Local atomic and electronic structure of tungsten ions in AWO_4 crystals of scheelite and wolframite types

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Abstract

X-ray absorption spectroscopy was used to study the local atomic and electronic structure of tungsten ions in polycrystalline scheelite $CaWO_4$ and wolframite-type $ZnWO_4$ and $NiWO_4$. The W L_1- and L_3-edges X-ray absorption near edge structure (XANES) signals suggest tetrahedral coordination of tungsten ions in $CaWO_4$ and strongly distorted octahedral coordination in $ZnWO_4$ and $NiWO_4$. Accurate analysis of the W L_3-edge extended X-ray absorption fine structure (EXAFS) signals by the regularization procedure was performed to reconstruct the radial distribution functions within the first coordination shell around tungsten atoms in AWO_4 crystals and polycrystalline WO_3, which was utilized for comparison. For the local environment around tungsten atoms in $CaWO_4$, we found very good agreement with known crystallographic data, suggesting the presence of four oxygen atoms at ~ 1.79 Å. The results obtained for $ZnWO_4$ and $NiWO_4$ show similarity of their local atomic structures: the oxygen atoms forming $[WO_6]$ octahedra can be divided into two groups — four atoms at 1.84 ± 0.01 Å and two atoms at 2.13 ± 0.01 Å. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

AWO_4 compounds are important materials due to their use as scintillator detectors, photoanodes, solid-state laser hosts and in optical fibre applications (Galasso, 1970; Kaminskii, 1981; Wang et al., 1992). They crystallise in scheelite- or wolframite-type structures. The scheelite structure (Gürmen et al., 1971) may be regarded as a cubic close-packed array of A^{2+} and $[WO_4]^{2-}$ units with the coordination numbers of 8 and 4 oxygen atoms for the A and W cations, respectively, whereas the wolframite structure (Wyckoff, 1963) may be described as made up of hexagonally close-packed oxygens with certain octahedral sites filled by A and W cations in an ordered way (Sleight, 1972).

The type of the tungstate structure depends crutially on the ionic radius of the A^{2+} cation (Sleight, 1972): for small A^{2+} cations (such as Mg^{2+} and 3d ions) the wolframite

structure is preferable, but in the case of Ca^{2+}, Ba^{2+} and Sr^{2+} the scheelite structure becomes favorable. In addition, the transition from scheelite (s) to wolframite (w) structure can be stimulated by a high pressure—about 1.2 GPa for $CaWO_4$ and 5 GPa for $BaWO_4$ (Kawada et al., 1974; Nicol and Durana, 1971). From the long-range point of view, it is accompanied by an abrupt increase in a_w, c_w or a_s lattice constants and an abrupt decrease in b_w or c_s (Sleight, 1972). From the short-range point of view, a shift of the W cation from the center of the $[WO_4]$ tetrahedron towards the center of the $[WO_6]$ octahedron occurs during the transition.

The local structure of tungsten ions can be successfully studied by X-ray absorption spectroscopy. In this work, we present recent results on the local atomic and electronic structure of tungsten ions, obtained from the analysis of the W L_1- and L_3- edges XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectra in $CaWO_4$, $NiWO_4$ and $ZnWO_4$. A set of structural parameters, determined from the modeling of the EXAFS signals, will be discussed in connection with

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known data. The analysis of the XANES spectra, related
to the conduction band states, will be presented within an
ab initio full-multiple scattering formalism.

2. Experimental details and data analysis

Polycrystalline $NiWO_4$ and $ZnWO_4$ powders were pre-
pared using thermal treatment in air at $700°C$ of amorphous
powders, obtained by co-precipitation at room temperature
(RT) from nickel or zinc nitrate and sodium tungstate aque-
ous solutions. Polycrystalline $CaWO_4$ and WO_3 powders
were commercial products. The single-phase structure of all
compounds was confirmed by X-ray powder diffraction.

