iron crucibles. Sintering was performed in a furnace at  $800^\circ C \pm 10^\circ C$  for 2 h. The fusion product was cleaned as in the traditional method. The insoluble matter was filtered, and leached with 150 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at  $60^\circ C$ . The acidic leachate, called Filtrate 2, Tb–Ce chloride concentrate, was obtained, while the Residue 2, which could not be dissolved, was returned to the alkali fusion process. The advantages of the novel method can be quantified by calculating the leaching rates of both methods.

### 2.3. Analysis

X-ray diffraction (XRD) analysis was performed using Philips APD-10 X-ray diffractometer with Cu  $K\alpha$  radiation, 40 kV voltage and 150 mA current at  $10^\circ/\text{min}$  scanning rate, from  $10^\circ$  to  $100^\circ 2\theta$  range. The morphology, aspect ratio and mean particle size were observed in the scanning electron microscope (Zeiss EVO-18, Germany). Chemical composition was analyzed by ICP-AES (Perkin Elmer Co., Ltd. OPTIMA 7000DV).



**Fig. 1.** Flow chart of REEs leaching from the waste phosphor: (a) traditional method and (b) DHA method.

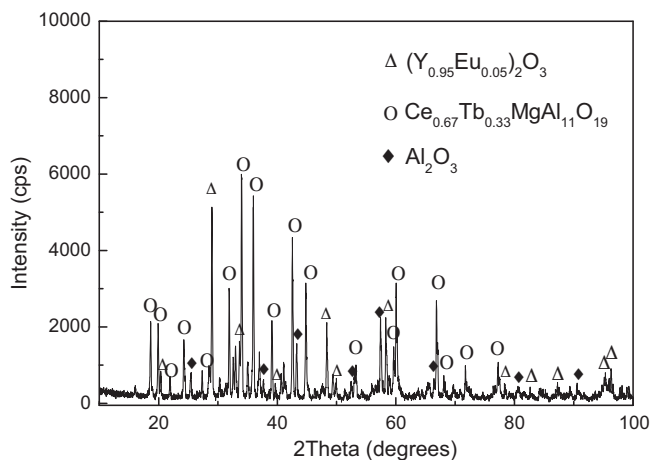


Fig. 2. X-ray diffractogram of the waste phosphor.

### 3. Results and discussion

#### 3.1. Waste phosphor

Fig. 2 shows X-ray diffractogram of the waste phosphor, where the powder consists of  $(Y_{0.95}Eu_{0.05})_2O_3$  (JCPDS 25-1011),  $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$  (CTMA, JCPDS 36-0073) phases and minor  $Al_2O_3$  (JCPDS 10-0173),  $Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$  (BMA, JCPDS 50-0513), phases.

#### 3.2. Traditional method

When waste phosphor/NaOH mass ratio is 1:1.5, a mixture of  $NaYO_2$  (JCPDS 32-1203) and  $NaAlO_2$  (JCPDS 33-1200) dominates, and the minor phase is  $BaFe_{12}O_{19}$  (JCPDS 27-1029), as observed in the X-ray diffractograms of the fused mass in Fig. 3.

After the fusion, solid was washed and dried, and 30 g of insoluble residue were employed. It was leached with 300 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at 60 °C. After oxalate precipitation and calcination, rare earth oxides were obtained.

#### 3.3. DHA method

First, 100 g of waste phosphor were leached by hydrochloric acid. As Fig. 4, it was observed that the metal components were

