



1.0



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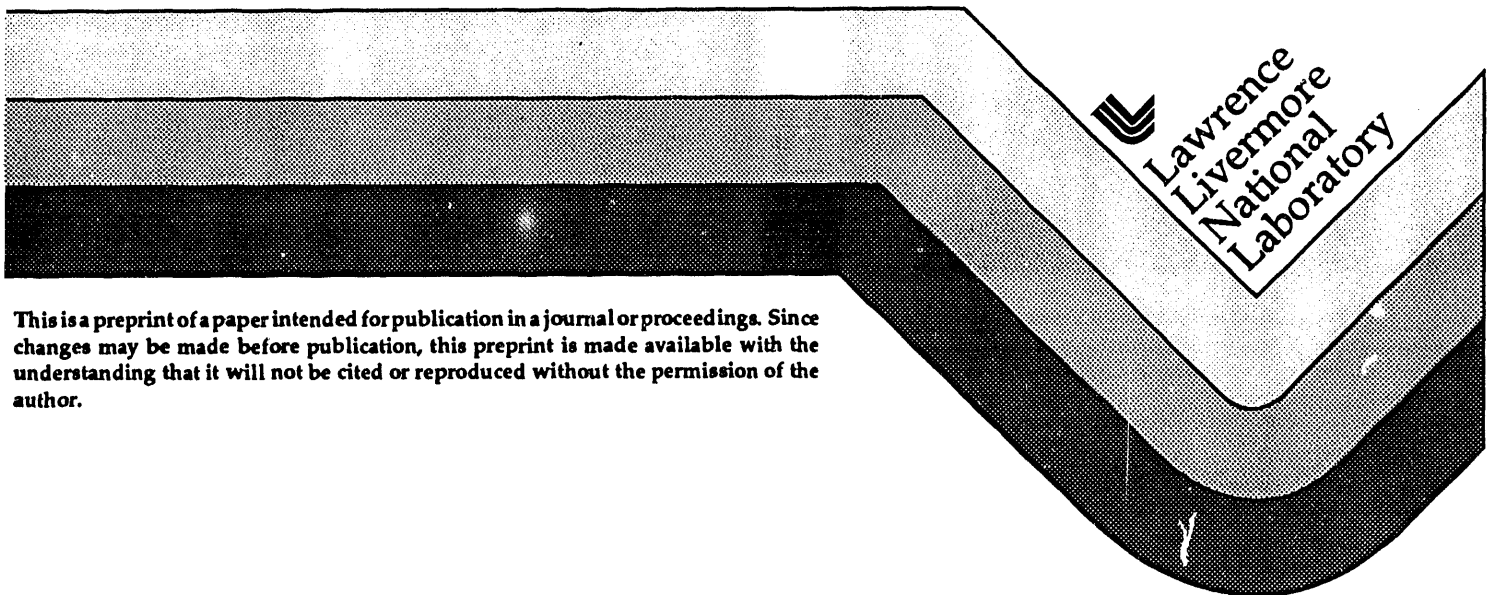
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D.K. Shuh  
L.J. Terminello  
LA. Boatner  
M.M. Abraham

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# X-RAY ABSORPTION SPECTROSCOPY OF THE RARE EARTH ORTHOPHOSPHATES

D.K. SHUH,\* L.J. TERMINELLO,\*\* L.A. BOATNER,\*\*\* AND M.M. ABRAHAM\*\*\*

\*Lawrence Berkeley Laboratory, Berkeley, CA 94720

\*\*Lawrence Livermore National Laboratory, Livermore, CA 94550

\*\*\*Oak Ridge National Laboratory, Oak Ridge, TN 37830

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## ABSTRACT

X-ray Absorption Spectroscopy (XAS) of the Rare Earth (RE) 3d levels yields sharp peaks near the edges as a result of strong, quasi-atomic  $3d^{10}4f^n \rightarrow 3d^9 4f^{n+1}$  transitions and these transitions exhibit a wealth of spectroscopic features. The XAS measurements of single crystal  $REPO_4$  (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er) at the 3d edge were performed in the total yield mode at beam line 8-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). The XAS spectra of the RE ions in the orthophosphate matrix generally resemble the XAS of the corresponding RE metal. This is not unexpected and emphasizes the major contribution of the trivalent state to the electronic transitions at the RE 3d edges. These spectra unequivocally identify the transitions originating from well-characterized RE cores and correlate well with previous theoretical investigations.

