

# Selective Separation of Yttrium and Cerium (IV) from the Prepared Abu Hamata Lanthanides Cake

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**Abstract:** The present work is concerned with selective separation of Y and Ce (IV) from the lanthanides cake prepared from the pregnant sulfate leach liquor of Abu Hamata sandy claystone ore material. This sulfate solution assays 0.32 g/L of Ln, 0.45 g/L of U together with 0.05 g/L V and 0.008 g/L B. It was used to prepare the lanthanides cake that contains 12.2% of Y and 37.4% of Ce. Ammonium carbonate solution in concentration of 200g/L was used for dissolving more than 95.1% of Y content selectively from the prepared lanthanides cake. The free Y lanthanides cake was then subjected to Ce (IV) separation via dissolving the other trivalent lanthanides in dilute hydrochloric acid while Ce(IV) remains insoluble.

**Keywords:** Sandy Claystone Ore, Agitation Leaching, Ln Direct Precipitation, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Y, Ce(IV)

## 1. Introduction

Lanthanides (Ln) have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high-temperature superconductors and secondary batteries, catalysis [1, 2, 3].

Abu Hamata sandy claystone rock facies of Um Bogma Formation, which occurs at Abu Zeneima area, Southwestern Sinai, Egypt, is considered as one of the most important occurrences of lanthanides beside the associated economic metal values such as uranium, vanadium, boron, copper,.... etc [4].

Yttrium shows selective solubilization with carbonate solutions while the other Ln are little dissolved or not dissolved at all [5, 6]. According to De Vasconcellos et al. (2006 & 2008) [7, 8], the carbonates of cerium group (La, Ce, Pr, Nd and Sm) are insoluble in water and in ammonium carbonate, while the yttrium group lanthanides (Gd-Lu) are soluble in this salt. On the other hand, Ce can be separated through changes in their oxidation state. The Ce(III) is oxidized to Ce(IV) by drying Ln-hydroxide in air at 120-130°C or by chlorination or electrolysis [9, 10].

In this context, the main target of the present work is to

separate both of Y and Ce(IV) selectively from Ln-cake in reasonable purity. For this purpose, the Ln-hydroxide cake prepared from Abu Hamata sulfate leach liquor was first dried at 160-200°C for 3h. Yttrium separation from the prepared Ln concentrate was first performed via its selective dissolution in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution. This was followed by separating Ce(IV) from the other trivalent Ln which was almost free from Y via HCl dissolution procedure.

## 2. Experimental

### 2.1. Preparation of Sulfate Leach Liquor

A sulfate leach liquor of the provided working material was prepared via its agitation leaching by using 5% H<sub>2</sub>SO<sub>4</sub> acid concentration at solid/liquid (S/L) mixing ratio of 1/2, leaching time of 1h and leaching temperature of 75°C. After filtration and washing, the total volume of the prepared leach liquor was adjusted to be 4 liters /Kg ore. The latter was found to assay in g/L: 0.32 Ln 0.45 U, 0.05 V, 0.008 B, 2.3 Cl and 26 SO<sub>4</sub><sup>2-</sup>.

### 2.2. Analytical Procedure

In this work, visible-ultra violet spectrometer (Shimadzu

UV-160) was used for the quantitative analysis of total Ln using 0.015% arsenazo III at  $\lambda_{654}$  nm using Ce as reference [11]. In addition, inductively coupled plasma-emission spectrometry (ICP-ES) was used for the chemical estimation of individually separated Ln.

Finally, the obtained products of total Ln as well as the separated Y and Ce(IV) was identified by using both of X-ray diffraction analysis (Philips X-ray generator model PW1140/90 fitted with a diffractometer model PW 1050/80) and scanning electron microscope (SEM-EXL 30 Philips type) coupled with X-ray analyzer (EDX unit system).

### 2.3. Extraction Procedures

#### 2.3.1. Direct Precipitation of Lanthanides

The working sulfuric acid leach liquor of Abu Hamata sandy claystone ore material was firstly adjusted to pH 1.8 and directed to anion exchange unit (Amberlite IRA<sub>400</sub>) to recover its U content. The effluent solution free from U was subjected to selective separation of total Ln via precipitation by using 10% oxalic acid solution. After filtration and washing, the precipitated Ln-oxalates cake was dissolved in 5% HCl solution and re-precipitated with NH<sub>4</sub>OH solution at pH 9.5 to remove the associated Ca impurities. The precipitate of Ln(OH)<sub>3</sub> was dried and used to perform selective separation of both Y and Ce(IV).

