“Unusual Ln^{3+} substitutional defects”: The local chemical environment of Eu^{3+} and Er^{3+} in nanocrystalline Nb_2O_5 by Ln-K edge EXAFS

Paolo Ghigna, Sonia Pin, Adolfo Speghini, Marco Bettinelli, Taiju Tsuboi

PII: S0022-3697(10)00011-9
DOI: doi:10.1016/j.jpcs.2010.01.010
Reference: PCS 6089

To appear in: *Journal of Physics and Chemistry of Solids*

Received date: 10 November 2009
Revised date: 19 January 2010
Accepted date: 20 January 2010

Cite this article as: Paolo Ghigna, Sonia Pin, Adolfo Speghini, Marco Bettinelli and Taiju Tsuboi, “Unusual Ln^{3+} substitutional defects”: The local chemical environment of Eu^{3+} and Er^{3+} in nanocrystalline Nb_2O_5 by Ln-K edge EXAFS, *Journal of Physics and Chemistry of Solids*, doi:10.1016/j.jpcs.2010.01.010

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

www.elsevier.com/locate/jpcs

“Unusual Ln³⁺ substitutional defects”: the local chemical environment of Eu³⁺ and Er³⁺ in nanocrystalline Nb₂O₅ by Ln-K edge EXAFS

Paolo Ghigna¹, Sonia Pin¹, Adolfo Speghini², Marco Bettinelli³, Taiju Tsuboi⁴

¹Dipartimento di Chimica Fisica “M. Rolla”, Università di Pavia, Viale Taramelli 16, I-27100 Pavia, Italy

²DiSTeMeV, Università di Verona and INSTM, UdR Verona, Via della Pieve 70, I-37029 San Floriano, Verona, Italy.

³Laboratory of Solid State Chemistry, DB, Università di Verona and INSTM, UdR Verona, Strada Le Grazie 15, I-37134 Verona, Italy.

⁴Department of Information and Communication Science, Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kita-ku, Kyoto 603-8555, Japan

Abstract

The local chemical environment of the trivalent lanthanide cations in Nb₂O₅ nanopowders doped with 1 mol % of Eu³⁺ and Er³⁺, prepared via a Pechini approach, has been studied by means of EXAFS at the Ln-K edge. It can be demonstrated that the lanthanide ions enter the Nb₂O₅ structure as substitutional defects with respect to Nb, giving rise to a very large amount of disorder: both Eu³⁺ and Er³⁺ ions substitute Nb in the 9-fold coordinated site, with clustering of oxygen vacancies around the substitutional defects. Valence Bond calculations have been used to validate the Ln-O distances obtained by the EXAFS fitting. The Er³⁺ doped nanocrystalline Nb₂O₅ sample shows efficient luminescence in the near infrared region around 1.5 μm. The emission and excitation spectra are affected by significant inhomogeneous broadening, in agreement with the presence of strong disorder around the dopant ions in nanosized Nb₂O₅.

* Corresponding author: Paolo Ghigna, Dipartimento di Chimica Fisica “M. Rolla”, Università di Pavia, Viale Taramelli 16, I-27100 Pavia Italy. Phone +39-0382-987574, Fax +39-00382-987575, E-mail paolo.ghigna@unipv.it.

