## Local Structure Analysis of Zr in Zirconia-mullite Glasses Prepared by a Levitation Technique

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Obtaining "hard" and "crack-resistant" glasses have always been of great important in glass science and glass technology. However, in most commercial glasses both properties are not compatible. Recently, we have found that  $60Al_2O_3$ - $40SiO_2$  (mullite) glass prepared by a levitation technique had extraordinary high cracking resistance with high hardness<sup>[1]</sup>. The addition of ZrO<sub>2</sub> to the mullite glass suppressed the cracking resistance, however, increased elastic moduli drastically. With increasing ZrO<sub>2</sub> content in the glasses, the packing density increased, which is crucial for elastic moduli. To investigate the structural effect of ZrO<sub>2</sub> addition on mechanical properties, Zr  $L_{2,3}$ -edge XANES spectra were obtained.

Glass syntheses of  $xAl_2O_3$ - $yZrO_2$ - $zSiO_2(x + y + z =$ 10) ternary system were examined by a levitation technique. The sample name was abbreviated as AxZySz corresponding to the chemical composition. High purity  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> were stoichiometrically mixed and pressed into pellets. The pellets were sintered at 1000°C for 12 hours in air, and they were crushed to pieces as targets for an aerodynamic levitation furnace (ADL). Targets were placed on the nozzle of the ADL furnace and levitated by O<sub>2</sub> gas flow. A CO<sub>2</sub> laser was applied to melt the levitated sample. The melt was rapidly cooled to room temperature by turning off the laser power and then solidified. Glass formation was confirmed by Cu Ka X-ray diffraction measurements. Zr L-edge XAFS measurements (2150-2530 eV)

were performed at the soft X-ray beam-line, BL-10, in the SR Center of Ritsumeikan University. The incident X-ray was monochromated with a double crystal, using Ge(111) planes. Powdered samples were put on the carbon seal on the sample holder in high vacuum chamber. Fluorescence spectra were recorded with the total electron yield method. Photon energy was calibrated at the energy of a peak (2153.00 eV) of white line of P *K*-edge XANES spectra of FePO<sub>4</sub> standard samples. The spectra of ZrSiO<sub>4</sub>, monoclinic (*m*-)ZrO<sub>2</sub>, and Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> were also obtained as references.

The Zr  $L_{2,3}$ -edge XANES spectra of crystalline reference compounds and Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub> glasses are presented in Figure 1. The Zr  $L_{2,3}$ -edge XANES spectrum reflects the ligand field splitting of Zr 4d level and is sensitive to local structure distortion and oxygen coordination number of Zr atom<sup>[2,3]</sup>. ZrO<sub>n</sub> polyhedra are distorted in  $ZrSiO_4$ , and m- $ZrO_2$ , while symmetric in Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub>. Coordination number of Zr atom is eight for  $ZrSiO_4$ , seven for m-ZrO<sub>2</sub>, and six for Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub>. It is clearly seen that the spectra of glasses were almost the same and resembled that of m-ZrO<sub>2</sub>. This means that Zr atoms are sevencoordinated and the ZrO7 polyhedra are highly distorted in the zirconia-mullite glasses. Generally, Zr in conventional oxide glasses is six-coordinated, ZrO<sub>6</sub> is symmetric and often participates in network formation. The large coordination number and local structure distortion of Zr in the zirconia-mullite glasses correspond to the densely packed structure that increases elastic moduli. Furthermore, the energy of peak B' and D' of glasses are almost the same as that of m-ZrO<sub>2</sub>, while the peak A' and C' shifted to the higher energy side compared to that of m-ZrO<sub>2</sub>. It was suggested that the ligand field splitting of Zr in glasses is smaller than that of m-ZrO<sub>2</sub> and Zr-O length in glasses are relatively longer.



Figure 1. (a) Zr  $L_3$ -edge and (b) Zr  $L_2$ -edge XANES spectra of zirconia-mullite glasses and reference materials.

## References

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