The RT X-ray absorption spectra of the W L_1- and
L_3-edges were recorded at the LURE DCI storage ring
(Orsay, France), operated at the energy $1.85\,GeV$ and
a maximum stored current $316\,mA$. A standard trans-
mission scheme with a $Si(3\,3\,1)$, $Si(3\,1\,1)$ and $Si(1\,1\,1)$
double-crystal monochromators and two ion chambers con-
taining argon/air was used. The energy resolution was about
$1–2\,eV$. The X-ray absorption spectra were analysed fol-
lowing a standard method using the EDA software package
(Kuzmin, 1995, 1997). The X-ray absorption coefficient
$\mu(E)$ was calculated as $\mu(E) = \ln(I_0/I)$ using the measured
intensities of the incident $I_0(E)$ and transmitted through
the sample $I(E)$ X-rays. Then, the EXAFS signal $\chi(k)$
was obtained as $\chi(k) = (\mu - \mu_b - \mu_0)/\mu_0$, where μ_b is the
background contribution, μ_0 is the embedded-atomic con-
tribution and $k = [(2m_e/\hbar^2)(E - E_0)]^{1/2}$ is the photoelectron
wavenumber (m_e is the electron mass, $\hbar$ is the Plank's con-
stant and E_0 is the energy, defining the zero photoelectron
wavenumber value ($k = 0$)) (Kuzmin and Purans, 2000).
The Fourier transforms of the EXAFS signals were cal-
culated as $FT(R) = (2/\pi)^{1/2} \int_\chi (k)k^2 W(k)\exp(-2ikR)\,dk$,
where $W(k)$ is the "window"-function.

The model-independent regularisation method (Kuzmin,
1997; Kuzmin and Purans, 2000) was used to reconstruct
the radial distribution functions (RDFs) $G_{W−O}(R)$ within
the first coordination shell of tungsten. The RDF $G_{W−O}(R)$
corresponds to the number of oxygen atoms located in the
spherical shell around the tungsten between R and $R + \delta R$,
so that the integration of $G_{W−O}(R)$ over the first shell range
gives the coordination number. The scattering amplitude and
phase shift functions, required in the EXAFS calculations,
were extracted from the EXAFS signal for $CaWO_4$, assum-
ing the following values of structural parameters (Gürmen
et al., 1971): the coordination number of tungsten $N = 4$,
the average interatomic distance $R(W–O) = 1.785\,Å$ and the
Debye–Waller factor $\sigma^2 = 0.002\,Å^2$.

XANES signals were modelled by the ab initio
full-multiple-scattering (FMS) FEFF8 code (Ankudinov
et al., 1998). The clusters having the appropriate crystal
structure and a size up to 8 shells around the absorber
(tungsten atom) were used. The self-consistent-field (SCF)
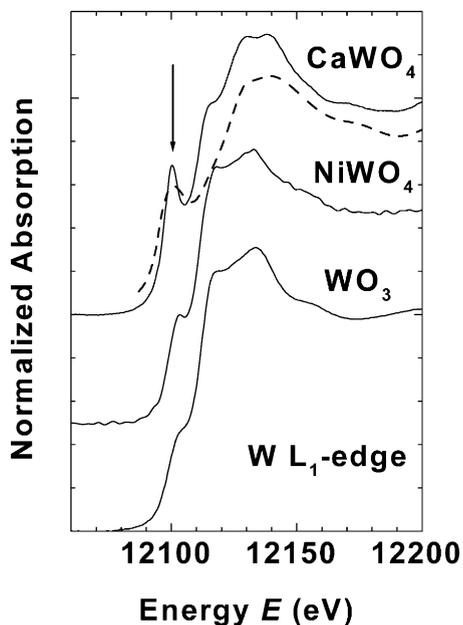cluster potential was utilized, including the complex energy

Fig. 1. Experimental W L_1-edge XANES spectra (solid lines) in
$CaWO_4$, $NiWO_4$ and WO_3. The FMS calculation of the XANES
signal for a cluster of 8 coordination shells around tungsten atom in
$CaWO_4$ is shown by dashed line. The pre-edge peak, corresponding
to the $2s(W) \rightarrow 5d(W)+2p(O)$ transition, is indicated by arrow.

dependent Dirac-Hara-Hedin- Lundqvist exchange-correlation
part (Ankudinov et al., 1998).