## INTRODUCTION

There is a rich history of Rare Earth (RE) 3d X-ray absorption measurements [1,2] that has been augmented recently by improvements in both experimental and theoretical techniques [3,4]. X-ray Absorption Spectroscopy (XAS) of the RE  $M_{4,5}$  edges (3d levels) exhibits sharp peaks near the edges as a result of strong quasi-atomic  $3d^{10}4f^n \rightarrow 3d^9 4f^{n+1}$  transitions which contain a wealth of spectroscopic features. These excitonic transitions appear a few electron volts below the true edges as a consequence of the strong core-hole/4f Coulomb interaction that lowers the  $4f^{n+1}$  final state by  $\sim 10$  eV with respect to the Fermi level ( $E_F$ ). The  $M_{4,5}$  spectra consist of two well-separated lines since the spin-orbit ( $\Delta_{SO}$ ) interaction of the  $3d^9$  hole is larger than the  $3d^9 4f^{n+1}$  exchange interaction. Although the purpose of XAS experiments is to obtain information on the RE ground state, the technique also probes the excited electronic final states [5]. The total  $3d^9 4f^{n+1}$  multiplets of the RE's are quite complex and even with dipole selection rules limiting the allowed transitions from the ground state, give rise to a large number of possible final states. The technique of total electron yield (TY) X-ray absorption spectroscopy has been shown to be a useful technique for investigation of 4f occupancy, 4f hybridization, and valence issues in RE materials since the TY measurements are known to be proportional to the X-ray absorption coefficient [3,4].

The electronic structures of the RE ions in the orthophosphates (La, Ce, Nd,...) $PO_4$  are of particular interest since the materials are geological standards, actinide material substitutes/prototypes, and the valence state is clearly defined as tripositive. Thus, the RE orthophosphates are suitable materials for the characterization of transitions originating from trivalent cores and will provide useful information for studies of mixed valence systems. The RE ions are also ideal from a spectroscopic perspective, since the  $M_{4,5}$  cross sections are large. In addition, several of the lightly-doped RE orthophosphates have recently been shown to be of interest as new scintillator materials [6]. The RE orthophosphates are also the analogs of the corresponding actinide orthophosphates, which have been considered as materials for primary nuclear waste containment and disposal [7].

## EXPERIMENTAL

The single crystal RE orthophosphates were prepared by a flux melt technique and have been extensively characterized by X-ray diffraction and microprobe [7]. The first seven REPO<sub>4</sub>'s have the monoclinic monazite structure, whereas the second half are the cubic zircon structure. With the exception of CePO<sub>4</sub>, the rare earth orthophosphates are insulating materials that have band gaps of ~10 eV. They are extremely stable and unreactive, requiring no special handling or preparations. The dimensions of the crystals employed in this investigation were approximately 2x3 mm.

