

Purification of cerium, neodymium and gadolinium for low background experiments

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Abstract. Cerium, neodymium and gadolinium contain double beta active isotopes. The most interesting are ¹⁵⁰Nd and ¹⁶⁰Gd (promising for 0ν2β search), ¹³⁶Ce (2β⁺ candidate with one of the highest $Q_{2\beta}$). The main problem of compounds containing lanthanide elements is their high radioactive contamination by uranium, radium, actinium and thorium. The new generation 2β experiments require development of methods for a deep purification of lanthanides from the radioactive elements. A combination of physical and chemical methods was applied to purify cerium, neodymium and gadolinium. Liquid-liquid extraction technique was used to remove traces of Th and U from neodymium, gadolinium and for purification of cerium from Th, U, Ra and K. Co-precipitation and recrystallization methods were utilized for further reduction of the impurities. The radioactive contamination of the samples before and after the purification was tested by using ultra-low-background HPGe gamma spectrometry. As a result of the purification procedure the radioactive contamination of gadolinium oxide (a similar purification efficiency was reached also with cerium and neodymium oxides) was decreased from 0.12 Bq/kg to 0.007 Bq/kg in ²²⁸Th, from 0.04 Bq/kg to <0.006 Bq/kg in ²²⁶Ra, and from 0.9 Bq/kg to 0.04 Bq/kg in ⁴⁰K. The purification methods are much less efficient for chemically very similar radioactive elements like actinium, lanthanum and lutetium.

1 Introduction

The study of the double beta (2β) decay gives important information about the properties of neutrino and of weak interactions [1, 2]. There are many potentially 2β active isotopes among the lanthanide elements [3] (cerium, neodymium, samarium, gadolinium, dysprosium, erbium and ytterbium, see Table 1), the most interesting are ¹⁵⁰Nd and ¹⁶⁰Gd (promising to search for neutrinoless 2β decay), ¹³⁶Ce (one of the highest $Q_{2\beta}$ among 2β⁺ candidates), ¹⁵⁶Dy and ¹⁶⁴Er (possible resonant 0ν2ε process).

The isotope ¹⁵⁰Nd is one of the most favourable nuclides to search for 0ν2β decay thanks to a high released energy ($Q_{2\beta} = 3371$ keV), a considerably high isotopic abundance (5.6%) and promising theoretical estimations (see [2] and references therein). The isotope ¹³⁶Ce is one of the most interesting 2β⁺ active nuclei with

the theoretical predictions for the two neutrino 2β decay half-lives on the level of $10^{18} - 10^{22}$ yr [3, 4, 5, 6]. The isotope ¹⁶⁰Gd is interesting object for double beta decay experiments thanks to a high isotopic abundance (21.9%) and promising theoretical predictions for the 0ν2β⁻ channels [7, 8], while ¹⁵²Gd is considered as a perspective nuclide to search for resonant neutrinoless double electron capture with a predicted half-life on the level of $8 \times 10^{23} - 8 \times 10^{26}$ yr for an effective neutrino mass of 1 eV [9, 10].

Both scintillation [7] and HPGe [11, 12, 13] detectors can be used to search for 2β decays of lanthanides. The main problem of compounds containing lanthanide elements is their high radioactive contamination by uranium, radium, actinium and thorium, as well as by radioactive lanthanides containing radioactive isotopes (¹⁴⁷Sm, ¹³⁸La, ¹⁵²Gd, ¹⁷⁶Lu). Even high purity grade (99.99% – 99.995%) lanthanide compounds contain

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Table 1. Double beta active isotopes among the lanthanide elements.