Accepted manuscript

1. Introduction

Luminescent niobium based compounds doped with trivalent lanthanide ions (Ln^{3+}) have been the subject of considerable attention in the past decades. For instance, LiNbO_3 has proved to be a very important host for Ln^{3+} ions, with widespread applications in the field of optoelectronics and light emitting devices [1, 2], and strontium barium niobate ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) (SBN) and barium sodium niobate $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (BNN) [3], activated with Ln^{3+} ions, are very promising materials in the field of photorefractive memories [4] and linear and self-frequency converter solid state laser materials [5, 6]. It is important to note that in all these crystals the location of the Ln^{3+} in the lattice is not obvious, as the trivalent lanthanide ions cannot easily replace the constituent cations (Li^+ , Na^+ , Sr^{2+} , Ba^{2+} , Nb^{5+}) due to evident size and/or charge mismatches. It is worth noting that for these niobate hosts the doping Ln^{3+} ions have a different charge with respect to the host cations (Li^+ , Sr^{2+} , Ba^{2+} and formally Nb^{5+}) and also a different ionic radius (the Sr^{2+} and Ba^{2+} cations are larger while the Li^+ and Nb^{5+} are smaller than the Ln^{3+} ions [7]). Also simple oxides like TiO_2 or Nb_2O_5 , in which a single cation is present, are characterised by similar problems due to large mismatch of both charge and ionic radii between the doping Ln^{3+} ions and the host constituent cations. However, recent investigations by our research group have demonstrated the feasibility of the synthesis, using solution methods, of both TiO_2 [8] and Nb_2O_5 [9] doped with lanthanide ions. Recently, in a paper dealing with the local chemical environment of Ln^{3+} dopants in anatase TiO_2 the incorporation of lanthanide ions in such class of hosts as been referred to as “unusual Ln substitution” [10]. By using a local structural probe such as EXAFS at the Ln-K edges, it has been demonstrated that the lanthanide ions enter in the anatase structure as substitutional defects with respect to Ti, but that the amount of disorder created by the substitutional defects is very large. Indeed, the Ln–O and Ln–Ti distances have been found to increase by as much as 0.45 Å, with respect to what is found for the Ti–O and Ti–Ti distances in pure anatase [10]. Aim of this paper is to extend this kind of study to Nb_2O_5 . As a matter of fact, samples considered in this paper retain the $T\text{-Nb}_2\text{O}_5$ crystal structure [11]. This structure is orthorhombic (space group $Pbam$) and Nb can be in a distorted octahedral

(coordination number 6) or pentagonal bipyramid (coordination number 7) environment. Further Nb centres are randomly located in the cell in a nine-fold coordination. For this reason, the structure is quite complicated and the location of the lanthanide ions in the cell could be a challenging task.

Experimental details

2.1 Samples preparation

Nanocrystalline powders of Ln^{3+} doped Nb_2O_5 were prepared by a sol-gel Pechini approach as described elsewhere [9]. The molar ratio between the niobium and the Ln^{3+} ions was kept 99:1. X-ray powder diffraction patterns collected on a Bruker D8 diffractometer, in the Bragg-Brentano geometry and using a Cu X-ray tube, confirmed the single phase nature of the reaction products. All the diffraction pattern could be indexed using the orthorhombic structure of $T\text{-Nb}_2\text{O}_5$ [11]. Moreover, from the broadening of the diffraction peaks and electron microscopy images, the average size of the nanoparticles was estimated to be about 25 nm [9].

2.2 EXAFS

Extended X-Ray Absorption Fine Structure (EXAFS) spectra were collected at the Er and Eu-K edges at the BM-29 beamline of ESRF. The data collection was made at 20 K in fluorescence mode using a Si (511) monochromator. For the measurements, a selected amount of sample (ca. 0.3 g) was thoroughly mixed with cellulose in an agate mortar and pressed to form a pellet. The data analysis was carried out taking advantage of the FEFF8 code [12]. The EXAFS extraction has been performed by the use of ATHENA code. The EXAFS fitting was performed by means of the IFEFFIT interface [13]. The goodness of fit (GOF) is given by the *R-factor* parameter which is scaled to the magnitude of the data itself

$$R = \frac{\sum_{i=1}^N \left\{ \left[\text{Re}(f_i) \right]^2 + \left[\text{Im}(f_i) \right]^2 \right\}}{\sum_{i=1}^N \left\{ \left[\text{Re}(\chi_{data}) \right]^2 + \left[\text{Im}(\chi_{data}) \right]^2 \right\}}$$

This number gives a sum-of-squares measure of the fractional misfit. For good fits to carefully measured data on concentrated samples, $R \leq 0.02$. The accuracy of amplitude and phase-shifts calculated by the program have been checked by fitting the spectrum of powdered lanthanide oxides, and comparing the fitted radial distances with crystallographic values, that have been recovered with an accuracy better than 0.01 Å.