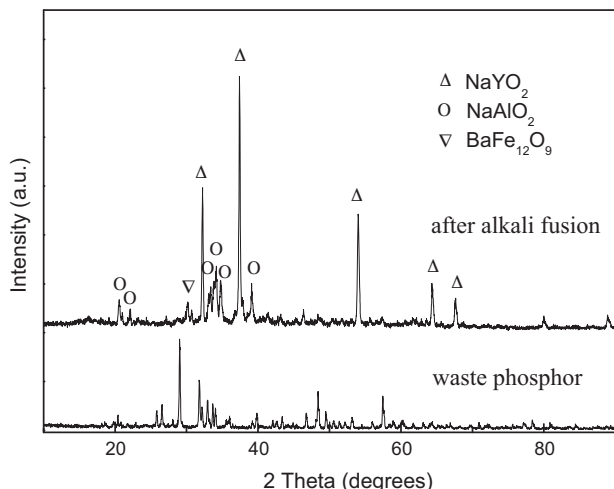


Fig. 3. X-ray diffractograms of the waste phosphor after alkali fusion.

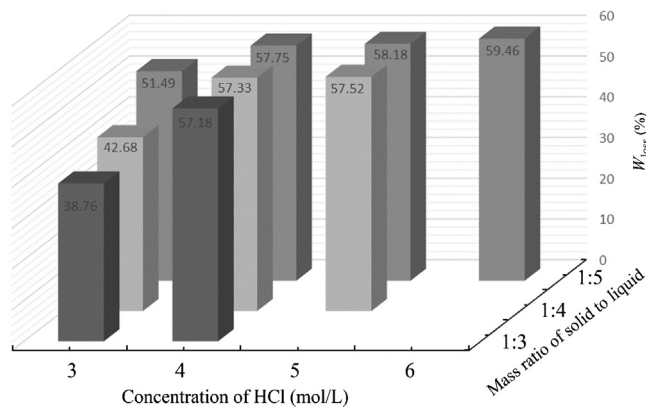


Fig. 4.  $W_{loss}$  of first acid hydrolysis.

Table 2  
REEs composition of Filtrate 1.

Oxide	REEs	Y	Eu	Tb	Ce	Others
Mass/g	15.371	14.312	0.924	–	–	0.135

leached out much more at the higher acid concentration and the lower mass ratio of solid to liquid. Considering the leaching cost, when concentration of HCl was 4 mol/L, mass ratio solid–liquid was 1:3, the  $W_{loss}$  was 57.18%, and the Red phosphor was leach out as Fig. 5, after first acid hydrolysis the diffraction peak of red ( $(Y_{0.95}Eu_{0.05})_2O_3$ ) was disappeared. The Residue 1 mainly consists of BMA and CTMA phase. And the Y–Eu chloride concentrate was obtained, REEs composition of filtrate 1 is showed in Table 2.

The main chemical reaction that occurs between Red phosphor and HCl by the first step acid leaching is:

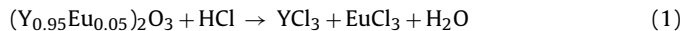


Fig. 6 shows XRD pattern of production after alkali fusion at different temperatures. When temperature was 400 °C, based on thermodynamics and kinetics analyses, the lower temperature was, the slower reaction rate was. The results showed that green (CTMA) phase was not fully decomposed. The main crystal phases were  $NaAlSiO_4$  (JCPDS 33-1203) and  $NaAlSi_2O_6$  (JCPDS 22-1338), which would lead to rare earth recovery not completely. When the alkali temperature increased to 600 °C, the main crystal phase was  $NaAlO_2$  (JCPDS 33-1200), the minor crystal phases was CaO

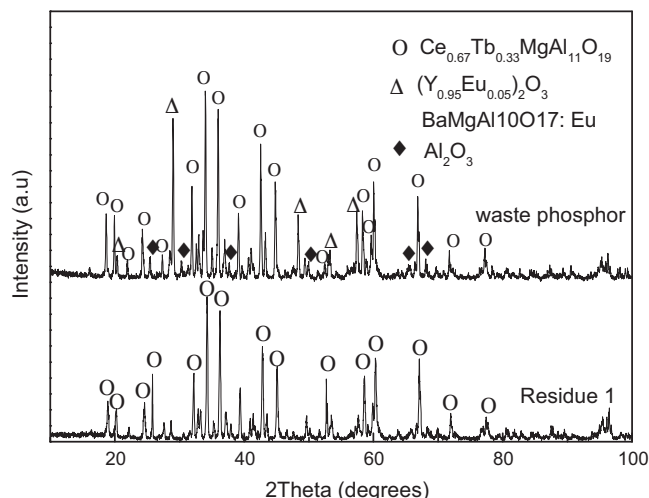


Fig. 5. X-ray diffractograms of the waste phosphor and Residue 1.

