Structural Analysis of Hydrolytic Condensed Zirconium Oxide by the Anomalous X-ray Scattering Method

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The anomalous X-ray scattering (AXS) technique has been applied to obtain the environmental radial distribution function (RDF) around a zirconium in amorphous ZrO_2 prepared by hydrolytic condensation of zirconium alkoxide. The environmental RDF was determined from the intensities measured at the Zr K absorption edge using synchrotron radiation and compared with the ordinary RDF. By combining the environmental and ordinary RDFs of amorphous ZrO_2 , zirconium is quantitatively confirmed to be surrounded by six oxygens at a distance of 0.214 nm and a considerably distorted ZrO_6 octahedron is likely to exist as a fundamental local ordering unit structure. A possible structural model of amorphous ZrO_2 in near neighbour region has also been proposed.

KEY WORDS: amorphous zirconia; radial distribution function; anomalous X-ray scattering; synchrotron radiation.

1. Introduction

The sol-gel method using metal alkoxides and other metal organic compounds as master materials has been extensively developed for making various advanced materials such as fine oxide powders, glasses and ceramic bodies and substrates with various superior properties.¹⁾ The advantages of this relatively new method may be explained as follows. The final products can be obtained by heating at relatively low temperature, because these master materials are highly reactive and the uniform mixing is likely obtained for multi-component systems. Moreover it is quite interesting to make various kinds of amorphous materials which cannot be prepared by the conventional melt quenching technique.

A number of interesting materials have been prepared by this sol-gel method. Zirconium oxide is included in this category and the thermal decomposition of amorphous ZrO_2 formed from zirconium alkoxides^{2,3)} and zirconium salts^{4,5)} are known to produce a metastable tetragonal ZrO_2 ($t\text{-ZrO}_2$), in addition to monoclinic ZrO_2 ($m\text{-ZrO}_2$) which is actually stable under about 1273 K. However, the formation of $t\text{-ZrO}_2$ at low temperature is still one of controversial subjects in the following results. Cypres *et al.*⁶⁾ and other two research groups^{7,8)} proposed that the stabilization of $t\text{-ZrO}_2$ is attributed to various anionic impurities such as OH^- , whereas Garvie⁴⁾ and some other people^{2,9)} suggest that it should be rather related to the particle size effect. According to Livage *et al.*⁹⁾ and Tani *et al.*,¹⁰⁾ the stabilization of the tetragonal form of ZrO_2 may be explained by the similarity of local ordering

structure between amorphous and crystalline tetragonal ZrO_2 . Garvie and Mitsuhashi *et al.*¹¹⁾ also pointed out the significance of strain on the stabilization of $t\text{-ZrO}_2$. In these contexts, the structure of amorphous ZrO_2 holds the key to give the conclusive remark regarding its particular crystallization behavior by low temperature heating. However, the quantitative accuracy of the presently available structural data of amorphous ZrO_2 was not sufficient to allow the definite comment on the structural similarity in comparison with those of crystalline ZrO_2 phases.

It is well known that the coordination numbers in disordered systems can be obtained from the radial distribution function (RDF) data using X-ray diffraction and such data provide a convenient picture of their local structure in near-neighbour region. The so-called pair function method by Mozzi and Warren¹²⁾ is one of the convenient procedures to estimate the interatomic distances and coordination numbers of a system containing more than two kinds of atoms, such as silicate glasses. On the other hand, Narten¹⁴⁾ determined the structural parameters of silicate glass using the least-squares technique by calculating the intensity profiles and the results were found to be similar to those reported by Mozzi and Warren.¹²⁾

The atomic correlations of the individual chemical constituents around a specific element are strongly required in order to describe the fine structure in multi-component systems. For these requirements, the relatively new method of anomalous X-ray scattering technique (hereafter referred to as AXS) is recently received much attention and its usefulness to determine the environmental structure around a specific element

in multi-component systems has been well demonstrated.¹³⁾ The structural analysis of the present interest of zirconium oxide requires more parameters than those determined from the single diffraction data alone and this prompts us to apply the least-squares method to the differential intensity profile obtained from the AXS measurements.

The main purpose of this work is to present our recent results for determining the atomic structure of hydrolytic condensed zirconium oxide at longer distance as well as the structure in the nearest-neighbor region including the AXS experiments of the differential intensity measurements.