2.3 Luminescence

The luminescence emission and excitation spectra were measured using a Spex Fluorolog-3 spectrofluorimeter equipped with a 450 W xenon lamp. The spectrofluorimeter consists of two monochromators, one for the excitation and the other for the detection of the emission. The slit width of the emission monochromator was fixed to band pass of 0.2 nm to obtain highly resolved luminescence emission spectra, while a narrow slit width (band pass of 0.2 nm) was selected for the excitation monochromator to obtain highly resolved luminescence emission spectra. The infrared emission signal was measured by a liquid-nitrogen cooled Jobin-Yvon DSSX-IGA010L InGaAs photodiode with sensitivity in the range 800-1650 nm.

3 Results and discussion

Fig. 1 shows the Eu-K edge XAS spectrum of the sample investigated in this work. The statistical noise in the $\chi(k)$ was estimated by fitting a straight line on the high energy tail of the absorption spectra, where the EXAFS oscillations are undetectable. The noise is, therefore, estimated from the standard deviation of the residual signal which is of the order of 10^{-3} after normalisation for the edge jump. It is well apparent that the EXAFS oscillations in both spectra are small and rapidly vanishing with increasing energy. This is a clear indication that doping with Ln^{3+} induces a great amount of disorder around the impurity in the Nb_2O_5 structure. Fig. 2 and 3 show the EXAFS signals for the spectra at the Eu- and Er-K edges, respectively, and the corresponding Fourier Transforms (FT). The two spectra look impressively similar: in both spectra the EXAFS oscillations

vanish for $k > 8 \text{ \AA}^{-1}$; this is again an indication of the large amount of disorder induced by Ln^{3+} incorporation in the Nb_2O_5 structure. In the EXAFS FT, moreover, just one peak, *i.e.* at distances around $2 \text{ \AA}$, is apparent in both spectra and can be attributed to oxygen atoms (nearest neighbours). The best fits, according to the structural models reported in Tab. 1, are shown in Fig. 2 and 3 as dotted lines for the Eu-K edge spectrum and the Er-K edge spectrum, respectively. According to the data reported in Tab. 1, the local chemical environments of Eu^{3+} and Er^{3+} in the Nb_2O_5 host structure are impressively similar. It should be noted that the models used for the EXAFS fitting implicitly assumed that the Ln^{3+} ions enter into the Nb_2O_5 host as substitutional defects on the Nb position. An additional comment is worth here on the fitting procedure that has been applied in this work. The large amount of disorder that is found in the samples reduces the k range in which observable EXAFS oscillations are found. This evidence makes the EXAFS analysis problematical, especially due to the heavy correlations between the coordination numbers and σ^2 . It is possible to overcome these limitations, by noticing that the coordination distance is much less affected, as it determines the frequency of the EXAFS oscillations. Therefore the coordination distances can be quite accurately found out by a first EXAFS fitting using “dummy” coordination numbers. Next, these distances can be used to estimate, by the well established Bond - Valence Sum method [14], the coordination numbers that give the best agreement between the calculated charges on the Ln^{3+} ions and the formal (III) oxidation state. The use of the Bond - Valence Sum method to restrain the number of variables in the EXAFS data analysis has been widely discussed by Newville [15]. Then, it is possible to test that these coordination numbers give a reasonable fit for the σ^2 parameters, and a further test can be performed by checking that the fitted values for the distances do not change in this final fit. Using the Ln^{3+} -O distances reported in Tab 1, and 7 as the coordination number, the calculated charges on both Eu and Er are 2.63. On the other hand, using for both Eu and Er a coordination number of 8, the calculated charge is 3.00, which is in better agreement with the formal (III) oxidation state. The present results, therefore, suggest that the most probable location of

Eu and Er is in the 9-fold coordinated sites, with a possible clustering of the oxygen vacancies, formed for charge compensating the Ln_{Nb}'' substitutional defects.