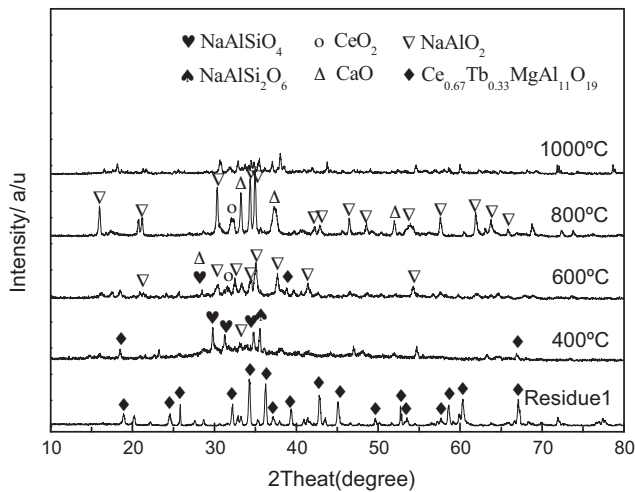


Fig. 6. X-ray diffractograms of alkali product at different temperatures.

(JCPDS 37-1497) and green diffraction intensity of peaks was significantly reduced. When the alkali temperature increased to 800 °C, NaAlO<sub>2</sub> diffraction intensity of peaks became stronger significantly, and green diffraction intensity of peaks was disappeared, green was dissolved completely at 800 °C, REO in the product would be dissolved by next acid hydrolysis. When the alkali temperature reaches 1000 °C, alkali product became non-crystalline. Therefore the best alkali temperature was 800 °C.

Fig. 7 showed XRD pattern of alkali product under different alkali dosages. When Residue 1 was mixed with NaOH at the mass ratio of 1:0.5, the main crystal phase of alkali product was still green (CTMA) phase. The possible cause was that the alkali product was not fully decomposed due to the less NaOH. So the minor crystal phases of CeO<sub>2</sub> (JCPDS 34-0394) and CaO (JCPDS 37-1497) existed in the product. When the ratio increased to 1:1, the crystal phase was consisted of the most NaAlO<sub>2</sub> and the minor phases of CeO<sub>2</sub> and CaO. The intensity of green (CTMA) diffraction peaks decreased significantly. When the ratio reached 1:1.5 or 1:2, green (CTMA) was fully decomposed, the main crystal phase was NaAlO<sub>2</sub>. Therefore the appropriate mass ratio was 1:1.5 at this method.

After the fusion, solid was cleaned and dried, while REEs were not detected in the cleaning water. The second step acid leaching was aimed at leaching the rare earth elements from the REOs

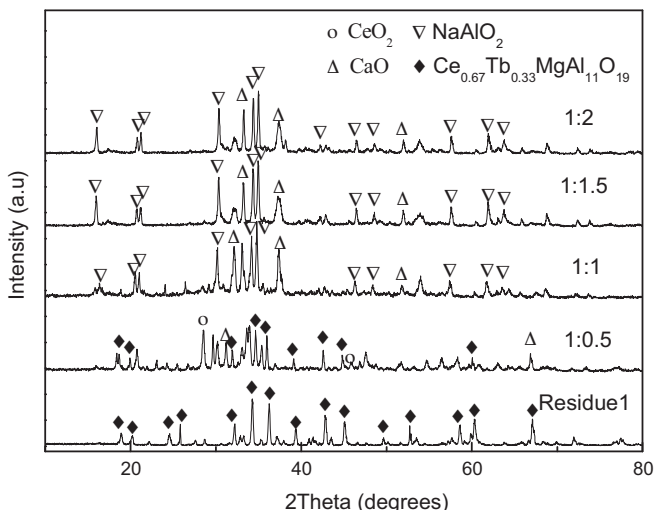


Fig. 7. X-ray diffractograms of alkali product under different alkali dosages.