#### 2.3.2. Separation of Yttrium

Yttrium separation from the prepared Ln(OH)<sub>3</sub> cake was performed via its selective dissolution in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution. For this purpose, different experiments were conducted to attain optimum dissolution conditions. These include (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>

concentrations, time of dissolution and temperature.

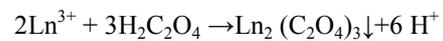
#### 2.3.3. Separation of Cerium (IV)

Separation of Ce(IV) from the dried Ln cake free from Y was performed through its insolubilization by dissolving the other trivalent Ln in HCl solution. For this purpose, the  $\Sigma$ Ln (III) were dissolved in 5% HCl solution at pH values ranging between 2 up to 4.

## 3. Results and Discussion

### 3.1. Preparation of Ln Cake

The total Ln in the prepared sulfuric acid leach liquor were selectively precipitated from the effluent solution which produced after the recovery of U by the addition of oxalic acid where the Ln form strong stable insoluble oxalates. Thus, they can be easily separated by precipitation [12]. The following equation illustrates the above reaction:



In the present work, complete precipitation of Ln was attained by addition of 10% oxalic acid at pH 1.1 with continuous stirring for 45 min. After filtration and washing, the obtained Ln-oxalate cake was dried at 120°C for 2h. The latter was subjected to EDX analysis technique to identify its content of Ln and the associated impurities as shown in Figure 1. It was found that, the purity of the Ln- cake achieved 85.2%. On the other hand, the chemical analysis by using ICP technique revealed the presence of 12% of Ca, 0.2% of Zn and 0.3% of Cu as the matching impurities.

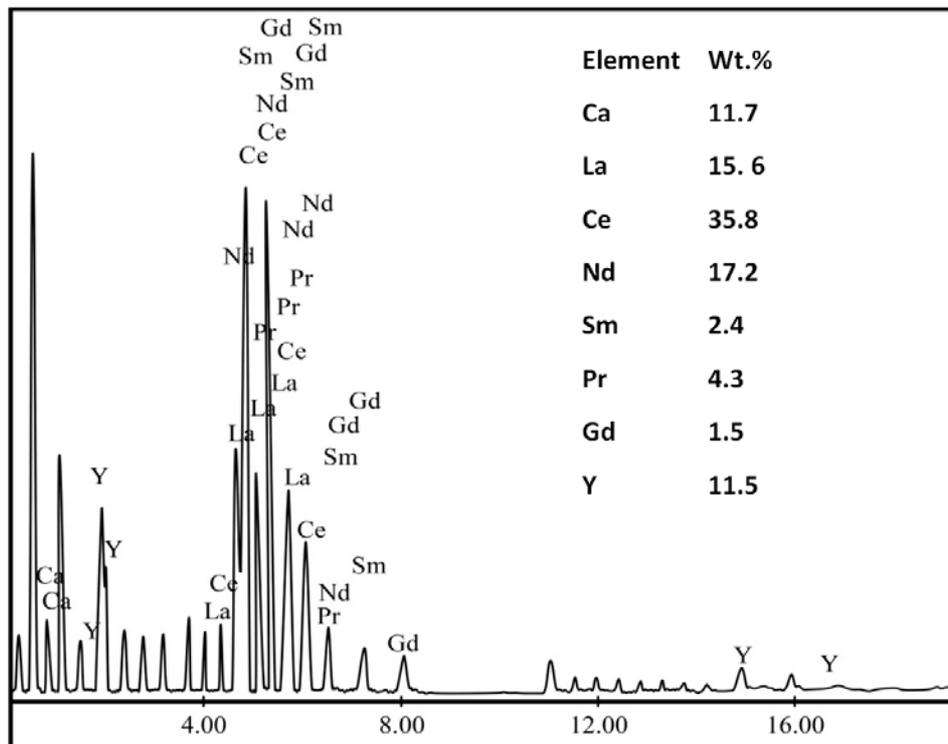


Figure 1. EDX analysis of the prepared impure Ln-cake associated with Ca.