Fig. 4 shows the room temperature emission and excitation spectra of the $Nb_2O_5:Er^{3+}$ nanopowder, measured with excitation and emission wavelengths 525 and 1516 nm, respectively. The spectra shows that excitation in the $^2H_{11/2}$ level gives rise to luminescence terminating on the $^4I_{15/2}$ ground state and originating from the excited levels $^4I_{9/2}$ (860 nm), $^4I_{11/2}$ (980 nm) and $^4I_{13/2}$ (1520 nm). The sharp band located at about 1230 nm is most probably due to an unidentified impurity. The Er^{3+} excited states below $^2H_{11/2}$ are populated by multiphonon relaxation bridging the energy gaps separating successive levels. This agrees with the relatively high energy phonons found in the Raman spectrum of nanocrystalline Nb_2O_5 (cut-off wavenumber of about 700 cm^{-1} [9]) and the relatively small energy gaps above $^4I_{13/2}$. On the other hand, the gap separating the latter level from $^4I_{15/2}$ is larger (about 6600 cm^{-1}) and therefore the $^4I_{13/2} \rightarrow ^4I_{15/2}$ band dominates the emission spectrum. The excitation spectrum indicates that NIR luminescence of nanocrystalline $Nb_2O_5:Er^{3+}$ can be excited efficiently in the visible region.

The profile of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ band clearly shows the presence of inhomogeneous broadening, as several relatively sharp peaks are superimposed to an underlying broad bandshape. Significant broadening is also present in the other features present in the emission and excitation spectra. These observations confirm the luminescence results obtained for nanocrystalline $Nb_2O_5:Eu^{3+}$ [9]. The general behaviour shown by the optical spectra of nanosized $Nb_2O_5:Ln^{3+}$ is clearly due to the presence of significant disorder around the dopant ions, in agreement with the EXAFS results discussed above. The broadening can be quantified through the estimation of the effective linewidth $\Delta\lambda_{eff}$ [16], defined as

$$\Delta\lambda_{eff} = \int \frac{I(\lambda)d\lambda}{I_{max}}$$

where $I(\lambda)$ is the luminescence intensity and $I_{\max}$ is the intensity at the peak maximum. In the present case, $\Delta\lambda_{\text{eff}}=44$ nm, a value not far from the ones measured for this transition in conventional oxide glasses (e. g. 57.1 nm in $\text{Sr}(\text{PO}_3)_2$ glass [17] and 32-51 nm for a series of soda-lime aluminosilicate glasses [18]). The high value of $\Delta\lambda_{\text{eff}}$ is a definite proof of a strong disorder around the luminescent ion.

4 Conclusions

The local chemical environment of the trivalent lanthanide cations in Nb_2O_5 nanopowders doped with 1 mol% of Eu or Er with respect to Nb, prepared via a Pechini route, has been studied by means of EXAFS at the Eu and Er-K edge. It can be demonstrated that the Ln^{3+} cations enter the Nb_2O_5 structure as substitutional defects with respect to Nb: the most probable site occupied by the Ln^{3+} cations being the nine-fold coordinate one randomly located in the unit cell. In addition, it is quite probable that oxygen vacancies, formed for charge compensation of the Ln''_{Nb} defects, cluster around the substitutional defects. These findings are compatible with the large amount of disorder that is found around the Ln^{3+} cations. The values obtained for the Ln-O distances have been validated by means of Bond Valence calculations. Luminescence spectra of the Er^{3+} doped sample shows significant inhomogeneous broadening, that indicates a large amount of static disorder, in agreement with the EXAFS findings.

Acknowledgements

This work has been supported by the European Synchrotron Radiation Facility (ESRF, experiment CH 1965 at the BM29 beamline). The BM29 staff, and in particular Simone de Panfilis, is gratefully acknowledged for help during the XAS data collection.