2. Experimental

The 0.1 mol/dm³ solution of the zirconium tetra-*n*-butoxide was prepared by dissolving Zr(OC₄H₉)₄ in *n*-butyl alcohol. This solution was then mixed with H₂O/*n*-butyl alcohol mixture (H₂O=10 vol%) so as to give final molar ratio; H₂O/Zr(OC₄H₉)₄ to be 6.0 and preliminary drying was made by rotary evaporator. Thus resultant condensed material was dried at 423 K for three hours. The details of sample preparation are almost identical to those reported by Saito *et al.*¹⁵⁾ This material was annealed at various temperatures from 423 to 823 K for 30 min and they were examined by the ordinary X-ray diffraction method using Cu K α radiation. Typical X-ray diffraction patterns are given in Fig. 1 using the results of original and two annealed samples, where 2θ is the scattering angle. Up to 573 K, only hallow patterns were obtained. Whereas the crystallization of such amorphous sample so as to produce *t*-ZrO₂ was detected with the increment of annealing temperature. At higher temperature such as 1373 K, only *m*-ZrO₂ remained. It may be noted that the diffraction peaks of *t*-ZrO₂ obtained in this work agree well with the JCPDS cards of No. 24-1164.

Fig. 1. X-ray diffraction patterns of amorphous ZrO₂ annealed at different temperatures by Cu K α radiation.

On the basis of these experimental facts, a sample was prepared by annealing at 573 K in an oxygen atmosphere for further structural investigation. This sample was found to contain at most 4.0 mass% of volatile species such as water and alcohol, from the estimation by the thermal gravimetric analysis. No further consideration of such volatile components was taken into account in the following analysis. The sample density was measured by the Archimedes method with toluene using the samples pressed in the shape of pellet.

A beam line (6B station) in the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan, where a double Si (111) crystal monochromator is provided upstream, was used for the present AXS measurements. The incident beam is monitored by an N₂ gas ion chamber placed in front of the sample, so as to keep the total number of the photon irradiating the sample constant. The fluorescent radiation from the sample, mainly arising from the tail of the band pass and the higher harmonic diffraction of the monochromator crystal is frequently not negligible, even if an energy below the absorption edges is used for the measurements like in the present case. Thus, the pure intrinsic germanium solid state detector was employed in order to separate such fluorescent component from the scattered intensity. Details of the experimental setting is given in Ref. 13).

The intensity profiles were measured at energies of 17.973 and 17.698 keV, which correspond to 25 and 300 eV below the Zr K absorption edge (17.998 keV). Then, these intensities were corrected for absorption and converted to the absolute intensities by the generalized Krogh-Moe-Norman method,¹⁶⁾ including the correction for Compton scattering.¹⁷⁾ The detected energy dependence of intensity results mainly from the variation of the real part of the anomalous dispersion terms of a zirconium atom, f'_{Zr} .¹⁸⁾ Therefore the resultant intensity difference, $\Delta i(Q)$, may be given by the following equation;

$$\Delta i(Q) = \frac{(I_{300}(Q) - \langle f_{300}^2 \rangle) - (I_{25}(Q) - \langle f_{25}^2 \rangle)}{c_{Zr}(f'_{Zr,300} - f'_{Zr,25})W(Q)} \\ = \int_0^\infty 4\pi r^2 \sum_{j=1}^2 \frac{Re[f_{j300}(Q) + f_{j25}(Q)]}{W(Q)} \\ \times (\rho_{Zrj} - \rho_{oj}) \frac{\sin(Qr)}{Qr} dr \quad \dots\dots\dots(1)$$

$$W(Q) = \sum_{j=1}^2 c_j Re(f_{j300}(Q) + f_{j25}(Q)) \quad \dots\dots\dots(2)$$

where $Q = 4\pi \sin \theta / \lambda$ is the wave vector and $I(Q)$ the absolute intensity, c_{Zr} the atomic fraction of zirconium, f_j the X-ray atomic form factor of the *j*-th element,¹⁹⁾ $\langle f^2 \rangle$ the mean square of the atomic scattering factors, ρ_{Zrj} the number density function of the *j*-th atom around a zirconium, and ρ_{oj} the average number density for *j*-th element. "Re" indicates the real part of the value in the parentheses. The subscripts 25 and 300 for $I(Q)$ represent the incident energies corresponding to 25 and 300 eV below the Zr K absorption edge; 17.973 and

17.698 keV, respectively. The summation in the above equation indicates the sum over the constituents of the present samples. The environmental RDF for Zr, which represents the local atomic distribution around a zirconium can be obtained by the Fourier transformation of the quantity $Q\Delta i(Q)$;

$$4\pi r^2 \rho_{Zr}(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q\Delta i(Q) \sin(Qr) dQ \quad \dots\dots\dots(3)$$

ρ_0 in Eq. (3) is the average number density of atoms in a system.

