

**Key Words**

lanthanide oxides

lanthanide fluorides

US\_Vis-NIR absorption spectra

4f-4f transitions

diffused-reflectance mode

charge transfer transitions

energy levels

absorption bands

spectroscopic properties

luminescence studies

bioimaging

raman spectroscopy

matrix absorption

crystal-field effects

nephelauxetic effect

**Objective**

1. Measurement of Absorption Spectra: To measure the UV-Vis-NIR absorption spectra of various lanthanide oxides and fluorides in the spectral range from 200 to 2500 nm.
2. Assignment of Energy Levels: To assign the energy levels (in both wavelength and energy scales) corresponding to the intraconfigurational 4f 4f transitions of lanthanide ions.
3. Comparison of Matrices: To compare the absorption characteristics of lanthanide oxides and fluorides, highlighting the differences in absorption band positions and intensities due to crystal-field

## REFERENCE: 20012

effects and matrix types.

4. Identification of Artifacts: To identify and discuss commonly observed additional bands in the spectra, such as those from water absorption, quartz holders, and intrinsic matrix absorptions, to facilitate correct identification of actual 4f 4f transitions.

5. Provision of Data: To provide a comprehensive spectral database in the form of editable datasets for scientists and engineers dealing with lanthanide-based functional materials, aiding in applications such as spectroscopy, optics, sensing, lighting, bioimaging, and forensics.

## Methodology

### 1. Materials and Synthesis:

- Lanthanide oxides ( $\text{La}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Tm}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ) of 99.99% purity were purchased from Stanford Materials (USA), except for  $\text{CeO}_2$ , which was synthesized from  $\text{CeCl}_3$  (99.99%; Sigma Aldrich).
- Lanthanide fluorides ( $\text{LnF}_3$ ) were prepared from the appropriate chlorides ( $\text{LnCl}_3$ ), obtained from the purchased lanthanide oxides. Detailed synthesis protocols and XRD data are provided in the supplementary information

### 2. Characterization:

- The UV-Vis-NIR absorption spectra of solid compounds were measured using a JASCO V-770 spectrophotometer, equipped with a spherical integrator ILN-925 (150 mm in diameter)
- Two detectors were used: a photomultiplier in the UV-Vis range (200 850 nm) and a PbS detector in the NIR range (850 2650 nm).
- Two light sources were used: deuterium (190 340 nm) and halogen lamps (340 2650 nm).
- The resolution in the UV-Vis range was 1 nm, and in the NIR range, it was 4 nm due to the lower sensitivity of the detector.

## REFERENCE: 20012

- X-ray powder diffraction (XRD) patterns were recorded using a Bruker AXS D8 Advance diffractometer in Bragg Brentano geometry, with Cu K 1 radiation ( $\lambda = 1.5406$  Å), in the  $2\theta$  range from 6 to 60°, in 0.05° step scan mode

### 3. Data Analysis:

- The absorption spectra were measured in diffused-reflectance mode using a spherical integrator.
- Energy levels ( $2S+1LJ$ ) of lanthanide ions (III) were assigned to the observed absorption bands.
- The determination of artifacts in the spectra was also focused on, such as absorption bands corresponding to water (absorbed by the samples), quartz (from the sample holder), and intrinsic absorption of matrices

## Key Findings

1. Absorption Spectra Range: The UV-Vis-NIR absorption spectra of lanthanide oxides and fluorides were measured in the range of 200 to 2500 nm.
2. Energy Level Assignments: Energy levels corresponding to intraconfigurational 4f-4f transitions of lanthanide ions were assigned to the observed absorption bands.
3. Comparison of Oxides and Fluorides: The absorption bands of lanthanide oxides are generally red-shifted compared to their corresponding fluorides due to crystal-field effects, which result in higher covalency and shorter bonds in fluorides.
4. Artifacts in Spectra: Commonly observed additional bands in the spectra were identified, including those from water absorption, quartz holders, and intrinsic matrix absorptions, to help distinguish the actual 4f-4f transitions.
5. Database Provision: The recorded spectra were provided as editable datasets in Excel format, facilitating the use of this spectral database by scientists and engineers for various applications.
6. Broad Absorption Bands:  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ , and  $\text{Tb}_4\text{O}_7$  exhibited broad absorption bands

## REFERENCE: 20012

corresponding to allowed charge transfer transitions from oxygen to lanthanide ions due to their stable +4 oxidation states.