3. Results and discussion

The XANES signals at the W L_1-edge are shown in
Fig. 1. They represent considerable interest, because the
pre-edge peak (indicated by the arrow) is sensitive to the
local symmetry of the tungsten sites (Kuzmin and Purans,
1993). The intensity of the pre-edge peak is the largest in
the case of tetrahedral coordination and becomes smaller for
the octahedral environment. The slightly higher intensity of
the pre-edge peak in $NiWO_4$ compared to WO_3 suggests a
stronger distortion of the $[WO_6]$ octahedra in the former.
Theoretical calculations (dashed line in Fig. 1, shown only
for $CaWO_4$) are able to reproduce the experimental signal,
however a large 8 shells cluster should be considered, and a
problem to reproduce the shoulder at ~$12115\,eV$, attributed
to the $2s(W) \rightarrow 6p(W)$ transition, exists.

The Fourier transforms (FTs) of the experimental EX-
AFS signals $\chi(k)k^2$ are shown in Fig. 2. The first peak at
~$1.5\,Å$ corresponds to the first coordination shell of tung-
sten atoms, built of oxygen atoms. The group of peaks at
~$3\,Å$ are mainly due to the second and third shell, com-
posed of tungsten and A^{2+} atoms. High intensity of this peak
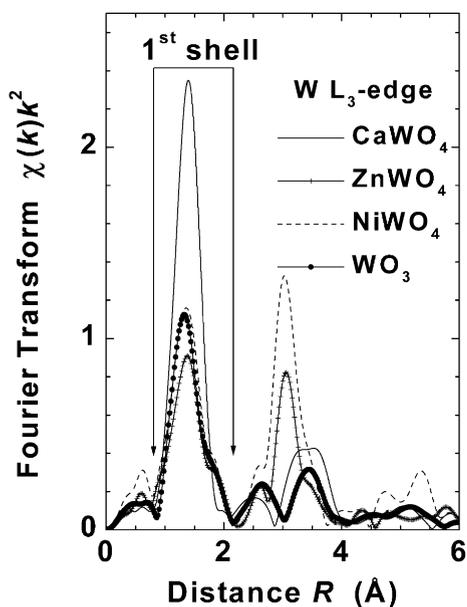for $NiWO_4$ and $ZnWO_4$ can be attributed to the presence of

Fig. 2. Fourier transforms of the experimental W L_3-edge EXAFS $\chi(k)k^2$ signals. The region of the first coordination shell of tungsten atoms is shown. Note that the positions of peaks do not correspond to the true crystallographic values due to the phase shift contribution in the EXAFS signal.

Fig. 3. Radial distribution function (RDF) $G_{W-O}(R)$ for the first coordination shell of tungsten atoms.

the so-called "multiple-scattering" contributions (Kuzmin et al., 1993). To determine structural parameters for the first shell in each compound, the peaks at $\sim 1.5\,\text{Å}$ were singled out by back-FT, and thus obtained EXAFS signals were best-fitted using the model-independent regularisation approach (Kuzmin, 1997; Kuzmin and Purans, 2000). The reconstructed radial distribution functions (RDFs) are given in Fig. 3. The shape of the RDFs suggests strong distortion of the $[WO_6]$ octahedra in tungstates and together with complementary data from Raman spectroscopy (Kuzmin et al., 2001) indicates a preferencial bonding of tungsten ions to the group of four nearest oxygen atoms at $1.84 \pm 0.01\,\text{Å}$.