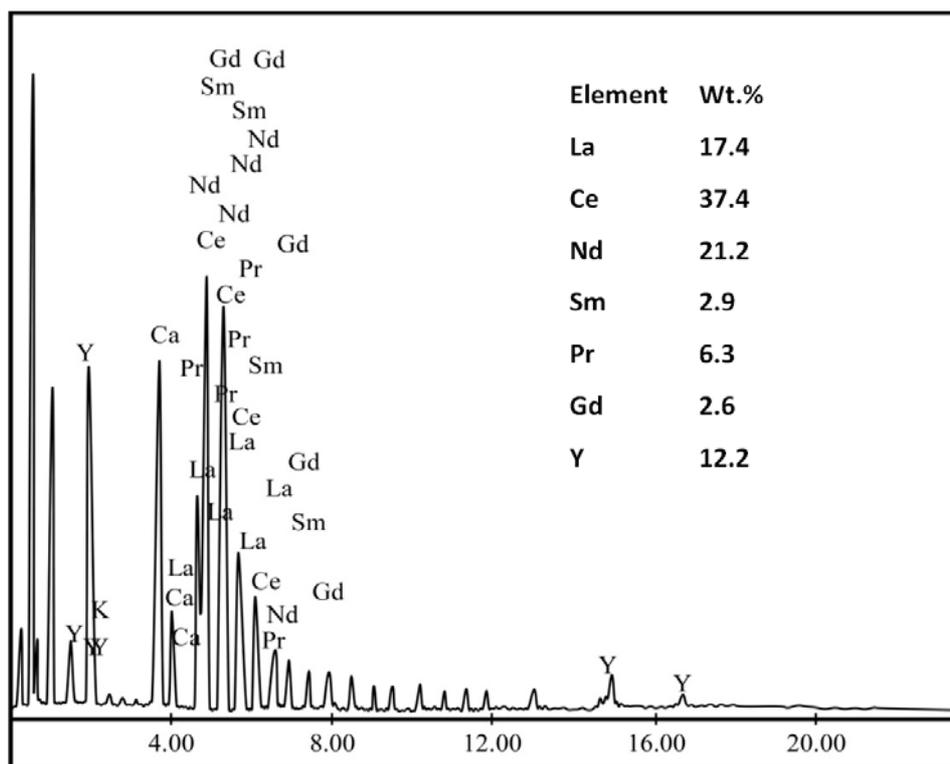


Figure 2. EDX analysis of the prepared pure Ln-cake.

For further purification, the precipitate of Ln-oxalates was dissolved in 5% HCl acid solution. The total Ln in the chloride solution were re-precipitated by adding  $\text{NH}_4\text{OH}$  solution to precipitate  $\text{Ln}(\text{OH})_3$  cake free from Ca ions at pH 9.5[13]. After filtration and washing, the obtained  $\text{Ln}(\text{OH})_3$  cake was dried at 160-200°C for 3h in order to oxidize its Ce(III) to Ce(IV). The obtained cake was identified by means of SEM-EDX analysis as shown in Figure 2. It was clearly evident that, the produced cake is composed of light Ln mainly Ce, La and Nd which represent about 75% beside 12% Y. The following equations illustrate the purification process:



The ICP-ES chemical analysis of the prepared Ln cake was shown in Table 1.

Table 1. The ICP-ES chemical analysis of the prepared Ln cake.

Element	Wt., %	Element	Wt., %
La	18.1	Nd	21.2
Ce	35.9	Sm	1.9
Pr	6.2	Eu	0.7
Gd	1.9	Dy	0.4
Y	12.1		

### 3.2. Separation of Y and Ce from the Prepared Ln-Hydroxide Cake

Due to the great technological and economic importance of individual Ln, it was decided to perform the proper separation procedures of pure individual products e.g. Y and Ce.

The obtained hydroxide cake was firstly dried at 160-200°C for 3 h to oxidize its content of Ce (III) into Ce(IV) which wouldn't readily dissolve in both alkaline or acid solutions [14, 15]. The purpose was to facilitate Y separation via its dissolution in ammonium carbonate solution. This was followed by Ce (IV) separation from the prepared cake which was almost free from Y via dissolving the other trivalent Ln in dilute hydrochloric acid while Ce(IV) remains insoluble.

#### 3.2.1. Selective Separation of Y

Y was selectively dissolved from the prepared Ln concentrate by using ammonium carbonate solution. This is due to the fact that, the heavy Ln especially Y are soluble in carbonate solutions while the others (Ce, La, Nd, Sm and Pr) are completely insoluble [7, 8]. Several relevant factors encourage Y selective dissolution such as:  $(\text{NH}_4)_2\text{CO}_3$  concentration, time of dissolution and temperature were studied at the suitable S/L ratio of 1/5.