Table 3  
REEs composition of Filtrate 2.

Oxide	REEs	Y	Eu	Tb	Ce	Others
Mass/g	1.269	0.360	0.017	0.307	0.534	0.051

Table 4  
Chemical composition of the Residue 2 in wt.%.

SiO <sub>2</sub>	Cl	CaO	Y <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	F
72.69	11.00	4.71	2.65	2.36	1.65	1.40
Fe <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>	Eu <sub>2</sub> O <sub>3</sub>	Tb <sub>4</sub> O <sub>7</sub>	SO <sub>3</sub>	Other
0.97	0.46	0.39	0.20	0.14	0.08	1.30

in alkali fusion products, and hydrochloric acid was chosen as the leaching agent. The mechanism is as follows:



30 g of insoluble residue were leached with 300 ml hydrochloric acid (5 mol/L) for 120 min with stirring (250 rpm) at 60 °C. Sulfate precipitation method was used to remove Ba<sup>2+</sup> and Mg<sup>2+</sup> from the Filtrate 2. Then the terbium and cerium chlorinated rare earth concentrates were obtained. The REEs composition of Filtrate 2 was showed as Table 3.

After filtering and drying, Residue 2 with the weight of 9.38 g was left. A mixture of SiCl<sub>4</sub> (JCPDS 10-0220) and Ca(AlSi)<sub>2</sub>O<sub>8</sub> (JCPDS 31-0248) dominates, as observed in the X-ray diffractogram of the fused mass in Fig. 8.

Based on Table 4, Residue 2 mainly contains 72.69% Si, 11% Cl, and 4.71% Ca, but only a small 3.16% amount of REEs. The silicon is in the form of silica gel. Thus, most of REEs were leached in the Filtrate 1 and Filtrate 2 by DHA. Silicon, which affected both the acid hydrolysis and subsequent extraction, originated from the tube glass fragment. So it would be better to add physical and chemical process, including sieving or leaching by hot aqueous alkali for separating the glass before the DHA process at the early stage.

### 3.4. Leach rate

The REEs leach results by the traditional method and DHA are shown in Table 5. Total REEs leach rate was 94.6% by DHA, which is much higher than 42.08% by the traditional method. Meanwhile, leach rate of Y, Eu, Ce and Tb reached 94.6%, 99.05%, 71.45%, and

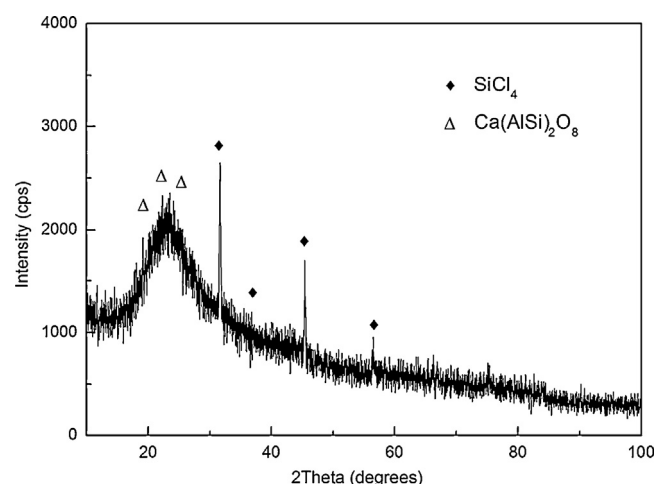


Fig. 8. X-ray diffractogram of the Residue 2.