The X-ray absorption measurements of the RE orthophosphates at the M<sub>4,5</sub> edges were performed in the TY mode on the LLNL/UC PRT beam line 8-2 Spherical Grating Monochromator (SGM) at the Stanford Synchrotron Radiation Laboratory (SSRL). The performance attributes of the beam line and the 55 m SGM have been described previously [8,9]. The spectra were measured with the monochromatic X-ray beam (700-1300 eV) incident at ~45° to the surface normal, monitoring the photon flux with a Au grid, and by recording the total integrated electron yield from a Channeltron electron multiplier. The SGM was calibrated from the higher order cut-offs from resident Fe, Cu, and Mg filters. The backsides of the samples were attached to a simple manipulator with conductive epoxy, baked to 150°C, and spectra recorded in an ion-pumped six-way cross that had a base pressure of better than 2x10<sup>-9</sup> Torr.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the XAS spectra of the M<sub>4,5</sub> edges of the RE orthophosphates. The Ce 3d of CePO<sub>4</sub> shown in Fig. 1 was collected with second order light and is representative of the total electron yield spectra of the REPO<sub>4</sub>'s. The spin-orbit split Ce 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks are the predominant features of the spectrum, whereas the exchange interaction provides the observed fine structure on each. The Ce spectra recorded utilizing first order light (not shown) did not resolve all of the multiplet the fine structure on the spin-orbit peaks. The resolution is estimated at about ~0.5 eV for the spectra taken with second order light, while spectra taken with the first order light are significantly degraded. The La M<sub>4,5</sub> lines are the narrowest core-hole states known at such high energies and the 1.5 eV FWHM obtained in this study is similar to those previously measured [3,4]. However, the intensity distribution between the spin-orbit pairs in the second order spectra are slightly skewed, since the photon flux monitor primarily accounts for the distribution of first order light. The Sm spectrum of Fig. 1 was collected in first order to avoid interferences with the O 1s edge of the SmPO<sub>4</sub>, as well as O 1s perturbations in the photon reference channel. The Gd and Dy spectra of Fig. 2 were recorded in first order since these sample were run independently when the amount of higher order light was significantly reduced. Comparison of these two spectra taken with first order light to previous experimental and theoretical calculations shows that none of the attendant fine structure of either spin-orbit peak is discernable. Thus, high-resolution measurements of RE materials at the M<sub>4,5</sub> edges on beam line 8-2 necessitates the use of second order light.

There has been a previous theoretical investigation of the full atomic multiplet in the intermediate coupling regime that included all of the states of the configuration 4f<sup>n</sup> for the ground state, 3d<sup>9</sup>4f<sup>n+1</sup> for the excited state, and including all of the ionization states known in the solid state for the rare earth ions [4]. This study utilized calculations from Cowan's program [10] with certain parameters modified and scaled by Thole et. al [4]. The experimentally determined absorption lines of the RE orthophosphates can, in all cases, be adequately described by comparison to these Hartree-Fock calculations of the initial and final states in the intermediate coupling regime. The calculations also suggest that there are some saturation effects in the data that weaken main peak intensity in relation to the smaller multiplet lines.