On the other hand, the so-called reduced interference function $i(Q)$ from the absolute intensity $I(Q)$ in the following form,

$$i(Q) = (I(Q) - \langle f^2 \rangle) / \langle f \rangle^2 \quad \dots\dots\dots(4)$$

where $\langle f \rangle$ is the average atomic scattering factor. By Fourier transformation of the function $Q\Delta i(Q)$, the ordinary RDF can be estimated:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q\Delta i(Q) \sin(Qr) dQ \quad \dots\dots\dots(5)$$

where $\rho(r)$ is the so called average number density distribution function.

3. Results and Discussion

The two scattering intensity profiles measured at two energies close to the Zr *K* absorption edge are shown in Fig. 2, where the differential intensity profile is also given at the top. The environmental interference functions $Q\Delta i(Q)$ of the present sample was estimated and shown in Fig. 3. The ordinary interference function $Q\Delta i(Q)$ calculated from the diffraction experiment of single energy of 17.698 keV is also illustrated in Fig. 3 for comparison. The profiles of these interference functions consist of the first peak at about 22 nm^{-1} followed by a

number of peaks, which indicate a considerable fraction of local ordering unit structures exist in this glass structures although their distribution appears to be no long range ordering. These features contrast to the case of metallic glasses, where the rapid damping of interference function is clearly observed.

The environmental and ordinary RDFs were calculated from the interference functions of Fig. 3 using Eqs. (3) and (5), respectively, and they are given in Fig.

Fig. 3. (Top) Interference function of amorphous ZrO_2 obtained from the intensity measurement at the energy of 17.698 keV. (Bottom) Environmental interference functions $Q\Delta i(Q)$ for zirconium of amorphous ZrO_2 obtained from the intensity data measured at energies close to the Zr *K* absorption edge.

Fig. 2. Differential intensity profiles of amorphous ZrO_2 (top) obtained from the intensity data (bottom) measured at incidence energies of 17.973 and 17.698 keV, which correspond to energies 25 and 300 eV below the Zr *K* absorption edge.

Fig. 4. Ordinary radial distribution function $4\pi r^2 \rho(r)$ and environmental radial distribution functions $4\pi r^2 \rho_{Zr}(r)$ calculated from the interference functions of Fig. 3.

4. In this work, the observed intensity data at Q less than 9 nm^{-1} were smoothly extrapolated to zero at $Q=0 \text{ nm}^{-1}$. The effect of the extrapolation or the truncation up to $Q=168 \text{ nm}^{-1}$ is known to make no critical contribution to the RDFs of a glassy sample calculated from the interference functions consisting of the broad peaks only in such Fourier method.²⁰⁾ Since the atoms do not approach one another inside the atomic diameter, the calculated RDFs should be zero in the small r region below the nearest-neighbor peak. Therefore the interference functions given in this work include a correction considering the experimental uncertainty so as to remove such spurious oscillations of the RDFs in the small r region by the usual method.^{16,21)}

The ordinary RDF corresponds to the sum of three partial RDFs of Zr–O, Zr–Zr and O–O. From the information of ionic radii of the constituent elements, the first peak around 0.22 and 0.34 nm can be suggested to be Zr–O and Zr–Zr pairs, respectively. The peak around 0.37 nm may be attributed to the mixed correlations of the Zr–Zr, Zr–O and O–O interactions. It is worth mentioning in the ordinary RDF that the Zr–Zr pair around 0.34 nm is well coincident with the atomic pairs characterized by the $m\text{-ZrO}_2$ structure. Therefore, the fundamental local structure of the present amorphous ZrO_2 sample seems to be rather close to that of $m\text{-ZrO}_2$ than the $t\text{-ZrO}_2$ one. On the other hand, the O–O atomic correlations are very difficult to ascribe in the present ordinary RDF, because of its low scattering power for X-ray compared to that of zirconium. Structural parameters of Zr–O and Zr–Zr pairs are likely to be obtained. However, the definite and precise information of the local atomic arrangements of amorphous ZrO_2 cannot be determined as a unique solution from the present ordinary RDF data alone. This is particularly true in the higher order correlations, because more than two kinds of atomic pairs usually overlap at longer distances.