References

- [1] D. Hreniak, W. Strek, A. Speghini, M. Bettinelli, G. Boulon, and Y. Guyot, *App. Phys. Lett.* **88**, (2006) 161.
- [2] S. Shimotsu, S. Oikawa, T. Saitou, N. Mitsugi, K. Kubodera, T. Kawanishi, and Izutsu, M. *Phot. Techn. Let. IEEE* **4**, (2001) 364.
- [3] J. E. Geusic, H. L. Levinstein, J. J. Rubin, S. Singh, and L. G. Van Uitert, *Appl. Phys. Lett.*, **11**, (1967) 269.
- [4] T. Imai, S. Yagi, H. Yamazaki, and M. Ono, *Jap. Jour. Appl. Phys.* **38**, (1999) 1984.
- [5] M. O. Ramirez, D. Jaque, L. E. Bausá, J. García Solé, and A. A. Kaminskii, *Phys. Rev. Lett.* **95**, (2005) 267401.
- [6] A. Yoshikawa, H. Itagaki, T. Fukuda, K. Lebboub, A. El Hassounib, A. Brenierb, C. Goutaudierb, O. Tillementb, G. Boulonb, *J. of Cryst. Growth.* **247**, (2003) 148.
- [7] R. D. Shannon and C. T. Prewitt, *Acta Cryst. B* **25**, (1969) 925.
- [8] M. Bettinelli, A. Speghini, D. Falcomer, M. Daldosso, V. Dallacasa, L. Romano, *J. Phys. Condens. Matter* **18**, (2006) S2149.
- [9] D. Falcomer, A. Speghini, G. Ibba, S. Enzo, C. Cannas, A. Musinu and M. Bettinelli, *J. Nanomaterials* **2007**, (2007), 949.
- [10] P. Ghigna, A. Speghini and M. Bettinelli, *J. Solid State Chem.* **180**, (2007), 3296.
- [11] K. Katsuo and S. Tamura, *Acta Cryst. B* **31**, (1975) 673.
- [12] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, *Phys. Rev. B* **58**, (1998) 7565.
- [13] M. Newille, *J. Synchrotron Rad.* **8**, (2001) 322.
- [14] I. D. Brown and D. Altermatt, *Acta Cryst. B* **41**, (1985) 244.
- [15] M. Newille, *Physica Scripta* **T115**, (2005) 159
- [16] M. J. Weber, D. C. Ziegler and C. A. Angell, *J. Appl. Phys.* **53**, (1982) 4344.
- [17] S. Zaccaria, M. Casarin, A. Speghini, D. Ajò and M. Bettinelli, *Spectrochimica Acta Part A* **55**, (1999) 171.

- [18] S. Berneschi, M. Bettinelli, M. Brenci, G. Nunzi Conti, S. Pelli, S. Sebastiani, C. Siligardi, A. Speghini and G. C. Righini, *J. Non-Cryst. Sol.* **351**, (2005) 1743.

Accepted manuscript

Table Captions

Tab. 1. – EXAFS fitting parameters for the spectrum of Fig. 2 and 3, with different structural models. *r*: distances (Å); *n*: neighbour numbers; σ^2 : distance variances (Debye-Waller factors, Å²); BVS: Bond Valence Sum.

Accepted manuscript

Figure Captions

Fig. 1. – Raw fluorescence data at the Eu-K edge for Nb₂O₅:Eu.

Fig. 2. – Er-K edge EXAFS spectra (upper panel) and EXAFS Fourier Transform (lower panel) of the samples investigated in this work. Continuous line: experimental data, dotted line: fit.

Fig. 3. – Eu-K edge EXAFS spectra (upper panel) and EXAFS Fourier Transform (lower panel) of the samples investigated in this work. Continuous line: experimental data, dotted line: fit.

Fig. 4. – Room temperature luminescence excitation ($\lambda_{\text{em}}=1516$ nm) and emission ($\lambda_{\text{exc}}=525$ nm) spectra of nanocrystalline Nb₂O₅:Er³⁺.

Tab. 1

Nb ₂ O ₅ doped Eu 1% Pechini				
Atom	n	r (Å)	σ^2 (Å ²) / BVS	R
O	7	2.41(1)	0.010(2) / 2.63	0.008

Nb ₂ O ₅ doped Er 1% Pechini				
Atom	N	r (Å)	σ^2 (Å ²) / BVS	R
O	7	2.35(2)	0.010(4) / 2.63	0.008

Nb ₂ O ₅ doped Eu 1% Pechini				
Atom	n	r (Å)	σ^2 (Å ²) / BVS	R
O	8	2.41(1)	0.010(2) / 3.00	0.008

Nb ₂ O ₅ doped Er 1% Pechini				
Atom	n	r (Å)	σ^2 (Å ²) / BVS	R
O	8	2.35(2)	0.010(4) / 3.00	0.008

Fig. 1

Fig. 2

Fig. 3

Fig. 4