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Modeling of the curve radial electronic density distribution for amorphous Me–Zr–O systems

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Abstract

Me–Zr–O systems were studied with X-ray Radial Electronic Density Distribution (RED) method. This method is based on the relation between the radial electronic density distribution function and intensity of coherent scattering of X-ray in the diffraction experiment. The intensity of scattering was measured for a wide range of angles using monochromator and $CuK\alpha$ radiation. RED curves was made by resolving in sum of Gauss function. Data on the known oxides and hydroxides structures, such as interatomic distances (r) and coordination number (Z) were used for the calculated curves. The values r and Z were calculated from the data of structural type, spatial group, coordinates of atoms and parameters of cell. For Fe–Zr–O system it has been demonstrated that all samples have similar structures, which related to that of cubic α-ZrO_2. The model with statistical arrangement of Fe^{3+} cations, vacancies in the cation and anion sublattices and modification of anion sublattice with OH^- groups is admitted as most probable. Numbers of cation and anion vacancies and number of OH^- groups were evaluated using experimental RED curves of samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: X-ray Radial Electronic Density Distribution; Zirconium oxides; Amorphous materials

1. Introduction

Zirconia-based compositions are widely used as catalysts and supports in the ceramic and refractory industries. The relevant studies are limited to two main directions: (a) stabilization of low-temperature modifications of zirconium dioxide (cubic and tetragonal) [1,2], and (b) formation of zirconia compounds with other oxides [3]. Low temperature transformations of the systems prepared by coprecipitation were studied insufficiently [2].

2. Preparation of samples

Zirconium oxides promoted by iron were prepared by precipitation of Zr(IV) and Fe(III) nitrates at pH = 9 followed by calcination at 383 K (sample 1) and 673 K (sample 2). Metal ratio Zr:Fe is 0.907:0.093. Specific surface area is 580 m^2/g and 340 m^2/g for sample 1 and sample 2, respectively.

3. Method

Samples were studied with RED method. This method is based on the relationship between the

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radial electronic density distribution function $\rho(r)$ and intensity of X-ray scattering. To calculate RED curve one needs to have experimental and reference characteristics of the materials under study. Experimental data: intensity of scattering measured for a wide range of angles using a monochromator, $2\theta = 2°–150°$; background scattering intensity; specimen thickness; chemical composition $(n_a, \ldots, n_m)$; pycnometric density. Reference data: number of electrons in atom; absorption coefficient, m_a; wavelength, $\lambda_{CuK\alpha} = 1.54$ Å, atomic factors, f_a.

4. Quantitative parameters of structure calculated with RED method

RED curve modeling is carried out by the sum of Gauss functions. One can determine the following values from the resolution: (1) Equilibrium interatomic distances (r) corresponding to electronic density maxima. (2) Coordination number Z determined from areas of coordination peaks; average square atomic shifts determined from the widths of coordination peaks. (3) Experimental areas of the coordination peaks corresponding to the given distance (r) can be compared to the calculated values: $S_c = 2n_a Z_{ab} K_a K_b$ for different types of atoms; $S_c = n_a Z_{aa} K_a^2$ for one type of atoms, where n_a is the number of a-type atoms, K_a, K_b — effective number of electrons in atoms, Z_{ab} — coordination number. Positions of coordination peaks from RED curves are determined within $Dr/r = \pm 0.5\%$ and accuracy of area determination is $\pm 5\%$. Data on the known oxides and hydroxides structures were used for modeling of the curve radial distribution: interatomic distances (r) and coordination number Z were calculated by the program «Policristall». The structural data were calculated from the space-group symmetry, coordinates of atoms, parameters of cell and structural type. The coordination peaks were simulated by Gauss functions.

5. Results and discussion

Effective molecule of $Zr_{0.907}Fe_{0.093}O_{1.952}$ was adopted for original RED curve calculation. RED curves of samples 1 and 2 are shown in Fig. 1. Interatomic distances and coordination peak areas obtained from RED curves are presented in Table 1.

An existence of several structural types of ZrO_2 is known [1]. However, monoclinic, tetragonal and orthorhombic modifications of highly disordered structures could not be revealed with RED method and besides it is known that cubic structure of α-ZrO_2 is stabilized with Me^{2+} cation [2,3]. Therefore, a-ZrO_2 structure was chosen as a basic for identifying the sample structure. Interatomic distances and coordination peak areas of a-ZrO_2 structure (structural type: CaF_2, S.G.: Fm3m, $a = 5.09$ Å) are presented in Table 2.