As shown in Fig. 4, the structural features observed in the environmental RDF for zirconium is essentially similar to those of ordinary RDF of amorphous ZrO_2 , although the environmental RDF includes only the atomic correlations of Zr–O and Zr–Zr pairs. This is mainly due to the reason that the contribution of O–O pairs to the ordinary RDF is not so significant. Nevertheless, it is worth mentioning that the correlation of Zr–Zr pairs in the environmental RDF is rather distinct at the distance of 0.34 nm, compared to that of the ordinary RDF. When such valuable different nature observed in the environmental RDF using present AXS technique is coupled with the ordinary RDF data, the resolution of the structural parameters for Zr–O and Zr–Zr pairs can be improved even in the higher order correlations. The following data processing was made along this data. The coordination number of Zr–O, Zr–Zr and O–O pairs estimated in this work by applying the least-square technique suggested by Narten¹⁴⁾ to the interference function. According to Narten, the reduced interference function $i(Q)$ may be given by the expression

$$i(Q) = \left[\sum_{i=1}^m \sum_k N_{ik} \exp(-b_{ik} Q^2) f_i f_k \frac{\sin Q r_{ik}}{Q r_{ik}} + \sum_{\alpha=1}^m \sum_{\beta=1}^m [\exp(-b'_{\alpha\beta} Q^2) f_{\alpha} f_{\beta} 4\pi r_{\alpha\beta} \times (Q r'_{\alpha\beta} \cos Q r'_{\alpha\beta} - \sin Q r'_{\alpha\beta}) / Q^3] \right] / \langle f \rangle^2 \quad (6)$$

where m is the number of elements, N_{ik} is the average number of type- k atoms around any type- i atom at the average distance of r_{ik} and the value of $2b_{ik}$ is the mean square variation. The quantities of $r'_{\alpha\beta}$ and $b'_{\alpha\beta}$ correspond to the mean and the variance of the boundary region which need not be sharp.¹⁴⁾ It may be also noted that the first and second terms of Eq. (6) represent the discrete Gaussian-like distributions and a continuous distribution with an average number density in the higher order correlations in the disordered system, respectively.

The quantities of N_{ik} , r_{ik} and b_{ik} for the nearest neighbor interactions were obtained by the least-squares calculation of Eq. (6) so as to reproduce the experimental interference function in Fig. 3. The differential interference function $Q\Delta i(Q)$ can be readily calculated by taking the difference of the calculated ordinary coherent intensity similarly estimated at the two energies in the AXS measurements using the Eqs. (1), (2) and (3) and compared with the experimental data of $Q\Delta i(Q)$ in Fig. 3. Thus, the resolution of the structural parameters can be improved at the reasonable level by the least-squares variational technique using the experimental and theoretical interference functions of not only $Q i(Q)$ but also $Q\Delta i(Q)$.

The present analysis qualitatively suggests that the structural features of amorphous ZrO_2 are rather close to those of $m\text{-ZrO}_2$ than $t\text{-ZrO}_2$ structure. Then, at the first step, the 22% random vacancy $m\text{-ZrO}_2$ structure model based on the density measurements was applied, similar to the approach of Narten¹⁴⁾ for explaining the experimental RDF data. The converged structural parameters could not reproduce the experimental RDFs particularly, the RDF data in the distance of 0.37 nm, which corresponds to first Zr–Zr pairs in $t\text{-ZrO}_2$ structure. It should also be kept in mind that the atomic configurations of amorphous ZrO_2 are not exactly identical to those of $m\text{-ZrO}_2$. Therefore, the 22% random vacancy model coupled with both $t\text{-ZrO}_2$ and $m\text{-ZrO}_2$ structures was used as initial parameters for the further calculation. After several iterations, the interference functions drawn with dotted lines in Fig. 3 were obtained. The RDFs calculated by the Fourier transformation of these interference functions are also shown with dotted lines in Fig. 4. The resultant parameters are summarized in Table 1 together with the crystalline zirconium oxides.^{22,23)} According to the O–O correlation, these parameters were fixed as suggested from $m\text{-ZrO}_2$ with 22% random vacancy model because the contribution of the O–O pairs are not significant as described above. Since that the variation of r and

Table 1. Structural parameters of the near neighbor correlations for amorphous ZrO_2 determined in the present work.

