

Structure Analysis Technology for Amorphous Materials by Synchrotron Radiation X-ray Measurements and Molecular Dynamics Simulations

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Structure analysis technology using X-ray measurements and molecular dynamics (MD) simulations has been established for amorphous materials such as optical fiber glass and diamond-like carbon thin films. X-ray scattering measurements using highly brilliant X-ray from synchrotron radiation was found very effective to obtain scattering spectra with a high signal to background ratio, despite the extremely small quantities of specimen. X-ray absorption fine structure (XAFS) was employed to investigate the local structure around trace elements in the materials. The synchrotron radiation was also useful in this analysis, due to its wide range of X-ray energy. MD simulations using optimized Born-Mayer type two-body potentials were performed to build structure models for the amorphous materials. These technologies were applied for erbium (Er) doped SiO₂ fibers (EDFs). The total and partial radial distribution functions from the MD simulations were found to reproduce the trends obtained by the X-ray experiments. In the EDF, aluminum (Al) is an effective co-dopant to improve the gain flatness as an optical amplifier. The structure analyses have clarified that the Al-doping expands the Er-O distance and increases the coordination number. The structure change is thought to lead to a variation in the electric field around Er³⁺ and in the Stark levels of Er 4f orbitals.

1. Introduction

Amorphous materials, such as optical fiber glasses and diamond-like carbon (DLC) thin films, are known to have so-called intermediate-range order (IRO) in their atomic structures. IRO is not the periodic structure that exists in crystalline, but a kind of structure order that exists in the distance of approximately 1nm. For instance, the silicate (SiO₂) glass, which is the principal ingredient in optical fibers, is composed of random network of SiO₄ tetrahedrons, as shown in Fig. 1. IRO can vary depending on the material composition or on the fabrication process conditions. The difference in the IRO is thought to affect the material properties.

Although the amorphous structure cannot be determined unambiguously like that of crystalline, the IRO can be modeled by combining analytical experiments with computer simulations. For instance, X-ray scattering and X-ray absorption fine structure (XAFS) are one of the most popular analysis methods for amorphous materials. From these analyses, we can obtain radial dis-

tribution functions (RDFs), $\rho(r)$, which correspond to the average number of atomic pairs that exist at radius between r and $r+\Delta r$. Regarding the simulation, molecular dynamics (MD) is often employed to build structure models, using appropriate interatomic potentials. The validity of the simulated models can be inspected by comparing the RDFs calculated from the models with those from X-ray experiments.

There are also some reports about the property calculation from simulated structure models of amorphous materials⁽¹⁾⁻⁽³⁾. However, either the structure analyses or property calculation has not been widely utilized in engineering, since they require highly advanced technologies.

Generally, in developing a new material, trial production needs to be carried out many times under a variety of process conditions, which are selected based on one's intuition and experience. This method is very useful especially to amorphous materials, to which structure analyses cannot be conducted easily. For quick development, however, it is necessary to reduce the number of trial productions, by establishing the technologies for structure analysis and property calculation.

In this study, we have developed the structure analysis technology for amorphous materials, combining X-ray scattering, XAFS, and MD simulations. In the X-ray measurements, we have utilized synchrotron radiation, which enables to analyze even very small quantity of optical fiber glasses and DLC thin films. We have also developed MD simulation technology using a pairwise potential function, in order to build structure models. We have successfully applied these analysis technologies to erbium-doped SiO₂ fiber (EDF), which is the key device in optical amplifier.

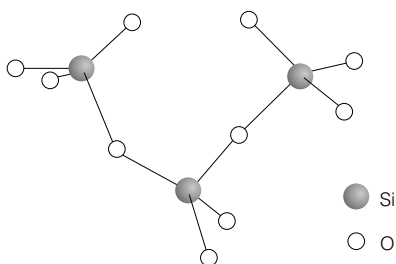


Fig. 1. Structure model of SiO₂ glass

2. X-ray Scattering Analysis

2-1 Outline ^{(4),(5)}

It is well-known that many sharp peaks corresponding to the Bragg reflections are observed in the X-ray diffraction spectrum of crystalline. On the other hand, several broad peaks so-called halos appear in the X-ray scattering spectrum of amorphous materials (see Fig. 2). RDFs can be obtained by normalization and Fourier-transformation of the scattering spectra. In the RDFs, the density of electron pairs, which corresponds to average numbers of atomic pairs, is plotted versus radius. Note that the higher concentration and the larger atomic number, the larger contribution an element has in the RDF by X-ray scattering.