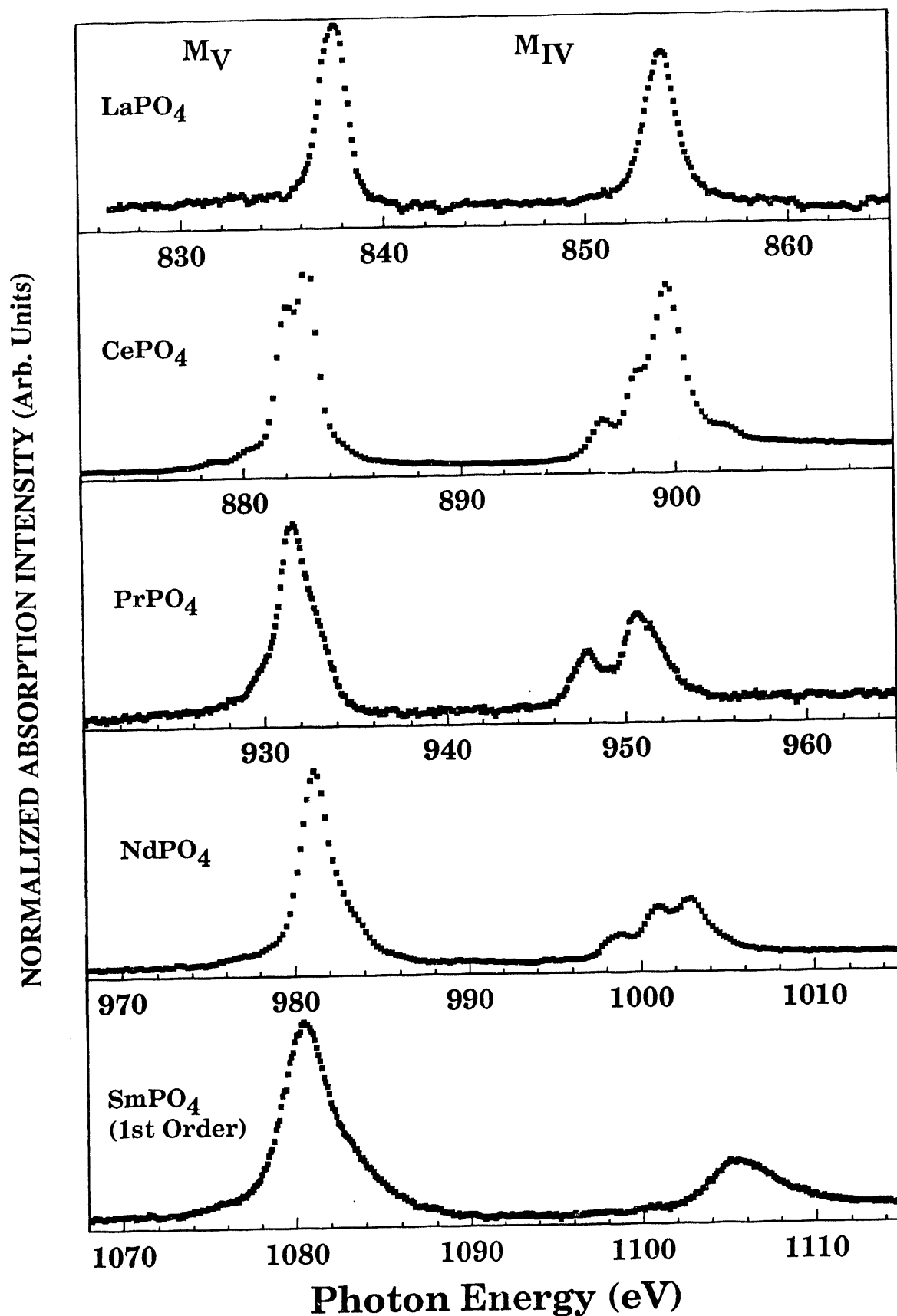


Figure 1. XAS spectra of the rare earth (La, Ce, Pr, Nd, Sm) orthophosphate M<sub>4,5</sub> edges collected with the monochromator diffraction grating satisfying the second order Bragg condition to improve the spectral resolution, except for Sm. The spectra have been normalized to the largest respective feature.