4. Summary and conclusions

Local atomic and electronic structures of tungsten ions in polycrystalline scheelite $CaWO_4$ and wolframite-type $ZnWO_4$ and $NiWO_4$ were studied by X-ray absorption spectroscopy on the W L_1- and L_3-edges. The analysis of both XANES and EXAFS signals allows to conclude that the tungsten atoms have regular tetrahedral coordination with the W–O distances about $1.79\,\text{Å}$ in $CaWO_4$, but they have very distorted octahedral coordination with four short (at $1.84\,\text{Å}$) and two long ($2.13\,\text{Å}$) W–O distances in $ZnWO_4$ and $NiWO_4$. Such difference in the local environment of the tungsten atoms agrees well with the one, expected upon the transition from scheelite to wolframite structure.
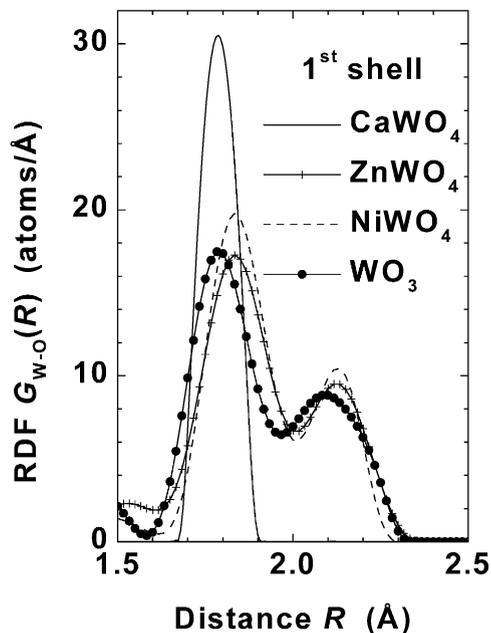
References

Ankudinov, A.L., Ravel, B., Rehr, J.J., Conradson, S.D., 1998. Real-space multiple-scattering calculation and interpretation of X-ray absorption near edge structure. Phys. Rev. B 58, 7565–7756.

Galasso, F.S., 1970. Structure and Properties of Inorganic Solids. Pergamon Press, Oxford.

Gürmen, E., Daniels, E., King, J.S., 1971. Crystal structure refinement of $SrMoO_4$, $SrWO_4$, $CaMoO_4$ and $BaWO_4$ by neutron diffraction. J. Chem. Phys. 55, 1093–1097.

Kaminskii, A.A., 1981. Laser Crystals. Springer, Berlin.

Kawada, I., Kato, K., Fujita, T., 1974. $BaWO_4$-II (a high pressure form). Acta Crystallogr. B 30, 2069–2071.

Kuzmin, A., 1995. EDA: EXAFS data analysis software package. Physica B 208 & 209, 175–176.

Kuzmin, A., 1997. Reconstruction of the radial distribution function from EXAFS: new trends and comparative analysis of different methods. J. Phys. IV (France) 7, C2-213–C2-214.

Kuzmin, A., Purans, J., 1993. The influence of the focusing effect on the X-ray absorption fine structure above all the tungsten L edges in non-stoichiometric tungsten oxides. J. Phys.: Condens. Matter 5, 9423–9430.

Kuzmin, A., Purans, J., 2000. Dehydration of molybdenum trioxide-hydrates $MoO_3 \cdot nH_2O$: in-situ X-ray-absorption spectroscopy at the Mo K-edge. J. Phys.: Condens. Matter 12, 1959–1970.

Kuzmin, A., Purans, J., Benfatto, M., Natoli, C.R., 1993. X-ray absorption study of rhenium L_3- and L_1- edges in ReO_3: multiple-scattering approach. Phys. Rev. B 47, 2480–2486.

Kuzmin, A., Purans, J., Kalendarev, R., 2001. Local structure and vibrational dynamics in $NiWO_4$. Ferroelectrics, in press.

Nicol, M., Durana, J.F., 1971. Vibrational Raman spectra of $CaMoO_4$ and $CaWO_4$ at high pressures. J. Chem. Phys. 54, 1436–1440.

Sleight, A.W., 1972. Accurate cell dimensions for ABO_4 molybdates and tungstates. Acta Crystallogr. B 28, 2899–2902.

Wang, H., Medina, F.D., Zhou, Y.D., Zhang, Q.N., 1992. Temperature dependence of the polarized Raman spectra of $ZnWO_4$ single crystals. Phys. Rev. B 45, 10 356–10 362.

Wyckoff, R.W.G., 1963. Crystal Structures, Vol. 3. Wiley, New York.