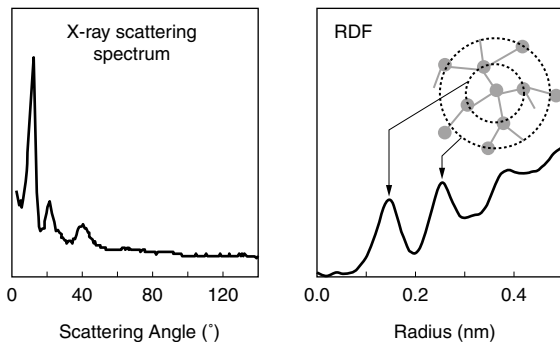


Fig. 2. Examples of X-ray scattering spectrum and RDF of amorphous materials

2-2 Synchrotron radiation X-ray scattering measurements

In the case of EDF and DLC, obtainable amounts of specimens are extremely small. For instance, the optical fiber core, whose diameter is approximately 15 μm , can be extracted by etching the outer layers of the coating resin and cladding glass. The mass of core glass specimen obtained from a 100 m long optical fiber is only some tens of mg. Things are the same in the DLC thin films, which can be collected by peeling off from substrates.

With such small amounts of specimens, only very weak scattering intensity can be obtained when using normal type X-ray source. To improve the signal to background (S/B) ratio in scattering spectra, it is effective to use a high flux X-ray source and to reduce the background in scattering measurements. In this study, we have attempted to utilize a synchrotron radiation for the X-ray source and to introduce some devices for the background reduction. The experiments were performed at SPring-8 in Japan, which is the world's largest third-generation synchrotron radiation facility, as a collaboration of five membership companies of Beam Line No.16 that is exclusive for Industrial Consortium ⁽⁶⁾.

Fig. 3 shows the outward appearance of the measurement system. The amorphous material specimen is crushed and crammed into a capillary or glass tube whose diameter is 1mm. An incident X-ray, whose height and width are trimmed by slits at 0.1mm and 1mm, respectively, goes through the capillary. The X-ray flux is

one billion times higher than that from commercially available rotating anode type X-ray sources. The X-ray is scattered by the specimen and detected by a scintillation counter, which is scanned from 5 to 140 degrees. A Soller slit is placed between the specimen and counter in order to improve the angle resolution of spectrum. For the background reduction, chambers for sample and Soller slit were substituted with helium (He) gas and low pressure tubes were placed for other X-ray paths.

Fig. 4 shows the X-ray scattering spectra of a DLC thin film. When using a rotating anode type X-ray source, no clear peaks have been detected in the spectrum. On the other hand, the combined use of synchrotron radiation X-ray source and background reduction has significantly improved S/B ratio.

We also performed X-ray scattering measurements for EDFs with different aluminum (Al) concentrations. Although Al is a well-known co-dopant that is effective to broaden and flatten the bandwidth of EDF for use as optical amplifiers, its mechanism has not been clarified

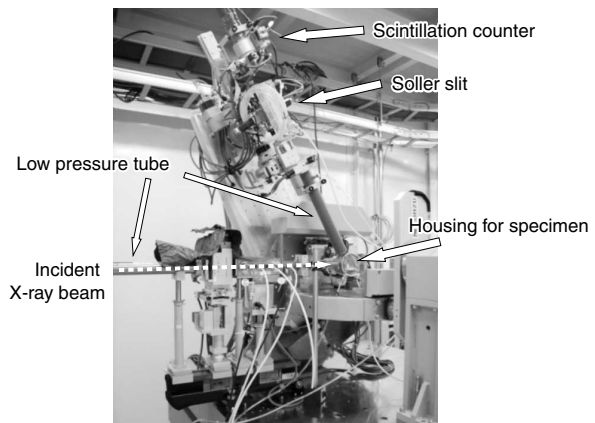


Fig. 3. Appearance of synchrotron X-ray scattering measurement system

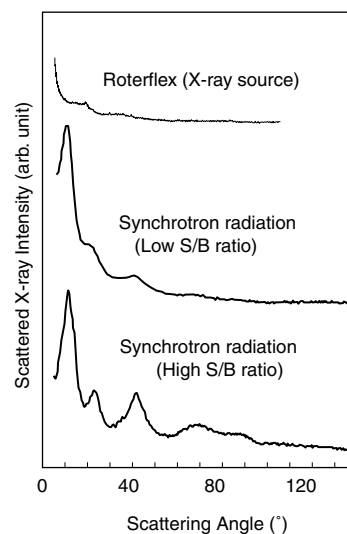


Fig. 4. X-ray scattering spectra of DLC at different measurement conditions

yet⁽⁷⁾. The results are shown in **Fig. 5**. No pronounced difference has been found between the two RDFs, which reflect mainly the SiO₂ amorphous network structure of each EDF. The RDFs demonstrate that the co-doping of several weight % Al does not affect so much the SiO₂ network structure.