Nuclide	Energy release, $Q_{2\beta}$, keV [14]	Isotopic abundance, % [15]	Decay channel [3]
$^{136}\text{Ce} \rightarrow ^{136}\text{Ba}$	2378.53(27) [16]	0.185(2)	$2\varepsilon, \varepsilon\beta^+, 2\beta^+$
$^{138}\text{Ce} \rightarrow ^{138}\text{Ba}$	693(10)	0.251(2)	2ε
$^{142}\text{Ce} \rightarrow ^{142}\text{Nd}$	1417.2(21)	11.114(51)	$2\beta^-$
$^{144}\text{Sm} \rightarrow ^{144}\text{Nd}$	1782.4(8)	3.07(7)	$2\varepsilon, \varepsilon\beta^+$
$^{154}\text{Sm} \rightarrow ^{154}\text{Gd}$	1250.8(9)	22.75(29)	$2\beta^-$
$^{146}\text{Nd} \rightarrow ^{146}\text{Sm}$	70.5(28)	17.189(32)	$2\beta^-$
$^{148}\text{Nd} \rightarrow ^{148}\text{Sm}$	1928.3(19)	5.756(21)	$2\beta^-$
$^{150}\text{Nd} \rightarrow ^{150}\text{Sm}$	3371.38(20) [17]	5.638(28)	$2\beta^-$
$^{152}\text{Gd} \rightarrow ^{152}\text{Sm}$	55.68(18)	0.20(1)	2ε
$^{160}\text{Gd} \rightarrow ^{160}\text{Dy}$	1730.5(13)	21.86(19)	$2\beta^-$
$^{156}\text{Dy} \rightarrow ^{156}\text{Gd}$	2005.95(10)	0.056(3)	$2\varepsilon, \varepsilon\beta^+$
$^{158}\text{Dy} \rightarrow ^{158}\text{Gd}$	282.7(25)	0.095(3)	2ε
$^{162}\text{Er} \rightarrow ^{162}\text{Dy}$	1846.96(30)	0.139(5)	$2\varepsilon, \varepsilon\beta^+$
$^{164}\text{Er} \rightarrow ^{164}\text{Dy}$	25.07(11)	1.601(3)	2ε
$^{170}\text{Er} \rightarrow ^{170}\text{Yb}$	655.6(17)	14.910(36)	$2\beta^-$
$^{168}\text{Yb} \rightarrow ^{168}\text{Er}$	1409.27(25)	0.123(3)	$2\varepsilon, \varepsilon\beta^+$
$^{176}\text{Yb} \rightarrow ^{176}\text{Hf}$	1088.7(18)	12.996(83)	$2\beta^-$

uranium, radium and thorium typically on the level of $\sim (0.1 - 1)$ Bq/kg. The new generation of 2β experiments to search for double beta decay of lanthanides requires development of methods for a deep purification from traces of uranium, thorium, radium and actinium.

Here we present results of R&D to purify cerium, gadolinium and neodymium oxides for 2β experiments.

2 Purification method

In this study we have used CeO_2 and Gd_2O_3 powders provided by Stanford Materials Corporation (USA), while the high purity neodymium oxide (Nd_2O_3) was produced by Soviet Union industry in the seventies.

The samples were purified with a combination of physical and chemical methods in several steps. At first the rare earths' oxides were dissolved in high purity mineral acids. Then obtained acidic aqueous solutions were used for the main purification procedures: liquid-liquid extraction and re-extraction. The liquid-liquid extraction (solvent extraction) is a method by which a compound is pulled from a solvent A to a solvent B, while the solvents A and B are not miscible (usually water and an organic solvent). Two immiscible liquids are mixed together, then the solutes with higher polarity dissolve in the solvent with a higher polarity, while the solutes with lower polarity solve in a solvent with lower polarity. This technique is widely utilised in chemical laboratories by using separatory funnels (see Fig. 1).

The solutes of lanthanide oxides were dissolved in water (phase A), while phosphor-organic complexing compound trioctylphosphine oxide (TOPO) in toluene was used as solvent B. At these conditions elements with a higher oxidation move to the organic phase with a higher distribution level rather than elements with a lower oxidation. Such a procedure allows to separate elements with different oxidation states [18]. Hydroxides of the purified elements were precipitated from aqueous solutions by neutralization using gaseous ammonia.

