Determination of contaminants in rare earth materials by prompt gamma activation analysis (PGAA)

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Prompt gamma activation analysis (PGAA) has been used to detect and quantify impurities in the analyses of rare earth (RE) oxides. The analytical results are discussed with respect to the importance of having a thorough identification and understanding of contaminant elements in these compounds regarding the function of the materials in their various applications. Also, the importance of using PGAA to analyze materials in support of other physico-chemical studies of the materials is discussed, including the study of extremely low concentrations of ions – such as the rare earth ions themselves – in bulk material matrices.

Introduction

The rare earth (RE) elements consist of those elements located in the $4f$ block of elements in the Periodic Table. Both the metals and their compounds are useful for an extremely wide variety of applications in chemistry and materials science, including applications that are dependent on both the metals' chemical and physical properties and their ability to form compounds and complexes. Their uses include hydrogen storage ("hydrogen sponges"), alloys, electronics, glass, ceramic pigments, and special alloys. The rare earth compounds, with the elements exhibiting several oxidation states, find uses as catalysts, phosphors, laser materials, and other materials that make use of their magnetic properties. Europium, for example, is used in conjunction with yttrium as color television phosphors[1,2] and as a dopant activator in nanoparticles for potential use in biochip-based analyses.[3] Europium chelates, cryptates, and other complexes with organic molecules have had their fluorescence properties exploited for use in distance measurements in biomolecules,[4] protein array applications,[5] fluoro-immunoassays,[6] and protein–protein interaction studies.[7] Materials science applications of europium also include silica-based matrix materials that make use of the fluorescent properties of europium(III) ions.[8] Other applications of rare earth metal ions include the use of samarium for crystal lattice structural studies,[9] yttrium and other rare earth ions for the syntheses of ferrite materials for use in recording media and microwave devices,[10,11] and divalent samarium in organic and polymer syntheses.[12] The use of the luminescent properties of rare earth metal ions is also incorporated into other devices such as chemical sensors, waveguides, and lasers.[13,14]

Neutron induced prompt gamma activation analysis (PGAA) is a non-destructive, self-calibrating, radioanalytical method capable of simultaneously identifying nearly the entire Periodic Table. It exploits the prompt capture gamma-rays themselves, while neutron activation analysis (NAA) utilizes the delayed gamma-rays from the radioactive daughter nucleus and is thus able to detect every element in the Periodic Table from hydrogen through uranium. The method has been applied to materials science, chemistry, geology, mining, archaeology, environment, food analysis, medicine and other areas. Development of high flux neutron generators and a new analytical PGAA database make it possible to apply PGAA/NAA techniques without requiring a nuclear reactor. The nuclear reactions to form the gamma-ray lines are independent of the physical form of the sample being analyzed, thus allowing the elemental composition of solids, liquids, and gases to be obtained. Also, the technique allows for the non-destructive analyses of samples with no prior chemical or other type of physical or experimental preparation.

The present paper describes the application of PGAA to the analysis and determination of contaminants in rare earth oxides of europium, erbium, gadolinium and other rare earth metal ion-based materials for which total characterization data, including that of trace contaminants, are often required. The technique also is discussed with respect to its use in monitoring trace amounts of elements used in the syntheses and processing of other materials that use such rare earths as precursor materials or as the desired final product.

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Experimental

Materials

The rare earth oxide samples were analyzed using prompt-gamma activation analysis as previously described.[15–17] Powders of oxide samples from praseodymium, neodymium, samarium, europium gadolinium, terbium, dysprosium, holmium, erbium, thulium and lutetium were represented and obtained commercially as being 99.999% purity.

PGAA method

The neutron-induced prompt gamma activation analyses (PGAA) were performed at the Institute for Isotopes and Surface Chemistry, Budapest, Hungary, which has been described previously.[15–17] The Budapest Reactor is a water-cooled, water-moderated research reactor with a thermal power of 10 MW. A beam of low-energy neutrons is transported for approximately 35 meters from the reactor core by a curved neutron guide fabricated from a glass coat with a nickel reflector. The prompt-gamma experimental apparatus is located at the end of the guide where the energy of the neutrons is less than that of thermal neutrons due to the higher energy neutrons not being reflected. The thermal-equivalent effective flux was approximately $2.5 \cdot 10^6$ n·cm^{-2}·s^{-1} at the target position.