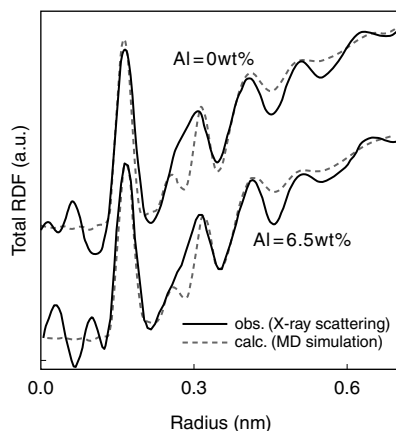


Fig. 5. Observed and calculated RDFs of EDFs with different Al contents

3. XAFS analysis

XAFS and X-ray scattering analyses complement each other. As described above, an RDF by X-ray scattering contains all atomic pairs in the analyzed amorphous material and usually has clear peaks for up to third neighboring atomic pairs. On the other hand, XAFS analysis can give an RDF for a particular element in the material, by tuning the incident X-ray energy for that element. In an RDF by XAFS, however, clear peaks are usually obtained only for first neighboring pairs. XAFS is very useful to analyze a trace element in a material, such as erbium (Er) in EDF, which cannot be detected by X-ray scattering.

Fig. 6 shows the schematic of XAFS analysis⁽⁸⁾. The X-ray absorption is measured by scanning the incident

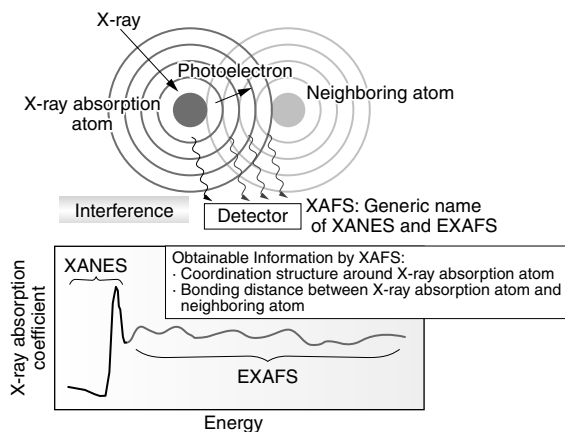


Fig. 6. Principle of XAFS

X-ray energy around the absorption edge of a target element. In some materials, the intensities of fluorescent X-rays or photoelectrons, which are equivalent to the X-ray absorption, are measured instead. X-ray absorption has an oscillation that reflects the local structure around the target element. An RDF can be obtained by Fourier-transforming of the absorption spectrum.

XAFS can be applied for not only amorphous materials but also crystalline, liquid, etc. The synchrotron radiation is useful also in XAFS, due to its high flux and wide energy range. We have succeeded in XAFS analyses for various kinds of materials, such as trace elements in indium phosphide (InP) semi-conductor and tungsten (W) ions in molten salt.

Regarding the XAFS analyses for EDFs, we reported in detail in the previous paper⁽⁸⁾. Some of the data are shown in **Figs 7 and 10**. It has been found that the Al doping extends the Er-O distance by approximately 0.03 nm and that the higher Al concentration leads to the larger Er-O coordination number. The results of X-ray scattering and XAFS analyses demonstrate that the major effect of Al doping is the change in local structure around Er⁽⁹⁾.

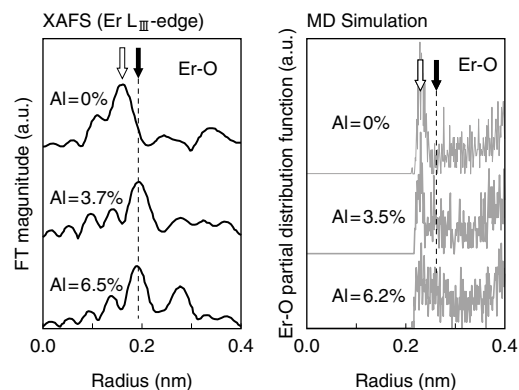


Fig. 7. RDFs for EDFs obtained from XAFS analyses and RDFs for Er-O portion obtained from MD simulations