	Amorphous		Monoclinic		Tetragonal	
Density (Mg/m ³)	4.47		5.74		5.86	
<i>i-j</i> pairs	<i>r</i> (nm)	<i>N</i> (atom)	<i>r</i> (nm)	<i>N</i> (atom)	<i>r</i> (nm)	<i>N</i> (atom)
Zr-O	0.214	5.8	0.216	7.0	0.226	8.0
Zr-O	0.395	2.3	0.385	8.0		
Zr-O	0.427	5.4	0.444	12.0	0.413	12.0
Zr-O	0.465	6.3			0.448	12.0
Zr-O	0.495	4.1	0.490	8.0		
Zr-Zr	0.341	4.4	0.347	7.0		
Zr-Zr	0.371	1.6			0.366	12.0
Zr-Zr	0.398	2.5	0.415	3.0		
Zr-Zr	0.449	1.4	0.456	1.0		
Zr-Zr	0.509	2.1	0.524	6.0	0.519	6.0
O-O					0.265	6.0
O-O	0.296	7.4*	0.285	9.5		
O-O					0.344	8.0
O-O	0.398	7.4*	0.394	9.5		
O-O					0.439	12.0
O-O	0.486	4.3*	0.474	5.5		

* fixed

Fig. 5. Schematic diagrams of the atomic structure of amorphous ZrO_2 .

N depend upon the initial structural model, the parameters in Table 1 should be read as not unique but possible solution with respect to the structure of amorphous ZrO_2 . For convenience, the interatomic distances obtained by the present analysis is shown by the arrows in Fig. 4.²²⁾

The present results quantitatively indicate that the fundamental local ordering unit of amorphous ZrO_2 investigated in this work is octahedrally coordinated zirconium and its distance is 0.214 nm. About the first neighboring Zr-Zr pairs, a zirconium is surrounded by about four zirconium at about 0.34 nm forming a particular structural unit. With these facts, a three-dimensional structural model illustrated in Fig. 5 is proposed as one of the possible amorphous structures by considering the simple geometrical factors. This model indicates that the zirconium octahedra link each other with sharing four edges of coordination polyhedra. The other Zr-Zr pairs ranging from 0.39 to 0.45 nm are also well attributed in this structural model, although

Zr-Zr pairs at 0.37 nm can not be elucidated. Another structural model was suggested by Livage *et al.*,⁹⁾ which is also feasible in the sight of the Zr-Zr configuration except for its extraordinary bi-dimensional character. Present data could not allow to obtain the definite conclusion on the reliability of these two model.

Monomeric zirconium alkoxides are suggested to undergo hydrolysis condensation reaction to form the linear oxide alkoxide polymers in which ZrO_6 octahedra are connected with each other by sharing their edges, although the polymerization degree is related to the molar ratio of initially added water to alkoxide.²⁴⁾ The present results clearly indicate that the progress of the hydrolysis condensation process makes the structure of monomeric alkoxide more dense, so as to increase of the shared edge number of coordination polyhedra and that calculated shared edge length in structural model of about 0.26 nm is rather shorter than the estimated edge length of the regular zirconium octahedron. Consequently, the very distorted feature of zirconium octahedra is readily suggested in the structure of amorphous ZrO_2 .

Murase *et al.*⁵⁾ examined the crystallization of amorphous ZrO_2 produced by sol-gel method at various conditions, and suggested that the crystallization behavior of amorphous ZrO_2 strongly depends on the conditions of sample preparation. Therefore, it is difficult to determine which mechanism is actually significant in the formation of *t*- ZrO_2 from amorphous ZrO_2 . Nevertheless, the present results, at least, suggest that it is quite unrealistic to identify the local ordering structure of amorphous ZrO_2 to be responsible for the formation of *t*- ZrO_2 as frequently discussed in the previous works. Moreover, the usefulness of AXS method coupled with least-squares technique has also been suggested as one of the most powerful tools for characterizing the structure of multi-component disordered system.

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