DETERMINATION OF THE RELATIVE CONCENTRATIONS OF RARE EARTH IONS BY X-RAY ABSORPTION SPECTROSCOPY: APPLICATION TO TERBIUM MIXED OXIDES

G. VAN DER LAAN

Department of Physical Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 16,
9747 AG GRONINGEN, The Netherlands

J. C. FUGGLE

Laboratory for Molecular Spectroscopy, Research Institute for Materials, Catholic University
of Nijmegen, Toernooiveld, 6525 ED NIJMEGEN, The Netherlands

M. P. VAN DIJK, A. J. BURGGRAAF

Department of Chemical Technology, Laboratory for Inorganic Materials Science, Twente University of
Technology, P.O. Box 217, 7500 AE ENSCHEDE, The Netherlands

and

J.-M. ESTEVA AND R. KARNATAK

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209c, Université
de Paris-Sud, 91405 ORSAY CEDEX, France

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Abstract—A method, based on X-ray absorption spectroscopy (XAS) in the range 0.8–1.5 keV, to determine the relative amounts of rare earth ions in different valencies is explained and tested for the case of terbium mixed oxides. The results are in agreement with those obtained by existing analytical methods. The XAS method is advantageous in that it can be applied where other, conventional, methods break down.

Keywords: X-ray absorption, rare earths, oxides, terbium, ionic conductivity, mixed valence.

INTRODUCTION

In this paper we show that, making use of the recently calculated spectra for the rare earth configurations and their tabulated properties by Thole [1], one can obtain information about the valency concentrations of rare earth ions in solid materials. These numbers are of technological importance and we will pick out an example.

Materials with conducting oxygen ions are frequently used in applications such as oxygen sensors, pumps and fuel cells in conjunction with platinum electrodes. It has been suggested that the electronic contribution to the conductivity of the solid electrolyte may improve the performance of the noble metal electrode or can even substitute these [2–5]. This has led to extensive studies of mixed oxides, like $(\text{Tb}_x\text{Gd}_{1-x})_2\text{Zr}_2\text{O}_{7+y}$ in which both Tb^{3+} and Tb^{4+} are found. From studies of electrical conductivity and ionic transport properties of these materials it is apparent that there is an electronic contribution to the conductivity due to hopping of electrons from Tb^{3+} to Tb^{4+} sites [6, 7]. The activation energy for this latter process is thought to arise from the lattice distortion around the Tb^{3+} and Tb^{4+} ions and can be treated in small polaron models [7–9]. In order to put the understanding of such electronic conductivity on a firm basis, it is necessary to know the relative quantities of reduced and oxidized forms of the ions in the lattices. There are not many methods

for making this analysis. In some cases this is possible using thermogravimetric analysis (TGA). In this method the oxygen weight loss as a function of temperature or oxygen partial pressure is measured and if the stoichiometry of the sample is known at one temperature and pressure, then the stoichiometry at all temperatures and pressures can be deduced. This approach is not possible if one of the components of the mixed oxide is volatile or if more than one of the atoms present can exist in multiple valencies. Other possible methods, such as X-ray photoelectron spectroscopy, are very surface sensitive and may suffer from surface decomposition in the ultra-high vacuum environments used.

In view of this paucity of methods to analyse the valency of metal ions in mixed oxide conductors we have attempted to use X-ray absorption spectroscopy (XAS) at the 3d edges of the rare earths. These spectra are known to have sharp peaks and multiplets which are characteristic of the metal ion valency [1]. We will show that the XAS method does yield semi-quantitative results for the rare earth valencies in these materials. Another example of this method for the case of mixed Ce valencies can be found in Ref. [10].

EXPERIMENTAL METHODS

All materials were prepared by means of thermolysis of a viscous solution of citrate complexes of the con-

stituent metal ions. After calcination at 800°C for 6 hours the powders were pressed isostatically and sintered into dense ceramics at a temperature between 1200 and 1550°C. X-ray diffraction revealed the fluorite structure for all materials investigated.

To study the stoichiometry of these compounds thermogravimetric analysis (TGA) runs were carried out for several compositions in the solid solution series $(\text{Tb}_x\text{Gd}_{1-x})_2\text{Zr}_2\text{O}_{7+y}$. Extensive results of TGA measurements together with results of electrical conductivity measurements have been reported elsewhere [7]. In summary, runs were carried out in air and under reducing conditions in the temperature range 300–1000°C. The latter conditions were realized with a gas mixture consisting of 1% CO and 99% CO₂, resulting in a sample stoichiometry for the $(\text{Tb}_x\text{Gd}_{1-x})_2\text{Zr}_2\text{O}_{7+y}$ compositions with all Tb in the 3+ state [7]. This was used as a starting point to determine the stoichiometry at all temperatures in air.