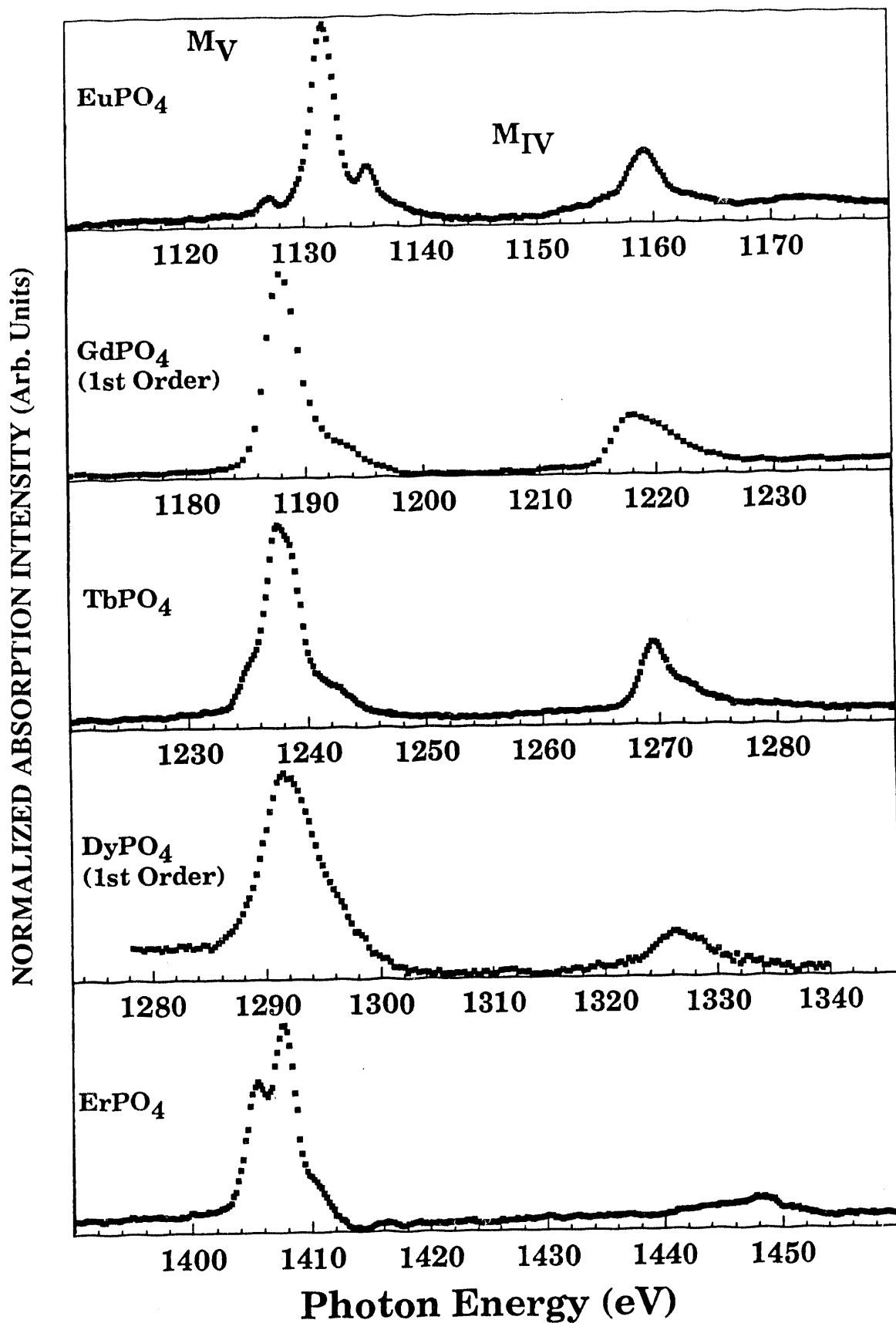


Figure 2. XAS spectra of the rare earth (Eu, Gd, Tb, Dy, Er) orthophosphate M<sub>4,5</sub> edges collected with the monochromator diffraction grating satisfying the second order Bragg condition to improve the spectral resolution, unless indicated. These data were also normalized to the largest feature.



The spectral data of the RE orthophosphates is summarized in Table 1. The peak energies are all systematically about 3 eV greater than expected from previous photoabsorption measurements of the RE metals, whereas the spin-orbit splittings are in complete agreement [3,4].

Table I. Summary of the absorption peak energies of the RE orthophosphates in eV.

REPO <sub>4</sub>	3d <sub>5/2</sub>	3d <sub>3/2</sub>	Difference ( $\Delta_{SO}$ )
La	837.6	853.8	16.2
Ce	885.5	902.7	17.2
Pr	931.6	950.7	19.1
Nd	981.2	1002.8	21.6
Sm	1080.3	1105.1	24.8
Eu	1131.7	1159.2	27.5
Gd	1188.1	1218.0	29.9
Tb	1237.6	1269.5	31.9
Dy	1292.0	1326.3	34.2
Er	1407.6	1448.4	40.8

## CONCLUSIONS

The XAS spectra of the RE ions in the orthophosphate matrix generally resemble the XAS of the corresponding RE metal. This is not unexpected and emphasizes the major contribution of the trivalent state to the electronic transitions occurring at the RE 3d edges. These spectra unequivocally identify the transitions originating from well-characterized RE cores and correlate well with previous theoretical investigations. The results of these measurements show that XAS of active elements and other hazardous materials safely contained in similar matrices, is feasible and can yield valuable electronic information.

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