**Table 5**  
Leach rate comparison of the traditional method with DHA.

Elements	Traditional method, %	DHA, %
Total	42.08	94.6
Y	41.53	94.6
Eu	67.88	99.05
Tb	94.52	71.45
Ce	86.14	76.22

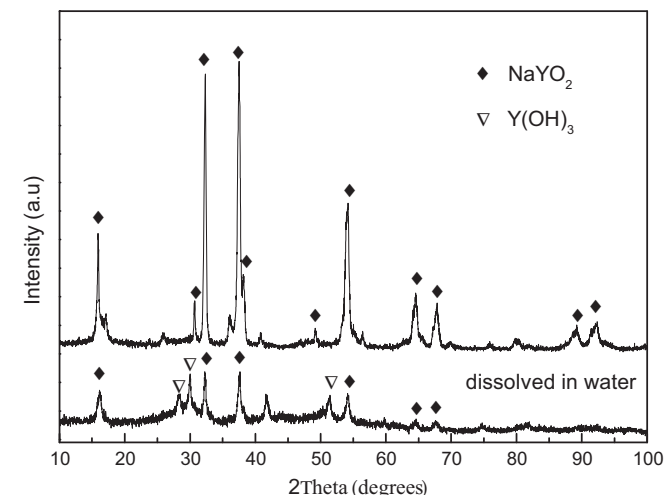


Fig. 9. X-ray diffractograms of  $\text{NaYO}_2$  before and after hydrolysis.

76.22%, respectively by DHA. After extraction, oxalate precipitation and calcination, a final product of 99% pure rare earth oxides was obtained.

$$\text{Total leach rate} = \frac{m_{\text{REEs1}} + m_{\text{REEs2}}}{m_{\text{REEs}}}$$

$$\text{Leach rate} = \frac{m_{\text{REE1}} + m_{\text{REE2}}}{m_{\text{REE}}}$$

where  $m_{\text{REE1}}$  is the mass of rare earth element (REE) in Filtrate 1,  $m_{\text{REE2}}$  is the mass of REE in Filtrate 2, and  $m_{\text{REE}}$  is the mass of REE in waste phosphor.

Y is the highest content REE element in the waste phosphor (Table 1), and recovery of Y was higher by DHA than by the traditional method. By the traditional method, during the alkali sintering, Red ( $\text{Y}_{0.95}\text{Eu}_{0.05}$ ) $_2\text{O}_3$  and NaOH went into melting stage

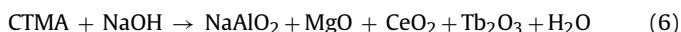
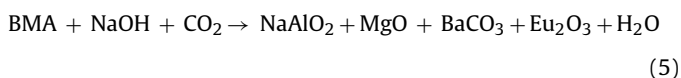
and reacted to produce  $\text{NaYO}_2$  (JCPDS 32-1203). It would mainly hydrolyze into  $\text{Y}(\text{OH})_3$  (JCPDS 24-1422) (as in Fig. 9) when the fused solid was cleaned, so a part of Y was lost in the cleaning water. However, by the DHA, Y loss will not occur that way either, since Red ( $\text{Y}_{0.95}\text{Eu}_{0.05}$ ) $_2\text{O}_3$  was dissolved in the first acid hydrolysis, and almost all of Y was recovered in the Filtrate 1.

### 3.5. Alkali fusion of pure phosphor

Pure three-band phosphor and sodium hydroxide were mixed, respectively, according to the Blue or Green/NaOH mass ratio of 1:1.5. Sintering was performed at 800 °C for 120 min. The main component is  $\text{NaAlO}_2$ , and minor REOs, MgO (JCPDS 45-0946) and  $\text{BaCO}_3$  (JCPDS 41-0373) phases are seen in the X-ray diffractograms of the fused mass in Fig. 10.