RED curve analysis revealed samples to have structure closely related to that of cubic a-ZrO_2. It was supposed that peaks at 3.36 Å in experimental curves correspond to the shortest Me−Me distance in disordered a-ZrO_2 type structure . 4.75 Å unit cell parameter was calculated using this assumption. RED curve of a-ZrO_2 type structure with parameter 4.75 Å and «effective» metal ion of $0.907 Zr^{4+} 0.093 Fe^{3+}$ composition is shown in Fig. 1. Calculated interatomic distances and coordination peak areas
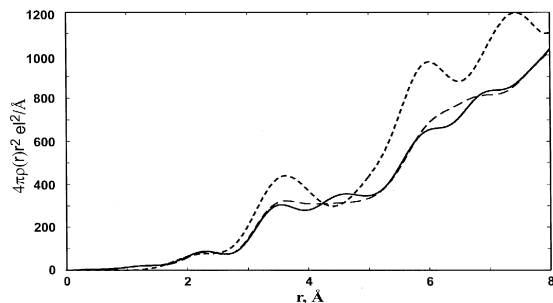

Fig. 1. RED curves of samples 1(—), 2(– –) and model RED curve of α-ZrO_2 type structure (- - -) with unit cell parameter 4.75 Å and ''effective'' cation of 0.907 Zr^{4+} + 0.093Fe^{3+} composition.

Table 1

Interatomic distances r, coordination peak widths b and coordination peak areas S of samples 1 and 2 with chemical composition of $Zr_{0.907}Fe_{0.093}O_{1.952}$

Sample 1			Sample 2		
r (Å)	b (Å)	S (el^2)	r (Å)	b (Å)	S (el^2)
2.17	0.35	70.4	2.19	0.35	68.53
3.36	0.39	251.8	3.37	0.39	245.9
4.06	0.41	89.8	4.07	0.42	196.0
4.59	0.48	358.1	4.8	0.48	281.7
5.8	0.46	641	5.87	0.48	627.5
6.81	0.46	776.8	6.76	0.49	730.6
7.72	0.45	763	7.7	0.49	821.0

Table 3

Interatomic distances r, coordination number Z and coordination peak areas S_c of a-ZrO$_2$ type model structure ($a = 4.75$ Å) with «effective» metal ion of $0.907Zr^{4+} + 0.093Fe^{3+}$ composition

Me−Me			Me−O			O−O		
r (Å)	Z	S (el^2)	r (Å)	Z	S (el^2)	r (Å)	Z	S (el^2)
3.36	12	465	2.05	8	99.6	2.38	6	6
4.75	6	232.7	3.94	24	298.9	3.36	12	12
5.81	24	930.5	5.11	24	298.9	4.12	8	8
6.72	12	465	6.17	32	398.5	4.75	6	6
7.51	24	930.5	7.03	48	597.8	5.31	24	24
						5.81	24	24

of model structure ($a = 4.75$ Å) are represented in Table 3.

The use of these data as the basis for some structural models was considered. (1) Fe$_2$O$_3$ clusters located in ZrO$_2$ bulk structure. This model is not valid because 2.06 Å standard interatomic distances related to Fe−O distance and 3.02 Å related to Fe−Fe distance are not observed in experimental RED curves. FeO clusters could not be formed because reduction of Fe^{3+} does not take place in the synthesis process. (2) a-ZrO$_2$ type cubic structure clusters with increasing iron concentration. Using the values of unit cell parameter 4.75 Å and ion radii of Fe^{3+} (0.67 Å) and Zr^{4+} (0.82 Å) it was calculated that clusters consist of Fe^{3+} and Zr^{4+} ions in the ratio of 1:2. But an existence of cubic a-ZrO$_2$ type structure with such Fe^{3+} content is rather problematic because every third

Table 2

Interatomic distances r, coordination number Z and coordination peak areas S_c of a-ZrO$_2$ structure (structural type: CaF$_2$, S.G.: Fm3m, $a = 5.09$ Å)

Zr−Zr			Zr−O			O−O		
r (Å)	Z	S_c, (el^2)	r (Å)	Z	S_c, (el^2)	r (Å)	Z	S_c, (el^2)
3.6	12	502	2.20	8	103.5	2.55	6	6
5.09	6	251	4.22	24	310.5	3.6	12	12
6.23	24	1004	5.47	24	310.5	4.41	8	8
7.20	12	502	6.61	32	414	5.09	6	6
			7.53	48	621	5.69	24	24
						6.23	24	24

cation of such structure should have valence of three and it should lead to strong deformations in cubic lattice. Besides, pure ZrO$_2$ phase with a set of interatomic distances should exist in this case, but such distances are not observed in RED curves. 3. Iron cations replaced statistically in α-ZrO$_2$ cation sublattice. (a) *Structure without vacancies*. It was found that ca. 9 at.% of Fe^{3+} ions inserted into the a-ZrO$_2$ structure caused a decrease of unit cell parameter to a value of 5.0 Å. But this model does not describe all interatomic distances in RED curves of the samples. (b) *a-ZrO$_2$ type structure with vacancies in the cation and anion sublattices*. Areas of coordination peaks of RED curve were calculated for model structure with vacancies by the formula: $S_c = 2n_a q_a K_a Z_{ab} K_b q_b$, for different types of atoms and by the formula: $S_c = n_a q_a^2 Z_{aa} K_a^2$ for one type of atoms. q_a is the part of positions occupied by a-type atoms, and therefore, the number of a-type vacancies is $(1 - q_a)$. Z_{ab} and Z_{aa} are coordination numbers in the structure without vacancies. K_a is the effective number of electrons in cation or anion.

