

Preparation of cerium oxide nanoparticles from monazite ore with microemulsion method

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*Pipat Pichestapong¹ **

Uthaiwan Injarean²

Abstract

Monazite ore in the South of Thailand was found to contain about 20% of cerium in the form of phosphate compound. This cerium has been chemically separated from the ore and purified by ion exchange columns at Rare Earth Research and Development Center, Thailand Institute of Nuclear Technology. Cerium in EDTA solution from the ion exchange columns was precipitated with NaOH and then dissolved with HNO₃ or HCl for the preparation of Ce(NO₃)₃·6H₂O or CeCl₃·7H₂O precursors by crystallization. Microemulsion of these cerium precursors was prepared in the mixture of n-hexane and butanol with cetyl trimethylammonium bromide (CTAB) surfactant and mixed with microemulsion of NH₄OH. Each mixture was dried at 250°C for 2 hr and calcined at 600°C for 1 hr to form nano-sized CeO₂ powder. The powder was characterized by XRD, TEM and BET. The average particle sizes of the prepared cerium oxide powders were found to be in the range of 9 – 12 nm and their surface areas were in the range of 44 – 57 m²/g.

Keywords: microemulsion, nanoparticles, cerium oxide, monazite ore

1. Introduction

Cerium oxide nanoparticles have been widely investigated because of the potential applications in catalysts, electrolyte of solid oxide fuel cells, oxygen storage capacitors, materials of high refractive index, UV blockers and polishing powder. Several processing routes have been carried out for the preparation of the nano-sized cerium oxide powder from different cerium precursors such as spray pyrolysis, direct combustion, microemulsion and

sol-gel methods. Each technique may have some chemical and physical advantages as well as the disadvantages. (Bumajdad et al., 2004; He et al., 2000; Hirans and Kato, 1999; Pillai and Shah, 1997 and Zhang, 2001) Microemulsion method is one of the promising process that employs the homogeneous precipitation of cerium salts confined in the micro-sized droplets to control the size of the reaction products before the calcinations to oxide compounds.

¹Nuclear Science Expert, Research and Development Division, Thailand Institute of Nuclear Technology

²Senior Nuclear Scientist, Research and Development Division, Thailand Institute of Nuclear Technology

*Corresponding author, E-mail: pipat@oep.go.th, pipat55@gmail.com

It has been found that monazite ore in the South of Thailand contains about 20% of cerium (Ce) in the form of phosphate compounds. This ore also contains some other rare earth elements such as lanthanum (La), neodymium (Nd), samarium (Sm), praseodymium (Pr), yttrium (Y) and gadolinium (Gd) including uranium (U) and thorium (Th) which are nuclear materials. Rare Earth Research and Development Center (RRDC), Thailand Institute of Nuclear Technology (TINT) has carried out the activities to break-down the monazite ore using alkali process to separate and purify each composed element. As shown in Figure 1, monazite ore is ground to 325-mesh size and digested with 50%

NaOH at 140°C for 3 hr. The caustic reaction converts phosphate compounds to hydroxides which later are dissolved by HCl and selectively precipitated at pH 4.5 to separate U and Th from the mixed rare earth elements. This alkaline process also yields Na_3PO_4 as by-product. Solvent extraction process with tributyl phosphate (TBP) extractant has been used to separate each individual element. As the rare earth elements in lanthanide series possess very similar chemical properties, this makes it difficult to separate them by solvent extraction process alone, ion exchange process with cation resins then has been employed for the purification of each rare earth element.

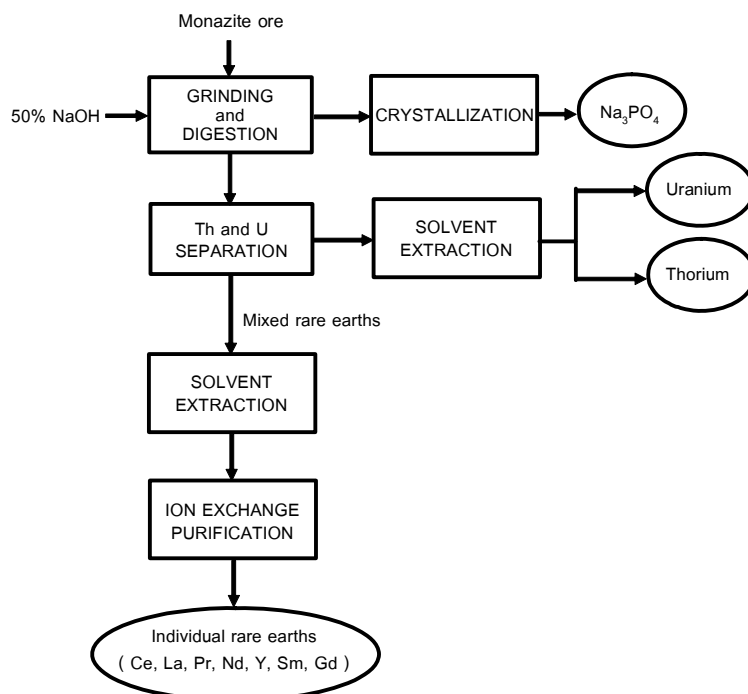


Figure 1. Diagram of monazite ore break-down by alkali process.