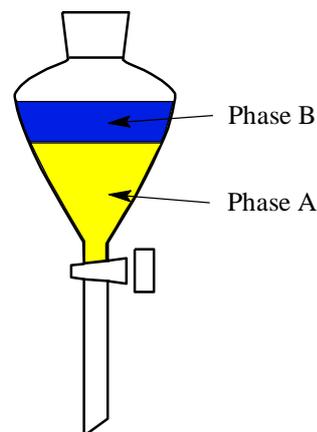


Figure 1. Separatory funnel with two immiscible liquids. Phase A – aqueous solution; Phase B – organic solution.

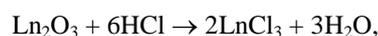
Finally cerium, neodymium and gadolinium oxides have been obtained by decomposition of the hydroxides at high temperature.

3 Purification of Gd_2O_3 and Nd_2O_3

3.1 Dissolving of Gd_2O_3 and Nd_2O_3

Nd_2O_3 and Gd_2O_3 oxides were dissolved in hydrochloric acid solution. Amounts of concentrated hydrochloric acid (of the super pure quality grade) and demineralized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) were calculated to obtain a solution with concentration of LnCl_3 20% and $\text{pH} \leq 0.1$.

Weighted powders of gadolinium and neodymium compounds were put into Teflon beaker. The hydrochloric acid solution was added very slowly to avoid boiling point due to exothermic reaction:



where Ln is Nd or Gd.

3.2 Extraction

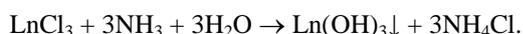
In case of gadolinium and neodymium extractions, the solvent A was 20% acidic solution of gadolinium or neodymium chloride. We have used TOPO with concentration 0.1 mol/L as the solvent B. Equal volumes of two phases were shaken in Teflon separatory funnel for one minute. In 0.5 hour the solutions were completely stratified. Extraction of thorium and uranium have been occurred by the reaction:



Then purified NdCl₃ and GdCl₃ solutions were separated and rinsed with toluene to reduce TOPO content in aqueous phase.

3.3 Precipitation

Further purification and separation were carried out by precipitation of the hydroxides by increasing of the pH level up to 7 [19]. We have used gaseous ammonia to neutralize the acidic media:

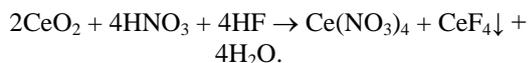


Amorphous hydroxides of gadolinium and neodymium were obtained.

4 Purification of CeO₂

4.1 Dissolving

CeO₂ powder with mass of 500 g was taken for purification. A mixture of concentrated nitric and hydrofluoric acids was used to dissolve CeO₂:

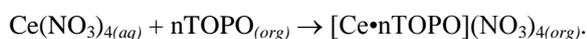


The reaction occurred only after heating up to 80–90 °C over at least 24 hours for complete dissolution of cerium oxide.

Some part of the cerium sample has been lost due to formation of insoluble cerium fluoride. Initial amounts of CeO₂ and HNO₃ were calculated in order to obtain a solution with a 10% concentration of Ce(NO₃)₄ and 5 mol/L of nitric acid.

4.2 Extraction

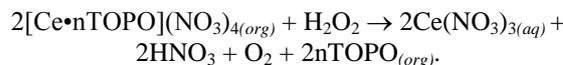
In case of cerium oxide, the solvent A was a solution of Ce(NO₃)₄ with a high content of nitric acid while the solvent B was 33% solution of TOPO in toluene. Stirring of the solutions leads to extraction of cerium to organic liquid together with thorium and uranium traces:



However the efficiency of cerium extraction was very low due to the lack of TOPO molar concentration in the solvent B (~ 1.03 mol/L).

4.3 Re-extraction

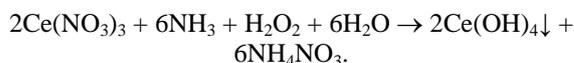
Re-extraction of cerium from the organic phase was performed into low acidic water solution with simultaneous decreasing of the Ce oxidation level. Hydrogen peroxide was utilized as a reducing agent:



Since solubility for Ce³⁺ in organic phase is less than for Ce⁴⁺, cerium concentration in aqueous phase was increased. However, a substantial part of cerium left in organic phase.