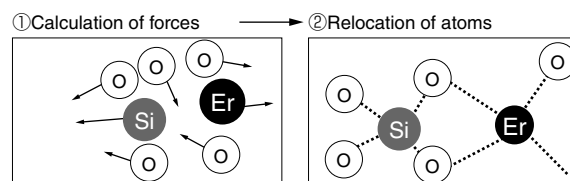


Fig. 8. Principle of MD simulations

4. MD simulation

4-1 Outline

MD simulations for amorphous materials usually proceed as follows (**Fig. 8**). First, the constituent atoms are randomly placed in a cell. In the case of an EDF,

3,002 atoms are placed in a cubic cell with a lattice constant of 3.57 nm, which corresponds to a density of 2.2 g/cm³. Then, (a) forces between all the atoms are calculated using interatomic potentials and (b) all atoms are moved by the forces during a very short time like 10⁻¹⁵ seconds. Steps (a) and (b) are repeated until the atoms arrive at a stable coordination in the cell under the given potentials.

The potentials affect significantly the reliability of simulated structure models. Although the strictest way is to use the first principal calculation, it takes too much time, even when a supercomputer is used. For the system containing more than 100 atoms, potential functions using empirical parameters are often employed at present.

Many authors have reported various types of potential functions^{(10),(11)}. Although some of them are regarded universally applicable and installed in commercially available MD software's, empirical parameters have not necessarily been optimized to be used for every material.

In this study, we attempted MD simulation for EDFs, using a conventional Born-Mayer type pairwise potential function. The potential parameters were optimized for EDFs and applied to the MD simulations. All these simulation analyses were performed by Professor Hiroyuki Inoue of the University of Tokyo, as a part of collaboration with Sumitomo Electric.

4-2 Optimization of MD potentials for EDF

Born-Mayer type potential can be written as follows:

$$\Phi(r) = \frac{e^2}{4\pi \epsilon_0} \frac{Z_i Z_j}{r} + B \exp\left(-\frac{r}{\rho}\right)$$

Here, e and ϵ_0 stand for the elementary electric charge and permittivity, respectively. The first and second terms of the right side correspond to coulomb's and repulsive interactions, respectively. Effective charges (Z_i , Z_j) and repulsive parameters (B , ρ) were optimized for the pairs of Si-O, Al-O, Er-O, etc, in an EDF. The effective charges were determined considering the number of valence electrons and the characteristic of each bond (ionic, covalent, or intermediate of them). B and ρ , which reflected the repulsive force and atomic size, respectively, were determined based on the stable bond

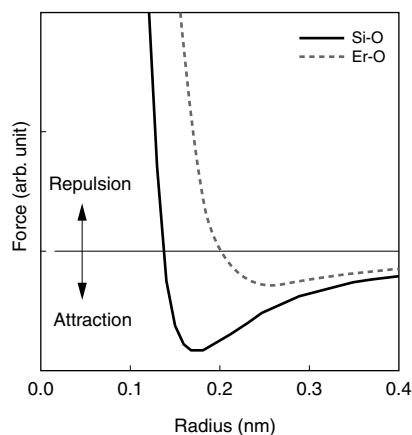


Fig. 9. Potentials of Si-O and Er-O pairs

length. The validity of these parameters was examined mainly by confirming the stability of crystal structures of similar compositions like Al₂SiO₅ under the potentials.

The forces between atoms can be obtained by differentiating the potentials. Fig. 9 shows the forces between Si-O and Er-O, which have their bottoms at 0.17 and 0.23 nm, respectively. These correspond to the stable distances of the atomic pairs.

4-3 MD simulation for EDFs

Using thus optimized potential parameters, the EDF structures of different Al concentrations were simulated. Then, the total and partial RDFs were calculated from the simulated models and compared with the results of the X-ray experiments.

The total RDFs by MD simulations are shown in Fig. 5, in addition to those by the X-ray scattering experiments. The simulated RDFs show a good agreement with the experimental ones. It has also been confirmed that the random networks of SiO₄ tetrahedrons are reproduced in the simulated models.

In Fig. 7, the partial RDF of Er-O pairs obtained from MD simulations are also shown. The trend of Er-O distance extension by Al doping, which was confirmed by the XAFS experiments, has been reproduced by the MD simulations. Another trend obtained by XAFS, regarding the Er-O coordination number increase by Al doping, has also been reproduced by the simulations, as shown in Fig. 10.

In conclusion, the MD simulations have qualitatively reproduced the results of both X-ray scattering and XAFS experiments for EDFs, though the results did not agree completely. The combination of the X-ray experiments and MD simulations allow understanding the three-dimensional structure of amorphous materials.