BMA [12] has the hexaaluminate structure and crystallizes in the  $\text{P6}_3/\text{mmc}$  space group. CTMA [13] has a distorted magnetoplumbite structure. They can be described as consisting of oxygen close-packed spinel blocks, separated by mirror planes. During the alkali fusion process, sodium hydroxide melts to form ionic liquids, in the  $\text{OH}^-$  environment, BMA, barium and europium are replaced by sodium in the mirror planes, and then spinel blocks of  $\text{MgAl}_{10}\text{O}_{16}$  composition are transformed into  $\text{NaAlO}_2$  and MgO. In CTMA cerium and terbium are replaced by sodium in the mirror planes, and then spinel blocks of  $\text{MgAl}_{11}\text{O}_{19}$  composition are transformed into  $\text{NaAlO}_2$  and MgO. After substitution and crystal structure transition, in order to keep the unit cell charge neutral, BMA and CTMA are decomposed into  $\text{NaAlO}_2$ , REO, MgO, CaO and  $\text{BaCO}_3$ .

The main chemical reactions that occur between Green, Blue and sodium hydroxide during the alkali fusion process are:



## 4. Conclusions

Compared with the traditional method, a novel dual dissolution by hydrochloric acid (DHA) method has been developed for recycling rare earth elements from the waste rare earth phosphor, avoiding the possible loss of Y by the traditional method. Total REEs recovery was 94.6%, which is much higher than the 42.08% by the

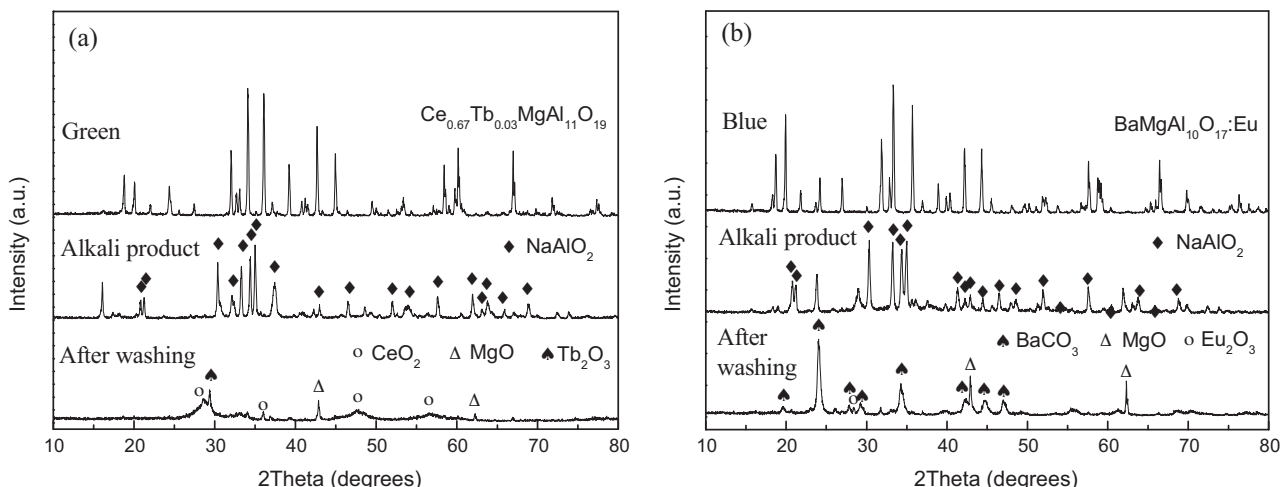


Fig. 10. X-ray diffractograms of alkali fusion: (a) Blue and (b) Green products.



traditional method. The leach rate of Y, Eu, Ce and Tb reached 94.6%, 99.05%, 71.45%, and 76.22%, respectively, while Y–Eu and Tb–Ce chloride concentrates were separated, reducing the burden of later extraction, separation and purification. Also, the used amount of caustic soda and extractant could be decreased by 1/3–1/2.

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