4.4 Precipitation

The same technique as described in section 3.3 was applied for cerium sedimentation. Gaseous ammonia was passed through the Ce(NO₃)₃ aqueous solution with an aim to neutralize the acidity of the solution. At the same time the oxidation level of cerium is increased due to the excess of hydrogen peroxide after the re-extraction procedure, which leads to amorphous hydroxide production:



4.5 Oxides recovering

Stoichiometric oxides CeO₂, Nd₂O₃ and Gd₂O₃ were reduced from the cerium, neodymium and gadolinium hydroxides at high temperature. The amorphous hydroxides sediments were rinsed several times with ultrapure water and placed into quartz beakers for drying and annealing. The beakers were put into muffle, heat up to 900 °C and kept for 4 hours.

The outputs of the purified oxides were ~ 90% for Nd₂O₃, Gd₂O₃ and ~ 20% for CeO₂.

5 Measurements of radioactive contamination

The radioactive contamination of the samples before and after the purification was tested by using ultra-low-background HPGe gamma spectrometry deep underground (3600 m w.e.) at the STELLA facility in the Gran Sasso National Laboratories of the INFN (Italy). The detectors, GeBer (244 cm³) in case of CeO₂, Gd₂O₃ and GePaolo (518 cm³) for Nd₂O₃, were located inside a passive shield made of low radioactivity copper (10 cm), lead (20 cm) and borated polyethylene (10 cm). The set-ups were flushed by highly pure nitrogen to remove radon. The energy resolution of the spectrometers are about 2 keV for 1333 keV γ quanta of ⁶⁰Co. The samples were placed directly on the end cap of the detectors. Detection efficiency has been calculated with the help of the GEANT4 code [20].

Radioactive contamination of the samples before and after purification is presented in Table 2.

Table 2. Radioactive contamination of lanthanide samples before and after purification (mBq/kg). Upper limits are given with 95% C.L., while uncertainties are presented with 68% C.L. The masses of the samples and the time of measurements are also given.

Nuclide	CeO ₂ (before) 501 g, 893 h	CeO ₂ (after) 98 g, 397 h	Gd ₂ O ₃ (before) 491 g, 942 h	Gd ₂ O ₃ (after) 495 g, 995 h	Nd ₂ O ₃ (before) 377 g, 631 h	Nd ₂ O ₃ (after) 374 g, 665 h
²²⁸ Ra	850(50)	72(18)	106(10)	<12	<2.1	<2.6
²²⁸ Th	620(30)	620(40)	79(6)	<4	<1.3	<1.0
²³⁴ Th	<590	<790	<1100	<670	<28	<46
^{234m} Pa	<870	<4600	<1000	<590	<46	<27
²²⁶ Ra	11(3)	<9.3	<7.4	<8.3	<2.8	<1.8
²³⁵ U	38(10)	<24	96(12)	<8.3	<1.7	<1.3
²³¹ Pa	–	–	1390(60)	1920(80)	–	–
⁴⁰ K	77(28)	<240	<80	<35	<29	<15
⁶⁰ Co	<1.2	<4.4	<1.1	<1	<0.21	<0.40
¹³⁷ Cs	<3.0	<8.5	<6	<3.8	<0.80	<0.53
¹³⁸ La	–	–	12(2)	26(3)	–	–
¹⁷⁶ Lu	–	–	32(3)	30(3)	1.1(4)	<1.3

6 Conclusions

The liquid-liquid extraction technique was used to purify CeO₂, Gd₂O₃ and Nd₂O₃. The radioactive contamination of the samples before and after the purification was tested by using ultra-low-background HPGe gamma spectrometry at the Gran Sasso National Laboratories of the INFN (Italy). Gadolinium oxide has been purified most effectively: radioactive contamination was decreased to <0.004 Bq/kg in ²²⁸Th, to <0.008 Bq/kg in ²²⁶Ra, and to <0.04 Bq/kg in ⁴⁰K. The purification methods are much less efficient for chemically very similar radioactive elements like actinium, lanthanum and lutetium. Further R&D of purification methods and preparation of experiments to search for 2β decay of several lanthanide isotopes is in progress.

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