##### i. Effect of $(\text{NH}_4)_2\text{CO}_3$ Concentration

To study the effect of  $(\text{NH}_4)_2\text{CO}_3$  concentration upon the selective dissolution of Y from the prepared Ln hydroxide cake, four dissolution experiments were conducted at room temperature by using different concentrations of  $(\text{NH}_4)_2\text{CO}_3$  varying from 50 to 250 g/L. The other parameters were kept constant at S/L ratio of 1/5 and dissolution time of 20 min. After filtration and washing the total volume was closed up to 100ml, where the dissolved Y was analyzed and its dissolution efficiency was calculated. The obtained results given in Table 2 revealed that, at  $(\text{NH}_4)_2\text{CO}_3$  concentration of 50g/L, the dissolution efficiency of Y was 17.4% while it has significantly improved gradually to be 43.3% by increasing

the concentration to 200g/L. Further increase in  $(\text{NH}_4)_2\text{CO}_3$  concentration shows limit improvement in Y dissolution efficiency which increased to 45.6% at  $(\text{NH}_4)_2\text{CO}_3$  concentration of 250g/L. Trials to improve the dissolution efficiency of Y more than 43.3% have been achieved through varying the time of dissolution as well as increasing the dissolution temperature as has been seen later.

**Table 2.** Effect of  $(\text{NH}_4)_2\text{CO}_3$  upon Y dissolution efficiency.

$(\text{NH}_4)_2\text{CO}_3$ Conc., g/L	Y dissolution efficiency, %
50	17.4
100	21.8
150	34.1
200	43.3
250	45.6

### ii. Effect of Dissolution Time

The effect of dissolution time upon Y dissolution efficiency from the prepared Ln-cake was studied at different intervals of time ranged between 20 to 60 min. The other dissolution factors were fixed at  $(\text{NH}_4)_2\text{CO}_3$  concentration of 200 g/L, S/L ratio of 1/5 at room temperature. The obtained data (Table 3) emphasized that, the dissolution efficiency of Y increased from 43.3 to 68% by increasing the dissolution time from 20 min to 40 min. Further increase in the dissolution time to 60 min has an opposite effect. This might be due to the hydrolysis of the dissolved Y.

**Table 3.** Effect of dissolution time upon Y dissolution efficiency.

Dissolution time, min	Y dissolution efficiency, %
20	43.3
30	53.1
40	68
50	69.1
60	55.9

### iii. Effect of Dissolution Temperature

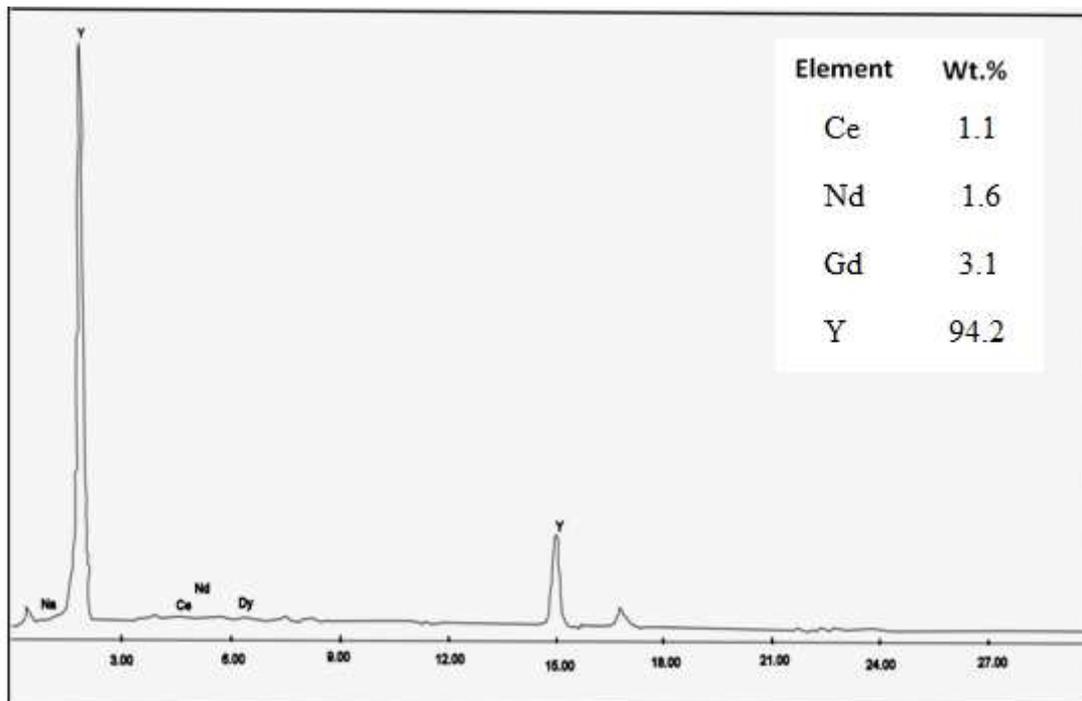
Four dissolution experiments have been performed to study the effect of increasing the dissolution temperature of Y from the prepared Ln hydroxide cake. In these experiments, the studied temperature ranged from room temperature up to 80°C, the other dissolution parameters were kept constant at  $(\text{NH}_4)_2\text{CO}_3$  concentration of 200 g/L, dissolution time of 40 min and S/L ratio of 1/5. The obtained data given in Table 4 revealed that increasing dissolution temperature has a great effect upon the dissolution efficiency of Y. The latter increased from 68 to 95.1% when the dissolution temperature increased from room temperature to 70°C. It was also noticed that further increase in the dissolution temperature to 80°C increased Y dissolution efficiency up to 99.1% but its purity decreased due to the dissolution of some other Ln elements especially Nd and La.

