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EXAFS Study of Nanocrystalline Solid Solutions Synthesized in the $\text{ZrO}_2\text{-Ga}_2\text{O}_3$ System

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Abstract. The local structure of $(\text{ZrO}_2)_{1-x}(\text{Ga}_2\text{O}_3)_{x/2}$ metastable solid solutions ($x \leq 0.5$) was investigated by EXAFS. These solid solutions crystallize in fluorite-like structures and are nanocrystalline. From the Ga K-edge spectra, the gallium atoms are found in an average fivefold coordination ($d_{\text{Ga-O}} = 1.89 \text{ \AA}$). No signal corresponding to a second coordination shell is observed on the radial distribution functions. From the Zr K-edge spectra, a splitting of the Zr-O distances is evidenced. For the lowest gallium content ($x \leq 0.14$) the zirconium environment is of tetragonal type (4+4), whereas for the higher gallium content (cubic solid solutions) it is more or less similar to that found in monoclinic zirconia (3+4). The signal associated with the second shell decreases with increasing gallium content. These results indicate an important displacement of the gallium atoms in relation to their ideal position in a fluorite structure, which leads to a strong relaxation of the cation network.

1. INTRODUCTION

The cubic modification of ZrO_2 , can be stabilized by the addition of lower valence oxides. Y_2O_3 is often used for this purpose and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solutions have already been investigated by EXAFS [1-2]. Some unusual solid solutions of ZrO_2 and other oxides as Fe_2O_3 or Al_2O_3 can also be synthesized [2-5]. These solid solutions are metastable and nanocrystalline. Similar metastable solid solutions may be synthesized in the $\text{ZrO}_2\text{-Ga}_2\text{O}_3$ system [6]; this paper reports the investigation of their local structure by EXAFS.

As showed by X-ray diffraction (XRD), these solid solutions crystallize in fluorite-like tetragonal ($x \leq 0.1$) or cubic structures and are nanocrystalline (table I). However, the broadening of the diffraction lines due to the small size of the particules limits the structural information which can be obtained by XRD. Conversely, EXAFS which does not require long range order can provide a convenient description of the local structure.

2. DATA ANALYSIS

EXAFS spectra were recorded at the zirconium and gallium K-edges on the EXAFS I beamline at LURE-DCI (ORSAY). Energy selection was accomplished using a channel cut Si (331) monochromator. Fig. 1 (a) and (b) show the radial distribution functions (RDF) obtained by Fourier transform of $k^3\chi(k)$ at the Zr and Ga K-edge for various gallium content. The first peak on the RDF correspond to nearest cation-oxygen shell and the second one to the nearest cation-cation shell. In order to determine the structural parameters of the partial EXAFS contributions, backscattering amplitudes and phase shifts were extracted from model compounds. BaZrO_3 was used for the Zr-O shell (6 oxygens at $2.09 \text{ \AA}$, $\sigma = 0.05 \text{ \AA}$) and GaAsO_4

Figure 1: RDF of $(\text{ZrO}_2)_{1-x}(\text{Ga}_2\text{O}_3)_x$ solid solutions annealed at 775°C (a) Zr K-edge and (b) Ga K-edge.

quartz for the Ga-O shell (4 oxygens at $1.825\text{\AA}$, $\sigma=0.05\text{\AA}$). For the second shell observed at the Zr K-edge, a metastable cubic solid solution (ZrO_2)_{0.96}(MgO)_{0.04} was used (11.5 zirconiums at $3.61\text{\AA}$, $\sigma=0.07\text{\AA}$).

3. RESULTS AND DISCUSSION

3.1 Oxygen shell

At the Zr K-edge, convenient fits of the oxygen contribution were obtained with a two subshell model and a normalization factor of 0.9. For $x \leq 0.14$, the best fits were obtained with the same number of oxygens in the two subshells. This environment of the zirconium atoms indicates a local order compatible with a tetragonal structure. Such structure is clearly evidenced by XRD for the lowest gallium content, but the tetragonal distortion seems to be too weak to be evidenced by XRD for the two other samples. The difference between the Debye Waller factors of the two subshells could be due to anisotropic thermal motions of the oxygen and zirconium atoms. For $x > 0.14$ zirconium is found in a sevenfold coordination, like in monoclinic zirconia. The two subshells, containing 3 and 4 atoms respectively, are similar to those found by neutron diffraction in a cubic yttria stabilized zirconia [7]. For the highest gallium contents, the increase of the number of vacancies leads to an important modification of the zirconium environment.

At the Ga K-edge, the coordination numbers and the Ga-O distances are typical of a fivefold coordination. Therefore, the symmetry of the gallium sites is quite different from that of the zirconium sites.

Table I : EXAFS results for $\text{ZrO}_2\text{-GaO}_{1.5}$ solid solutions with various gallium content

*Fixed values

GaO _{1.5} content (mol %)	Bonding	$\Delta k(\text{\AA}^{-1})$	Zr K-edge			Ga K-edge			Lattice parameter($\text{\AA}$)	
			N	R($\text{\AA}$)	$\sigma(\text{\AA})$	$\Delta k(\text{\AA}^{-1})$	N	R($\text{\AA}$)		$\sigma(\text{\AA})$
4	cation-oxygen	2.8-13.6	4.00 [#]	2.09	0.072	-	-	-	-	a=5.08 c=5.16
	cation-cation	6-13.9	9.0	3.61	0.048					
10	cation-oxygen	2.9-13.8	4.00 [#]	2.09	0.075	2.5-10.3	5.2	1.88	0.091	a=5.09
	cation-cation	6-13.9	9.0	3.59	0.054					
14	cation-oxygen	2.9-13.5	4.00 [#]	2.09	0.077	2.4-12.7	5.1	1.89	0.091	a=5.08
	cation-cation	6-13.9	9.0	3.59	0.053					
24	cation-oxygen	2.8-13.3	3.00 [#]	2.09	0.065	2.4-13.2	5.2	1.89	0.095	a=5.05
	cation-cation	6-13.1	6.5	3.57	0.068					
39	cation-oxygen	2.8-13.3	3.00 [#]	2.08	0.061	2.4-13.1	5.0	1.89	0.091	a=5.00
	cation-cation	6-13.2	5.0	3.54	0.079					
48	cation-oxygen	2.9-13.3	3.00 [#]	2.09	0.066	2.4-13.0	5.1	1.89	0.104	a=4.97
	cation-cation	6-13.2	5.2	3.54	0.082					

3.2 Cation shell

On the RDFs obtained at the Ga K-edge, the amplitude of the second peak is very weak. This indicates an important displacements of the gallium atoms in relation to their ideal position in a fluorite structure. Therefore, the Ga-Zr distances are widely distributed and the second peak observed in the RDFs at the Zr K-edge are only due to scattering by zirconium atoms. For a $(\text{ZrO}_2)_{1-x}(\text{GaO}_{1.5})_x$ solid solution, the number of Zr atoms in the second coordination shell around zirconium is given by $N_{\text{Zr}}=12*(1-x)$. Even taking account uncertainties close to 20%, the experimental values are always lower than the calculated ones, which suggests some distortions of the cation network. However, the Zr-Zr distances are in good agreement with those deduced from the lattice parameters ($a/\sqrt{2}$ for the cubic structure).

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