For XAS experiments discs of the ceramic specimen were equilibrated at 600°C in air and quenched to room temperature rapidly. Reduced samples were obtained as above for the TGA measurements.

X-ray absorption spectra of the Tb $M_{4,5}$ excitations were obtained using the synchrotron radiation emitted by the Anneau de Collisions d'Orsay (ACO) at Orsay. The use of a constant deviation double crystal monochromator equipped with beryl crystals results in an energy resolution of 0.4 eV [11]. The spectra were recorded by the electron yield method so that no samples of thin foils were required. Checks were made on the X-ray flux using an Al sample, displaying a flat X-ray flux in the energy region of the Tb $M_{4,5}$ absorptions. The energy scale was calibrated by setting the La $3d_{3/2}$ and Mg $1s$ edges to an energy of respectively 850.5 and 1303.0 eV.

The samples were measured under ultra high vacuum conditions. The spectra were identical for a sample without any surface treatment and for scraping the surface in the vacuum, indicating that bulk and surface have the same composition.

RESULTS

Fig. 1 shows the measured XAS spectrum from Tb³⁺ in TbAl₂ compared with the calculated XAS spectra from Tb³⁺ and Tb⁴⁺. The spectra have been explained as being transitions from the Hund's rule ground state to final states where a $3d$ core electron has been excited to the $4f$ level: $3d^{10}f^8 (^7F_6) \rightarrow 3d^9 4f^9$ and $3d^{10}f^7 (^8S_{12}) \rightarrow 3d^9 4f^8$ for the Tb³⁺ and Tb⁴⁺, respectively. The final states are multiplet split but the dipole selection rules severely limit the number of accessible states [1]. The spectra are roughly separated in a $3d_{5/2}$ (M_5) and a $3d_{3/2}$ (M_4) multiplet at ~1240 and ~1270 eV respectively, due to the large $3d$ spin-orbit splitting. It is clear that the Tb³⁺ and Tb⁴⁺ spectra are quite distinct, but that they will overlap when the two species are present together. We use the M_5 peaks for analysis because they are sharper, stronger, and less influenced by Fano effects [1].

Fig. 1. Experimental $M_{4,5}$ X-ray absorption spectrum of TbAl₂ compared with the calculated spectra for Tb³⁺ and Tb⁴⁺.

Fig. 2 shows the XAS spectra of various Tb mixed oxide samples. It is seen that the spectrum of the reduced mixed oxide of Tb is very similar to the calculated Tb³⁺ ion spectrum and Tb in TbAl₂ (Fig. 1). In this spectrum we should surely have detected a 5% contribution from Tb⁴⁺ but none was found, in agreement with the conclusions of thermogravimetric analysis [7].

If we now look at the oxidized forms of Tb_{1.2}Gd_{0.8}Zr₂O₇ and Ce_{0.7}Tb_{0.3}O_{1.85+y} we see distinct shoulders on the high energy side of the main peaks. These are attributed to the Tb⁴⁺ contributions in the spectra.

In order to extract the amount of Tb³⁺ and Tb⁴⁺ from the experimental spectra, one could deconvolute the theoretical spectra. However, there are minor differences between theory and experiment, partly due to the fact that only atomic effects and no solid state effects have been taken into account in the calculated spectra. In order to avoid possible complications we simply use the experimental Tb³⁺ curve from the reduced compound and subtract it from the total spectra of the oxides. This procedure is demonstrated in Fig. 2. We already have seen from Fig. 1 that at the relative maximum at the left side in the Tb³⁺ peak (~1238 eV), hardly any Tb⁴⁺ contribution is present. Thus we can use this point to normalize the spectra. The dashed line in Figs. 2(a) and (b) is the Tb³⁺ contribution whereas the full line represents the Tb⁴⁺ contribution.

There is a small background problem in some of the GdTbZr oxides (as seen in Fig. 2a), which may be due to the slowly varying EXAFS oscillations from the nearby Gd $M_{4,5}$ excitations at about 23 and 53 eV lower excitation energy. This complication is not present in the Ce-Tb oxides where the Ce $M_{4,5}$ transition is at much lower excitation energy. Choice of the back-

Fig. 2. The experimental $M_{4,5}$ spectra from $Tb_{1.2}Gd_{0.8}Zr_2O_{7+y}$ (a), from $Ce_{0.7}Tb_{0.3}O_{1.85+y}$ (b) and from material a in reduced form (c) are given by the dotted curves. The Tb^{3+} and Tb^{4+} contributions in the oxides are given by the dashed line and the solid line, respectively; also given is a suggested background (lowest solid line).

ground is somewhat arbitrary and is certainly a limitation, although not a dramatic one. Note that the position of the Tb^{4+} contribution is within 0.2 eV of that predicted [1].