**Table 4.** Effect of dissolution temperature upon Y dissolution efficiency.

Dissolution temp., °C	Y dissolution efficiency, %
35	68
45	69.2
60	80.3
70	95.1
80	99.1

From the forgoing study of selective Y dissolution from the prepared Ln-cake, it can be concluded that the optimum dissolution conditions for dissolving about 95.1% of Y content are as following:

$(\text{NH}_4)_2\text{CO}_3$ concentration	:	200 g/L
Dissolution time	:	40 min
Dissolution temperature	:	70°C



**Figure 3.** EDX analysis chart of the prepared pure  $\text{Y}_2\text{O}_3$ .

Finally, the alkaline carbonate solution rich in Y and almost free from the other associated Ln was subjected to Y precipitation via neutralization. Acidification of the prepared alkali solution was carried out by the addition of dilute HCl. However, the complete precipitation of Y hydroxide was achieved at pH 6. The Y precipitate was then filtered, washed and calcined at 750°C for 1h to obtain the final product of Y<sub>2</sub>O<sub>3</sub>. The latter was identified by means of EDX analysis technique as shown in Figure 3. On the other hand, the chemical analysis of Y in the final Y<sub>2</sub>O<sub>3</sub> product revealed that it has a purity of 94.2%.

**3.2.2. Selective Separation of Ce(IV)**

The process of Ce(IV) separation from the other Ln (III) is more economic and widely applied. However, the dried Ln-cake free from almost Y was leached by gradual addition of 5% HCl solution to dissolve the trivalent Ln elements leaving behind the insoluble Ce(IV) [16]. Separation efficiency of Ce(IV) and its purity depends mainly on the pH value of the chloride solution as well as the time of Ln-cake dissolution.

**i. Effect of pH Value**

The pH value of the chloride solution is considered as the most effective variable parameter affecting Ce(IV) recovery and its purity from the dried Ln cake free from Y. In the present work, different chloride solutions with different pH values varied from 2 to 4 were used for 20 min as stirring time at room temperature. Results given in Table 5 show that, Ce (IV) recovery increased from 93.6 to 98.3% with increasing the pH values of chloride solutions from 2 to 4. It was noticed that the chloride solution at pH 3.5 gave the more suitable Ce(IV) separation efficiency(97.9%) and purity (95.4%).