2. Experimental

Cerium precursors used in the preparation of nano-sized powder by microemulsion method are $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. These precursors have been prepared from cerium in EDTA solution from the ion exchange columns of the monazite ore break-down process at RRDC. The purity of cerium is more than 99.2% and the rest are traces of mixed rare earth elements from the ore. Cerium was precipitated from the solution using dilute NaOH and washed once with deionized water. Cerium hydroxide then was dissolved with HNO_3 or HCl and the solution is evaporated for the crystallization of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ accordingly. These cerium crystals were recrystallized twice to remove the remained Na ions which were present during the precipitation with NaOH solution.

Microemulsions of cerium precursor and NH_4OH were prepared separately before they were

mixed together as shown in Figure 2. In the preparation of microemulsion, 4 ml of butanol and 5 g of cetyl trimethylammonium bromide (CTAB) surfactant were added into 75 ml of n-hexane under vigorous agitation. Cerium precursor as 0.1 M solution of 10 ml was added and 2 ml of 10% NH_4OH was added in the other microemulsion for the precipitation of cerium hydroxide. Cerium hydroxide was formed during the mixing of these two microemulsions and the mixture was dried at 250°C for 2 hr. The dry solid hydroxide was calcined at 600°C for 1 hr to form nano-sized CeO_2 powder. The powder was characterized by TEM, XRD and BET. The study was carried out using cerium precursors from RRDC as well as lab grade cerium precursors. The particle sizes of the CeO_2 powder were determined from the TEM micrographs using ImageJ (National Institute of Health, 2007) as image analyzer program.

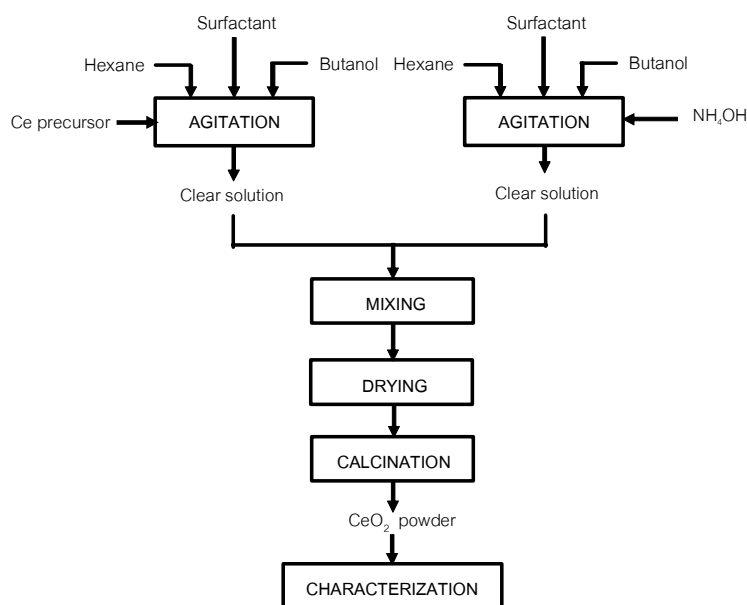


Figure 2. Flow diagram for the preparation of CeO_2 from cerium precursor ($\text{Ce}(\text{NO}_3)_3$ or CeCl_3) using microemulsion method.

3. Results and discussion

The resulted CeO_2 powders from each precursor appear similarly as a pale yellow-white powder. The TEM micrographs of the CeO_2 powder are shown in Figure 3. The average particle size of CeO_2 powder prepared from the following cerium precursors: $\text{Ce}(\text{NO}_3)_3$ [lab grade], $\text{Ce}(\text{NO}_3)_3$ [RRDC], CeCl_3 [lab grade] and CeCl_3 [RRDC] are 10.5, 11.6, 10.0 and 9.2 nm, respectively. The XRD pattern of CeO_2 powder prepared from CeCl_3 [lab grade] is shown in Figure 4 which matches well with the referent pattern of CeO_2 . These are also the same with the XRD patterns of CeO_2 powder prepared from the other precursors. The surface areas of the oxide powders determined by BET are in the range of 44 – 57 m^2/g .

The CeO_2 nanoparticles prepared from RRDC cerium precursor and lab grade cerium precursor are closely alike. However, it is noted that $\text{Ce}(\text{NO}_3)_3$

precursor produces slightly smaller particle size of oxide powder compared to CeCl_3 precursor. The preparation of microemulsion using different surfactants such as polyoxyethylene-4-lauryl ether and polyoxyethylene-10-oleyl ether were also studied and they produced similar results.