7. Narrower Bands In Fluorides: Most absorption bands in lanthanide fluorides are narrower than those in oxides, attributed to the different coordination environments around the lanthanide ions in these matrices.

8. Different Relevant Intensities: The relative intensity ratios of the bands corresponding to the same 4f-4f transitions are different for fluoride and oxide matrices, as observed in compounds like  $\text{EuF}_3$  vs.  $\text{Eu}_2\text{O}_3$  and  $\text{DyF}_3$  vs.  $\text{Dy}_2\text{O}_3$ .

### Relevance to Study

**Spectroscopic Properties:** Provides detailed UV-Vis-NIR absorption spectra of lanthanide compounds, which are essential for understanding the electronic environments of lanthanides in different ligand fields

**Energy Level Assignments:** Offers energy level assignments for 4f-4f transitions in lanthanides, aiding in the prediction of electronic behavior in various ligand environments

**Comparison of Matrices:** Compares the spectroscopic properties of lanthanide oxides and fluorides, highlighting how different ligand fields (e.g., oxide vs. fluoride) influence absorption spectra and electronic transitions, which is crucial for selecting appropriate ligands in nuclear fuel cycle chemistry

**Identification of Artifacts:** Identifies common spectral artifacts (e.g., water and quartz absorption) that can interfere with accurate spectroscopic analysis, ensuring more precise ligand selection and characterization

**Database Provision:** Provides a comprehensive spectral database, facilitating the comparison of experimental data with theoretical predictions, which is useful for the design and selection of ligands

## REFERENCE: 20012

in the nuclear fuel cycle

### Critical Parameters Identified

High Importance

Chemical Stability

Relevance: The document discusses the stability of lanthanide oxides and fluorides in various matrices, which is crucial for understanding how these compounds would behave under different chemical conditions, including their stability in the presence of ligands used in nuclear fuel reprocessing.

Details: The absorption spectra analysis includes identifying stable forms of lanthanides in different oxidation states, which informs their chemical stability.

Radiolysis Resistance

Relevance: While not directly discussed, understanding the electronic structure and absorption spectra of lanthanides provides insights into their susceptibility to radiolysis. Stability under irradiation can be inferred from the stability of electronic transitions.

Details: The article's focus on UV-Vis-NIR absorption helps predict how lanthanide compounds might react to radiation.

Thermodynamics

Relevance: The document provides fundamental data on the energy levels of lanthanide ions, which is critical for thermodynamic calculations related to ligand binding and separation processes.

Details: Energy level assignments and absorption band analysis offer data necessary for understanding the thermodynamics of ligand-metal interactions.

Medium Importance

## REFERENCE: 20012

### Kinetics (forwards and reverse)

Relevance: Although not explicitly covered, the absorption spectra and electronic transitions data can be used to model reaction kinetics in ligand exchange processes.

Details: The information on 4f-4f transitions can help predict the kinetics of ligand binding and release.

### Loading Capacity

Relevance: Indirectly addressed through the discussion of absorption spectra, which can help in understanding the saturation limits of ligands in complexation with lanthanides.

Details: Knowledge of the electronic environment aids in designing ligands with optimal loading capacities.

### Operational Condition Range

Relevance: The study's analysis of lanthanide behavior in different matrices provides insights into the operational ranges of these compounds under various conditions.

Details: The stability and absorption properties in different environments suggest operational flexibility for ligands in separation processes.

### Low Importance

### Solubility

Relevance: The document does not focus on solubility, but understanding the electronic structure can help infer solubility properties in different solvents.

Details: Information on matrix absorption and stability can indirectly inform solubility considerations.

### Dispersion Numbers

Relevance: Not directly addressed, but the data can be used to infer how well lanthanide-ligand complexes might disperse in various solvents.

Details: The absorption spectra provide a basis for further studies on dispersion properties.

## **REFERENCE: 20012**

### Phase Disengagement

Relevance: Not a primary focus of the study, but understanding the electronic transitions and stability can help in designing systems for efficient phase disengagement.

Details: The spectral data might be used to optimize phase separation processes in applied systems.