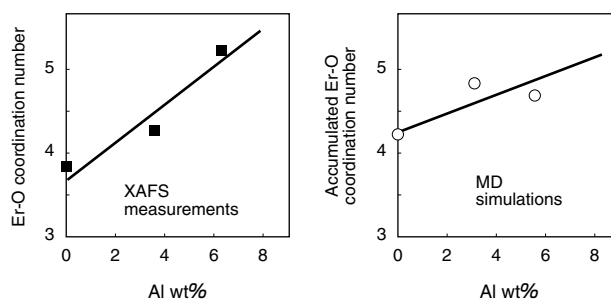


Fig. 10. Increase of Er-O coordination number by Al₂O₃-doping (Coordination numbers in MD simulation were obtained by accumulating up to 0.3nm radius.)

4-4 Discussion

It is of quite interest how the Al doping changes the local structure around Er and the optical properties of an EDF as an amplifier.

The further investigation of the simulated models shows that the local structure is affected by the second neighboring atom to Er (Fig. 11). Without Al doping, there are two types of second neighboring atoms: (a) one Si atom (Er-O-Si) and (b) two Si atoms (Er-O-Si₂).

Applying Al doping adds another type (c) one Si atom and Al atom (Er-O-(Si, Al)). The frequency of appearance of two Al atoms (Er-O-Al₂) was found to be extremely low in the simulated models. The Er-O distance in (c) is an intermediate between that of (a) and (b). Although many of the Al atoms are found to be in AlO₄ tetrahedron just like SiO₄ in the simulation, the effective charge of Al was supposed to be different from that of Si. Therefore, the extension of Er-O distance and increase in coordination number are considered to be caused by the difference in effective charges.

Regarding correlation with optical properties, it is well-known that the 1.55 μm fluorescence is due to transitions between Er4f orbitals. The energy levels of orbitals shift by Stark effect, depending on the electric field around Er³⁺. Electric field is significantly affected by the Er-O distance and coordination number. The local structure change by Al doping should cause a variation in electric field and Stark levels. This is seen as the change in the bandwidth of the optical amplifiers.

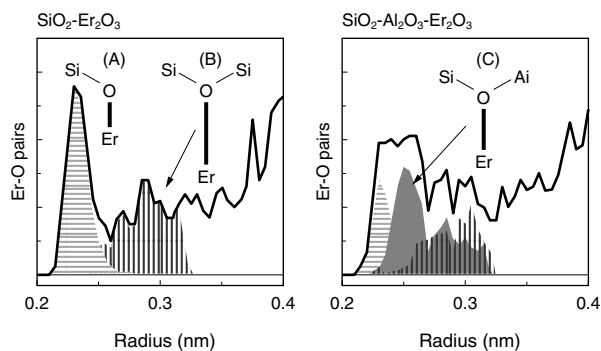


Fig. 11. Er-O coordination types classified by second neighboring atom

5. Conclusion

We have developed a structure analysis technology for amorphous materials by combining X-ray experiments with MD simulations. In the X-ray scattering analysis, even very small amount specimens of optical fiber and DLC thin film were successfully measured, using synchrotron radiation as X-ray source and some devices for background reduction. XAFS analysis is also found to be a very useful method for investigating the local structures of trace elements contained in amorphous materials. In MD simulations, the results of X-ray experiments for EDFs have been reproduced qualitatively, using the originally optimized Born-Mayer type potential parameters. From these results, the effect of Al doping on the local structure around Er in EDF was clarified.

As the next step, material properties such as optical emission of EDFs and friction coefficient of DLC thin films are now being calculated, using the simulated structure models. These technologies are expected to reduce the number of trial productions and promote the developments of innovative new materials in the future.

6. Acknowledgement

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Technical Terms

Radial Distribution Function (RDF):

RDF can be obtained by Fourier-transforming of observed X-ray or neutron scattering spectra. RDF corresponds to the average number of atomic pairs that exist at each radius.

X-ray Absorption Fine Structure (XAFS):

X-ray absorption is measured by scanning the incident X-ray energy around the absorption edge of a particular element. The absorption has an oscillation that reflects the local structure around the selected element. By Fourier-transforming of the absorption spectrum, RDF can be obtained.

Molecular Dynamics (MD)

In MD simulations, forces between atoms in a cell are calculated using interatomic potentials and the atoms are moved by the forces during a very short time like 10⁻¹⁵ seconds. These steps are repeated until the atoms arrive at a stable coordination under the given potentials. The potentials are of fundamental importance since they affect significantly the reliability of simulated structure.

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