The preparation of nanoparticles by microemulsion method in this study is conceptually based on the reaction in water-in-oil microemulsions where reactant species, cerium precursor and NH_4OH are totally confined within the dispersed water droplets of nano to micro sizes. Upon mixing, there will be collision and coalescence of the droplets and the reactants come into contact with each other to form hydroxide precipitate. This precipitate is confined in the interior of the microemulsion droplets which is the main principle applied in producing nanoparticles with microemulsion method.

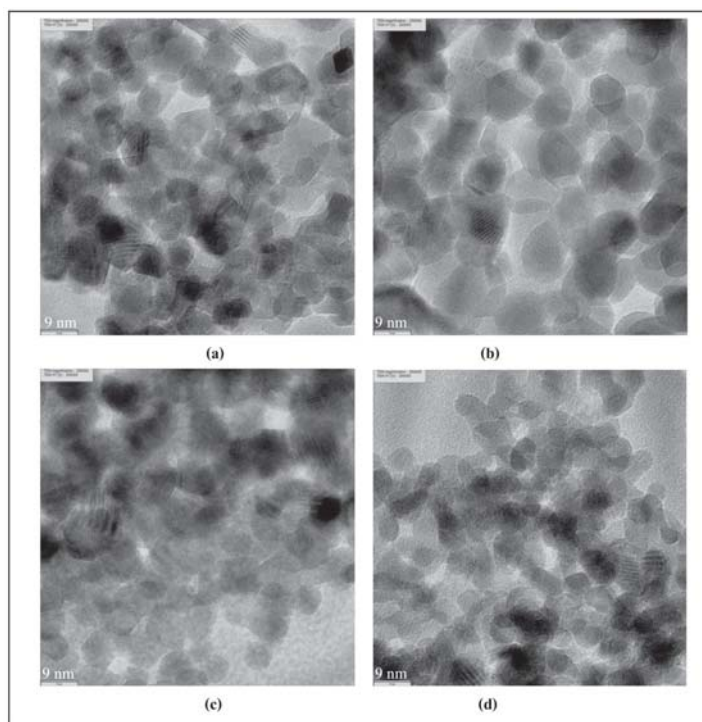


Figure 3. TEM micrographs of CeO_2 nanoparticles prepared from different precursors: (a) $\text{Ce}(\text{NO}_3)_3$ [lab grade], (b) $\text{Ce}(\text{NO}_3)_3$ [RRDC] (c) CeCl_3 [lab grade] and (d) CeCl_3 [RRDC].

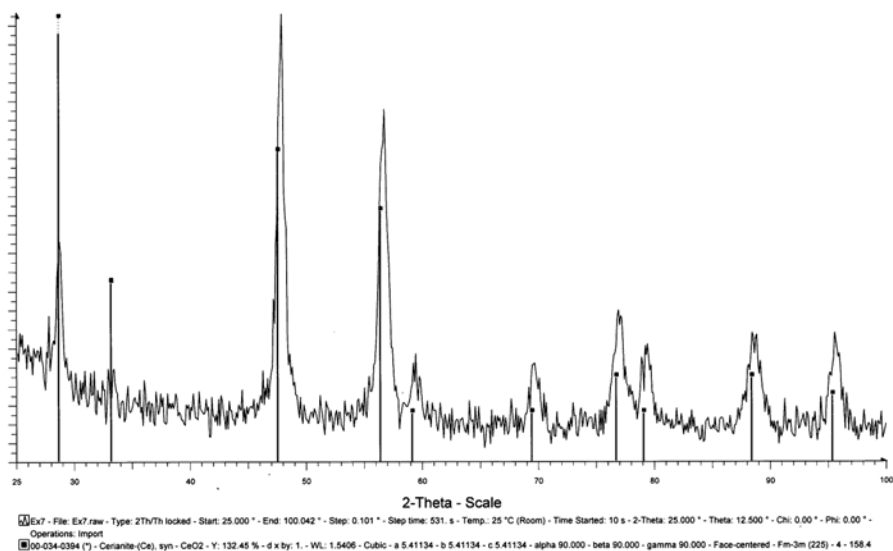


Figure 4. XRD pattern of CeO_2 nanoparticles prepared from lab grade CeCl_3 precursor matches the referent XRD pattern of CeO_2 .

4. Conclusion

Cerium in the monazite ore can be separated and purified by chemical process and converted to precursors for the preparation of cerium oxide powder. Cerium oxide nanoparticles prepared by water-in-oil microemulsions of either cerium chloride or cerium nitrate precursors and ammonium hydroxide using CTAB surfactant have the average size about 10 nm. The oxide powders obtained from both cerium precursors are very similar in both shape and size. However, cerium nitrate precursor produces slightly smaller particle size of oxide powder than the oxide powder from chloride nitrate precursor.

References

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