Local Environment of Co$^{2+}$ Ions in $\beta''$-Alumina Crystals

By

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Introduction In the past few years, X-ray absorption spectroscopy (EXAFS, XANES) has become increasingly popular as a technique for studying valence states of incorporated ions, their local site symmetry and coordination numbers in complex multicomponent compounds. EXAFS is most useful as a probe of the crystallographic structure and static or dynamic disorder. The near-edge structure (XANES) is determined by multiple scattering (MS) processes and is a probe of higher order correlation functions of local atomic distributions in complex systems. It is sensitive to the geometrical arrangement of the environments of the absorbing atom via MS. These techniques provide different but complementary information. Recently EXAFS and X-ray crystallographic studies, which examined the local structure around Co ions, showed that in Co-doped $\beta''$-alumina Co$^{2+}$ ions are in distorted tetrahedral environment [1], and the average Co-O bond length (0.195 nm [2]) is significantly longer than the average Al(2)-O distance (0.1838 nm). It is not clear why it is the $\beta''$-alumina structure that can accommodate the larger concentration of the dopant Co ions. The aim of this note is to find the local environment around Co ions in Co exchanged $\beta''$-alumina crystals by EXAFS and XANES techniques.

Experimental Transmission EXAFS and XANES spectra were taken on the CoK edge using the EXAFS station (Si[220] channel-cut crystal monochromators) of one of the wiggler beam lines (BX-1, "PWA" ADONE LNF INFN). The storage ring "ADONE" operated at 20 to 50 mA and 1.51 GeV with a wiggler current of 4000 A. The powder samples were prepared from single crystals by dusting on the Scotch tape as a holder.

Sodium $\beta''$-alumina crystals, e.g. Na$_{1.67}$Mg$_{0.67}$Al$_{10.33}$O$_{17}$, were grown by a flux evaporation method in which a mixture of Na$_2$CO$_3$, MgO, and Al$_2$O$_3$ was

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Fig. 1. Experimental CoK edge XANES for a) $\beta''$-alumina, b) CoCr$_2$O$_4$ /3/, and c) Co$_3$O$_4$

Fig. 2. FT of the EXAFS $\chi(k)k^2$ ($k = 20$ to $145 \text{ nm}^{-1}$) for a) Co-$\beta''$-alumina and b) Co$_3$O$_4$

heated in an yttrium crucible in air at 1700 °C for one day. Dimensions of specimens were generally about 4×4×0.2 mm$^3$. The samples were buried in CoCl$_2$ and heated to 770 °C in argon atmosphere and full exchanged after 1 h. The crystals were deep blue and of good optical quality. The optical absorption spectrum has a triplet centered at 600 nm, which is attributed to Co$^{2+}$ ions in tetrahedral environment /1/. The Raman spectrum is typical for $\beta''$-alumina.

Results and discussions Since the K-edge XANES is most sensitive to the geometrical arrangement of the environment of the absorbing ion, one would expect a dominant feature close to one of reference compounds.

Fig. 1 shows the near-edge region (XANES) of the spectra in Co-$\beta''$-alumina and reference compounds with the tetrahedral (CoCr$_2$O$_4$) /3/ cobalt arrangement and a mixture of tetrahedral and octahedral positions (Co$_3$O$_4$). The pre-edge feature is a result from transitions to the localized empty mixed p-d state. The p-d orbital mixing (on the metal atom) occurs in complexes which do not have a center of inversion (as tetrahedrally coordinated complexes in spinels CoAl$_2$O$_4$, CoCr$_2$O$_4$, etc.) /3/. In the edge region (extending to about 50 eV above the absorption edge) the outgoing photoelectron has a relatively long mean free path and can scatter strongly from atoms surrounding the absorber. Thus multiple scattering effects can become important and peaks in Co-$\beta''$-alumina are determined by the atomic geometrical arrangements in a local cluster around the absorbing atom. The general shape of the XANES spectra in Co-$\beta''$-alumina is qualitatively similar to the spectra in the spinels CoCr$_2$O$_4$ /3/, FeAl$_2$O$_4$ /4/. So,
Fig. 3. a) The best fit of the EXAFS $\chi(k)k^2$ of the second shell in Co-$\beta''$-alumina (dotted line shows experiment, solid line the model). Contributions to the total EXAFS from different bonds: b) Co-Co, c) Co-Al, d) Co-O

the XANES measurement supports the idea that the Co$^{2+}$ dopant ions are in a tetrahedral position with a spinel-like environment.

Fig. 2 shows the Fourier transform (FT) of the EXAFS spectra $\chi(k)k^2$ in the intervals 20 to 145 nm$^{-1}$ for Co-$\beta''$-alumina and the reference compound Co$_3$O$_4$. The back FT mean peaks in different R-space intervals allowed us to separate contributions in EXAFS spectra from different shells: 0.08 to 0.22 nm - the first coordination shell (Co-O); 0.22 to 0.35 nm - the second and third shells. The analysis was done by fitting the back FT in the single scattering approximation with amplitudes and phases calculated in the curved wave approximation (Co-O [5], Co-Co, Al [6]). The least-squares procedure by the modified Levenberg-Marquardt method [7] was used to obtain a set of the most suitable parameters: $N_1$ coordination number, $R_1$ distance, $\sigma_1^2$ Debye-Waller factor. Some parameters ($E_0$ continuum threshold, $S_o^2$ sealing factor, $\Gamma$ whole state width) were used as fixed parameters from the reference compounds.

The first coordination shell in Co-$\beta''$-alumina has a set of structural parameters with $N_1 = 4.0 \pm 1.0$, $R_1 = (0.196 \pm 0.001)$ nm, and $\sigma_1^2 = (0.008 \pm 0.001) \times 10^{-2}$ nm$^2$. This value of distance is characteristic of a four-fold coordination for two-valence Co ions.

Using a multishell theoretical model to fit the second peak in FT we obtained a set of structural parameters:
Co-Co: $N = 4.0 \pm 1.0$, $R = (0.356 \pm 0.002)\text{nm}$, $\sigma^2 = (0.003 \pm 0.001) \times 10^{-2} \text{nm}^2$,
Co-Al: $N = 9.5 \pm 1.0$, $R = (0.332 \pm 0.002)\text{nm}$, $\sigma^2 = (0.008 \pm 0.001) \times 10^{-2} \text{nm}^2$,
Co-O: $N = 12.0 \pm 1.0$, $R = (0.319 \pm 0.002)\text{nm}$, $\sigma^2 = (0.009 \pm 0.001) \times 10^{-2} \text{nm}^2$.

Fig. 3 shows the best fit of the EXAFS signal of the second peak in FT and different contributions from Co-Co, Co-Al, and Co-O pairs. Since the back-scattering amplitudes as well as phase shift functions of Co, Al, and O differ strongly, these elements are distinguishable in the fitting process in the k-space. For small and middle values of the wave vector (20 to 100 nm$^{-1}$) the Co-Al and Co-O bonds give a comparable contribution to the EXAFS spectrum and have negative interference. For large values of the wave vectors (≥100 nm$^{-1}$) only oscillations from the Co-Co bond are important.

The obtained EXAFS data are in good agreement with the structural parameters of Co$^{2+}$ in tetrahedral site CoAl$_2$O$_4$ spinels. So, we can conclude that in Co-$\beta''$-alumina Co$^{2+}$ ions are tetrahedrally coordinated and built in the spinel structure.

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References

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