Number of vacancies in the cation and anion sublattices was determined using a correlation between the calculated (Table 3) and experimental (Table 1) RED peak areas. Number of cation vacancies was calculated using areas of 3.36 Å (sample 1) and 3.37 Å (sample 2) peaks corresponding to the Me−Me distance. Number of anion vacancies was obtained by averaging
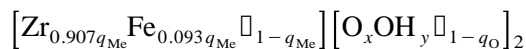
Table 4
Number of cation $(1 - q_{Me})$ and anion $(1 - q_O)$ vacancies and structural formulae for $(3b)$ structural model of samples

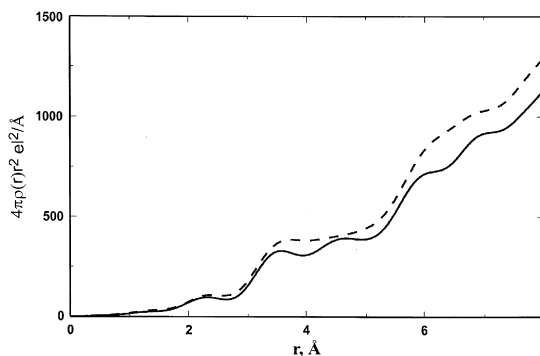| Sample	$1 - q_{Me}$	$1 - q_O$	Structural formula
1	0.266	0.038	$Zr_{0.666}Fe_{0.0683}\square_{0.266}O_{1.434}\square_{0.076}$
2	0.273	0.054	$Zr_{0.659}Fe_{0.0676}\square_{0.273}O_{1.412}\square_{0.108}$

Fig. 2. RED curves of samples 1(—), 2(- - -) calculated with final chemical composition for (3c) structural model.

the vacancies calculated for areas of 2.17 Å and 4.06 Å (sample 1) and 2.19 Å and 4.07 Å (sample 2) peaks. These peaks correspond to the Me–O distances. These data and structural formulae for both samples are presented in Table 4.

These structural formulae (Table 4) do not describe a-ZrO_2 structural type because total number of cations (containing cation vacancies) is equal to 1 $(0.666 + 0.068 + 0.266 = 1)$ but total number of anions is not equal to 2 $(1.434 + 0.076 = 1.51)$. (c) *Structure with vacancies and modification of anion sublattice with OH^- groups*. General formula for both samples:

$$\left[Zr_{0.907q_{Me}}Fe_{0.093q_{Me}}\square_{1-q_{Me}}\right]\left[O_xOH_y\square_{1-q_O}\right]_2$$

x and y values should satisfy the following conditions:

1. conformity to a-ZrO2 structural type $(x + y = q_O)$,
2. neutral molecule $2(2x + y) = q_{Me}(4 \cdot 0.907 + 3 \cdot 0.093)$.

To obtain the self coordinated structural formulae q_{Me}, q_O, x and y values were determined by successive recalculations of RED

curves. Final values of these parameters are presented in Table 5. RED curves calculated with the obtained final chemical compositions are presented in Fig. 2.

Final structural formulae are as follows:

$$\left[Zr_{0.695}Fe_{0.071}\square_{0.234}\right]\left[O_{0.495}OH_{0.505}\right]_2$$
for sample 1
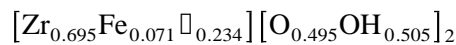
$$\left[Zr_{0.744}Fe_{0.076}\square_{0.18}\right]\left[O_{0.616}OH_{0.370.14}\right]_2$$
for sample 2

In a previous work [4] the local structure of iron in Fe-doped zirconium oxide produced by self-sustained high-temperature synthesis was studied by different methods. Iron was found to be in its II oxidation state and to occupy two different sites of the fluorite ZrO_2 structure. By method of Fe–K edge extended X-ray absorption fine structure (EXAFS) were identified as usual for cubic ZrO_2 structure distances (Me–Me 3.6 Å) and also a short Fe–Zr distance (2.64 Å). In our case Zr^{4+} ions were statistically substituted by Fe^{3+} ions and averaged distance (3.36 Å) was observed.

Table 5
Number of occupied cation (q_{Me}) and anion (q_O) positions and content of oxygen (x) and OH-groups (y) in the samples for (3c) structural model

Sample	q_{Me}	q_O	x	y
1	0.766	1	0.495	0.505
2	0.82	0.986	0.616	0.37

6. Conclusions

1. Near order of X-ray amorphous Zr–Fe–O system has a-ZrO_2 structural type.

2. Addition of Fe^{3+} ions leads to the appearance of cation vacancies in the samples structure along with a decrease of interatomic distances as compared to those of pure a-ZrO_2.

3. Anion sublattice has no vacancies but contains OH^- groups, which is indicative of the low temperature Zr–Fe–O hydroxide.

4. Calcination at 673 K leads to a decrease in the concentration of cation vacancies and partial removal of OH^- groups.

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