The samples were placed directly in the beam that had been collimated to an area of 2×2 cm^2. The determined chemical composition of the sample was an average value for the entire irradiated volume of the sample due to the almost total transparency of the sample to neutrons. The prompt gamma rays were detected by a detector system[15] whose main component was a Canberra high-purity germanium (HPGe) detector which was surrounded by a bismuth germanate (BGO) scintillator annulus used to reject Compton-scattered photons. The detector assembly could be moved to variable lengths from the target, with the main detector being moved to within as close as 12 cm to the target. Complete details of the experimental arrangement and detector system have been published elsewhere.[16]

Spectra for the samples were collected using a 16,384-channel multichannel analyzer card from Canberra, Model No. S100 MCA. The energy and efficiency calibrations for the system were made using known γ-lines emitted by radioactive sources and (n,γ) reactions. The collected spectra of the rare earth oxides were analyzed by "Hypermet PC," a γ-spectrum analysis program developed at our laboratory at the Institute for Isotope and Surface Chemistry in Budapest.[17]

Element identification

The elemental identification involved with these samples is based on the nuclear database here at the Institute for Isotope and Surface Chemistry, Budapest, Hungary. The elements are identified according to the energy values of their most intense prompt-gamma peaks. The reliability of the element identification is controlled through different statistical parameters which are derived from the deviations of measured energy and intensity values from literature values.[18] The intensity ratios between the different gamma-peaks must also be considered, along with the possible background lines. The background gamma-rays mostly originate from the (n,γ) reactions in the surrounding material. The most important sources are from oxygen and nitrogen in the air, iron and aluminum in the equipment's material, and fluorine from the Teflon packaging material surrounding the samples.

Determination of chemical composition

The detected gamma-ray intensity, represented by the peak area (A), is directly proportional to the mass of a given chemical element (m), the neutron flux and the measuring time, t:

$$A = \frac{m}{M} N_A \; \sigma_\gamma \; \Phi \; \varepsilon(E) \, t \qquad (1)$$

where M is the atomic weight, N_A is the Avogadro number, σ_γ is the partial gamma-ray production cross section of the given element at the given energy, Φ is the neutron flux, $\varepsilon(E)$ is the counting efficiency at a given gamma-energy and t is the live measuring time.

The mass ratio for an element x can be determined according to:

$$\frac{m_x}{m_R} = \frac{A_x}{A_R} \frac{\sigma_{\gamma,R}}{\sigma_{\gamma,x}} \frac{\varepsilon(E_{\gamma,R})}{\varepsilon(E_{\gamma,x})} \frac{M_R}{M_x} \qquad (2)$$

where R is an arbitrary reference element contained in the sample. This ratio is independent of the neutron flux, it depends only on nuclear constants and the detector efficiency. The latter are known with good accuracy.[19] The partial gamma-ray production cross sections were determined by internal standardization measurements. The masses were calculated according to Eqs (1) and (2). The gamma-lines used and the corresponding cross sections are listed in Reference 19. The possible interferences between different gamma-peaks were individually examined, and the peaks affected by spectral interference were neglected. The concentrations were calculated from the mass ratios assuming that all components are detected with the exception of the oxygen, whose quantity was calculated from the stoichiometry.

The total uncertainties (standard deviations) were calculated from the statistical (counting) uncertainties of the peak areas, the uncertainties of the cross sections and the uncertainties of the detector efficiencies. As the last two typically have standard deviations of a few per cent, the total uncertainty is mainly determined by the counting statistics reflected in the analytical sensitivities.

Measurements

Elemental compositions of the samples were analyzed by means of PGAA. Samples of rare earth oxide powders with masses of 10 to 500 mg were sealed in Teflon bags. The thicknesses of the sample were below 1 mm. The samples were irradiated for 15 minutes to 17 hours to obtain several hundred thousands of counts in the spectra. Compton suppressed prompt gamma-ray spectra were measured as usual. The details are listed in Table 1.

Results and discussion

Prompt gamma activation analysis is based on the nuclear phenomenon by which gamma-rays are detected that originate from neutron radiative capture or (n,γ) reactions. The obtaining of the elemental composition of a sample is made possible by comparing the energies and intensities of the gamma-ray spectrum of the sample. Figure 1, for example, shows gamma-lines for europium, gadolinium, samarium, erbium, and praseodymium in a PGAA spectrum of Nd_2O_3. The analytical results for the trace elements contained in the rare earth oxides are given in Table 2. Not surprisingly, the contaminants are exclusively other rare earth ions which are extremely difficult to separate from one another[20,21] during processing. As can be seen in Table 2, the concentration range of impurities can vary widely. In the Gd_2O_3 sample, for example, 3.5 parts per million of praseodymium were detected and over 900 parts per million of terbium can be observed in Dy_2O_3.