The relative valency concentrations are obtained by dividing the areas of the Tb^{3+} and Tb^{4+} contributions by the theoretical M_5 cross sections. Theoretical cross sections for all rare earths are found in Thole's tables [1]. The XAS values obtained for the Tb^{4+} and Tb^{3+} percentages are given in Table 1. Also presented are the percentages for other Tb mixed oxides studied, $Tb_{0.8}Gd_{1.2}Zr_2O_{7+y}$ and $Tb_{0.6}Bi_{1.4}O_{3+y}$. The values are comparable to values from TGA. Note that the independent determination of the amount of Tb^{4+} using TGA measurements is almost impossible in the Ce-Tb oxide, due to the presence of both Ce and Tb in two valencies.

DISCUSSION

The ability to determine by XAS the Tb^{3+} and Tb^{4+} quantities in the mixed oxides depends on the sepa-

ration of the Tb^{3+} and Tb^{4+} contributions to the spectrum. There are three tests for the validity of this separation.

- 1) Is the Tb^{4+} contribution at the predicted energy? Here the answer is yes within 0.2 eV.
- 2) Is the shape of the residue attributed to Tb^{4+} reasonable? Here we find a larger width to the Tb^{4+} contribution than calculated. There are various possible explanations for this but most probably it is a result of small changes in the shape of the Tb^{3+} contribution from one compound to another.
- 3) Is the Tb^{4+} weight derived from these measurements comparable to that from the standard methods? The standard method for these materials is thermogravimetric analysis and we have compared various results from TGA with our XAS data in Table 1. The agreement is remarkably good.

The accuracy of XAS measurements of the valency of Tb is difficult to assess. Systematic errors can enter due to the background subtraction or small changes in the Tb^{3+} line shape. We estimate an accuracy of ~ 3 –5% in the Tb^{4+} content.

The sample of $Ce_{0.7}Tb_{0.3}O_{1.85+y}$ showed a very large Tb^{4+} contribution of $\sim 25\%$, which was much higher than for the TbGdZr mixed oxides. This is in accord with preliminary conductivity measurements [6, 12]. We also find a very low Tb^{4+} concentration in the $Tb_{0.6}Bi_{1.4}O_{3+y}$ sample exposed to the same oxygen treatment. Clearly the lattice has a significant effect on the equilibrium Tb^{3+} : Tb^{4+} ratios. Considering effects of strain energy, one might expect larger fractions of Tb^{3+} to be present in the host lattice with the larger cations, since the ionic radius of Tb^{3+} (1.04 Å, Shannon and Prewitt values for 8-coordination [13]) is larger than the ionic radius of Tb^{4+} (0.88 Å). Thus the Tb ions fit better in their host lattice and the lattice has a lower free energy. This concept explains the result obtained for $Ce_{0.7}Tb_{0.3}O_{1.85+y}$ compared to the result obtained for $Tb_{0.6}Bi_{1.4}O_{3+y}$. Extending this concept to TbGdZr mixed oxides, the results indicate that the Tb ions occupy Gd ion lattice sites, which are nonequivalent to the Zr lattice sites. This is in accord with the observations of short range order in the fluorite lattice and the formation of pyrochlore ordered microdomains for the TbGdZr mixed oxides [6, 14].

CONCLUSIONS

We have shown that X-ray absorption is a suitable quantitative tool for analysis of the valency of Tb in

Table 1. % of Tb^{4+} as obtained from XAS and TGA measurements

	XAS	TGA
$Tb_{1.2}Gd_{0.8}Zr_2O_{7+y}$	15	14
$Tb_{0.8}Gd_{1.2}Zr_2O_{7+y}$	13	14
$Ce_{0.7}Tb_{0.3}O_{1.85+y}$	25	—
$Tb_{0.6}Bi_{1.4}O_{3+y}$	5	—
$Tb_{0.8}Gd_{1.2}Zr_2O_{7+y}$ (reduced)	0	0

mixed oxide materials. In some cases the concentration of Tb was as low as ~ 5 atomic% Tb, but we still obtain usable results with recording times as low as ten minutes. Thus the sensitivity of XAS is adjudged to be high. Also for the $\text{Ce}_{0.7}\text{Tb}_{0.3}\text{O}_{1.85+y}$ and $\text{Tb}_{0.6}\text{Bi}_{1.4}\text{O}_{3+y}$ the standard method, thermogravimetric analysis, is not applicable. We thus conclude that XAS is a suitable adjunct to the standard analytical methods for study of such systems.

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