*Table 5. Effect of pH upon Ce(IV) recovery and purity.*

pH value	Ce(IV)recovery, %	Ce-purity, %
2	93.6	98.4
2.5	94.0	97.2
3.0	94.9	96.9
3.5	97.9	95.4
4.0	98.3	92.8

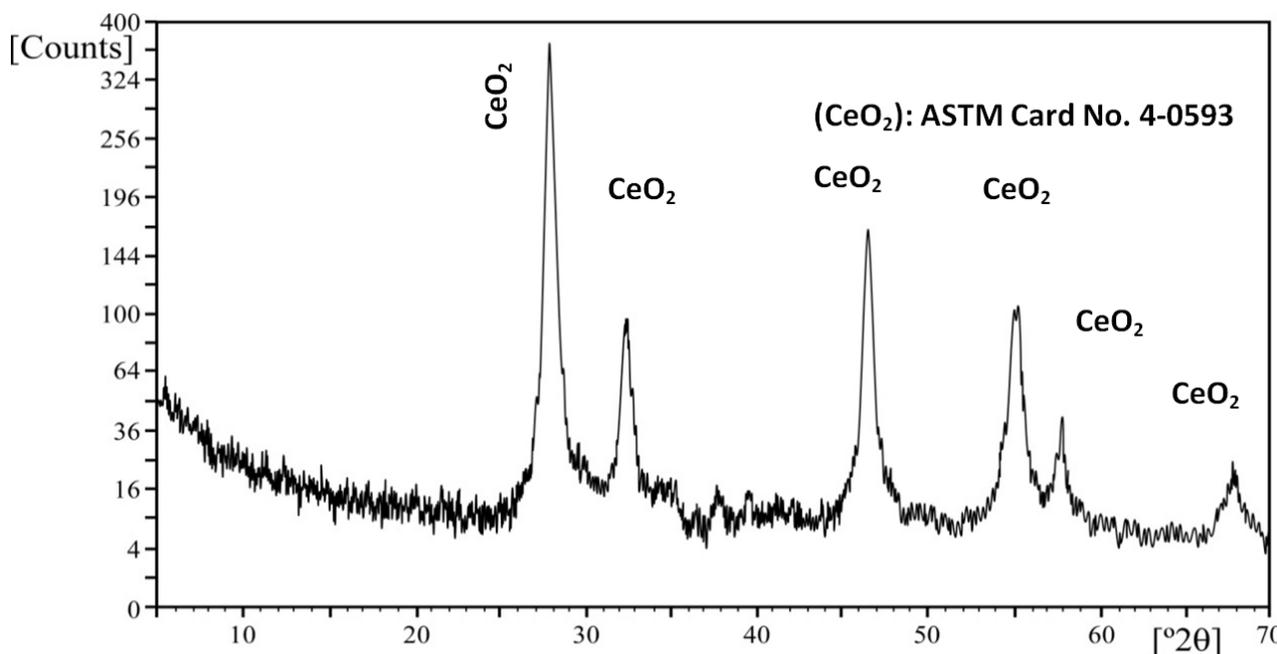
**ii. Effect of Time**

The effect of stirring time upon the separation efficiency of Ce(IV) from the dried Ln cake free from Y appears during the dissolution process by using HCl solution. It was noticed that, increasing the dissolution time from 20 to 40 min increase the dissolution of the other trivalent Ln elements in chloride solution at pH 3.5. In the meantime, the purity of the prepared Ce(IV) increased up to 98.6%. Further increase in the dissolution time to 50 and 60 min increases the dissolution efficiency of the other trivalent Ln elements and decreased the purity of the recovered Ce(IV), Table 6.

*Table 6. Effect of dissolution time upon Ce(IV) recovery and purity.*

Time, min	Ce(IV) recovery, %	Ce (IV) purity, %
20	97.9	95.4
30	97.8	97.2
40	97.5	98.6
50	96.9	98.9
60	95.3	99.0

The obtained yellowish Ce(IV) precipitate at the applied optimum separation conditions (pH 3.5 & 40min) was then filtered, washed several times with distilled H<sub>2</sub>O to remove the excess of Cl<sup>-</sup> anions and dried to gave pure CeO<sub>2</sub>. The latter was confirmed by means of XRD analysis as shown in Figure 4.



*Figure 4. XRD analysis of the prepared pure CeO<sub>2</sub>.*

## 4. Conclusion

Almost Y dissolution (95.1%) from the prepared Ln-hydroxide cake of Abu Hamata sulfate leach liquor was achieved by using 200g/L  $(\text{NH}_4)_2\text{CO}_3$  at solid/liquid ratio of 1/5 with stirring for 40 min at 70°C. In addition, Ce (IV) was then separated from the Ln-cake almost free from Y by dissolving the other Ln in 5% HCl at the optimum pH value of 3.5 leaving Ce (IV) behind as un-dissolved material.

The procedures described in this study are simple, adequate and economical that can be applied successfully at pilot scale for separating Ln beside Y and Ce with high efficiencies and relatively purity.

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