Table1. Analysis of rare earth metal oxides by PGAA

Element (Z)	Sample	Measurement time, s	Total counts
Praseodymium (59)	Pr_2O_3	61,320	1,738,909
Neodymium (60)	Nd_2O_3	6894	427,995
Samarium (62)	Sm_2O_3	2796	4,319,462
Europium (63)	Eu_2O_3	5699	38,605,635
Gadolinium (64)	Gd_2O_3	6620	20,530,263
Terbium (65)	Tb_4O_7	18,458	1,078,895
Dysprosium (66)	Dy_2O_3	911	816,152
Holmium (67)	Ho_2O_3	1405	467,221
Erbium (68)	Er_2O_3	1033	2,039,865
Thulium (69)	Tm_2O_3	5375	1,331,440
Lutetium (71)	Lu_2O_3	10,743	1,188,078
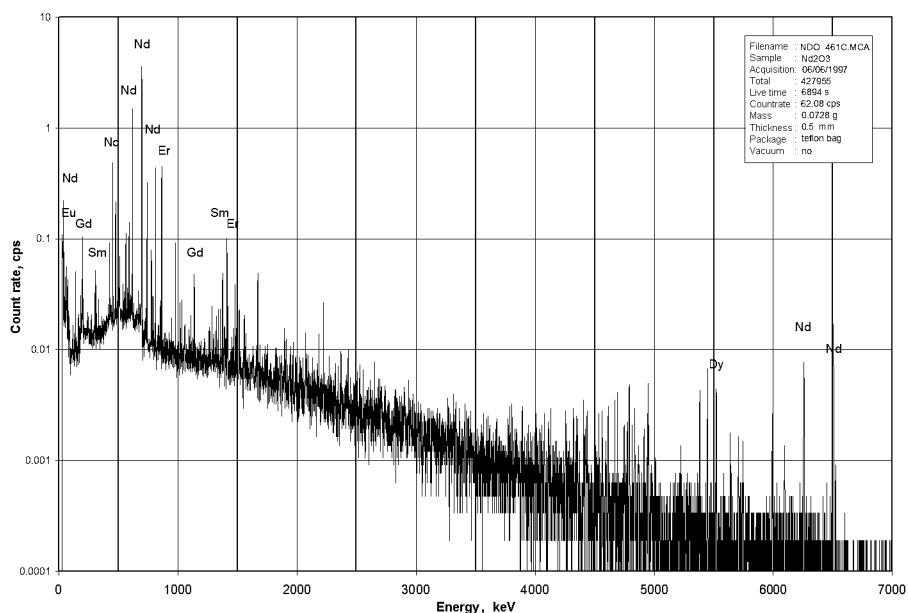
Fig. 1. The PGAA spectrum of Nd_2O_3

Table 2. Analytical results for rare earth oxides by PGAA

Oxide	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Lu
Pr_2O_3	99.5(4)%										
Nd_2O_3		99.5(4)%									
Sm_2O_3	9.6(3)p	17(2)p	99.94%	0.23(2)%		58(2)p			11(3)p	42(8)p	27(3)p
Eu_2O_3	7.0(14)p	120(20)p		99.5%							
Gd_2O_3	3.5(4)p	8.0(10)p	58(5)p	0.23(2)%	100%	120(4)p			48(7)p	29(9)p	55(5)p
Tb_4O_7						99.6(3)%					
Dy_2O_3		0.050(6)%				940(94)p	100%				
Ho_2O_3								100%			
Er_2O_3	0.32(6)%	0.46(5)%				0.29(3)%			99.994%		
Tm_2O_3										99.993%	
Lu_2O_3	0.14(2)%										99.99%

Concentrations of the rare earth elements are expressed in both percentage (%) and parts per million (p).

Missing are boron and cadmium, two elements which exhibit very high cross sections with respect to PGAA and which results in very high sensitivity. These elements are normally trace contaminants in rare earth materials. This is possibly due to the processing and separation scheme used to extract the rare earths from their ore and their subsequent further purification. Another possibility is that the original ore containing the rare earth elements did not contain these elements which are normally associated with those ore bodies.

A thorough analytical knowledge of rare earth ions can be very important from a number of standpoints, being the rare earth either the material matrix itself, or a contaminant in another material host. First, many times it is important to have a precise and very accurate analysis of a material with respect to the concept of quality control. This is true in the materials manufacturing sector, where the bulk electronic materials, for example, must have extremely low levels of impurities due to the impurities' possible effects on the performance characteristics of the material.

It also is beneficial to know the levels of contaminant elements in industrial batches of materials in general, so as to be able to use this knowledge to understand causes and postulate mechanisms in case of material failures. This is especially true of materials that have applications in electronics, such as conductors, semiconductors, and different materials that are components of integrated circuits. In the case of semiconductors, for example, dopant levels of different elements are critical to both the quality and performance of the material. The ratios between the cations and anions in the semiconductor can determine the type of semiconductor.

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