

論文の内容の要旨

論文題目

Application of Electron Energy Loss Spectroscopy for Probing Local Structure
and Thermal Properties in Ceramic Materials

(電子エネルギー損失分光法によるセラミック中原子構造と熱物性の局所解析)

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Understanding structure-property of matter is of the essence in the field of solid state science. Materials characterization, especially, plays a central role for bridging structural information to the physical properties. While a variety of characterization techniques has been developed for decades, transmission electron microscope (TEM) remains as powerful method for structure determination because of its ultrahigh spatial resolution. Nowadays, atomic resolution image can be robustly obtained in crystalline materials by TEM with the support of spherical aberration corrector. Such improvement on image resolution has benefited a number of studies on crystalline defects, interfaces and nanomaterials. However, there remain two great challenges for the electron microscopy including structure determination of amorphous solids which lacks long-range periodicity, as well as the measurement of local thermal properties by microscopic techniques.

In this thesis, I aimed at overcoming these two issues by using electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). With this purpose, advanced EELS techniques were developed to investigate local structure and thermal properties of oxide ceramics.

In Chapter 1, general introduction of this work as well as theoretical background are described in this chapter.

In Chapter 2, the fundamental of EELS, the experimental methodology used in this dissertation, is introduced in this chapter. The origin of EELS signal and the excitations involved in varied energy range are described.

In Chapter 3, a novel method for local structural analysis for glasses is demonstrated using energy loss near-edge fine structure (ELNES) and vibrational EELS. With this method, local structural information including both cation and anion environments can be obtained in a real space with high spatial resolution. A phase-separated aluminosilicate glass (50%Al₂O₃-50SiO₂) has been chosen as a model system. The glass showed a phase-separated morphology, where Si-rich domains with size of 20nm is embedded in the Al-rich matrix. Using the fine structure of Al L_{2,3}-edge, spatial distribution of differently coordinated Al species is unraveled for the first time. The highly coordinated 5,6-fold Al species is found to form in Al-rich phase, while most Al sites in Si-rich phase remain 4-fold coordinated. This finding serves as the first real-space observation of local structure inside phase-separated glass and is in general agreement with simulated result from molecular dynamics (MD).

In addition to Al coordination, O coordination in a phase-separated region was also investigated by vibrational EELS. Local atomic vibration, Si-O stretching modes in particular, was successfully resolved at about 140 meV using monochromatic EELS. The real-space mapping of this stretching mode reveals the presence of triply coordinated O species in Al-rich phase, serving as the first direct evidence of O tricluster species in glasses since it was first proposed at 1980s. With cation and anion environment resolved from EELS experiments, structural model of phase-separated aluminosilicate glass can be made. Careful comparison of structural information from EELS and MD simulation allows us to suggest the possible origin of strong crack-resistance in a phase-separated aluminosilicate glass.

In Chapter 4, we developed a novel EELS technique for measuring local coefficient of thermal expansion (CTE) in bulk ceramics and grain boundaries (GBs). Temperature-dependent valence EELS was recorded in several oxide ceramics, in a temperature range between 373 and 973K. Using the peak shift of bulk plasmons induced by temperature change, CTEs of SrTiO₃ (STO), magnesium oxide (MgO),

yttria-stabilized zirconia (YSZ), aluminosilicate glass (4.9%Al₂O₃-95%SiO₂), and α -alumina (Al₂O₃), were successfully determined. The accuracy of EELS approach was confirmed as about 20% deviation from the bulk measurement. Furthermore, this technique was employed in a STO thin-film lamella to investigate thickness dependence of CTE. Our finding shows that CTE of STO increase almost linearly as the film thickness reduce below 110 nm.

The local CTE near STO GBs was also studied in chapter 4, since the presence of GBs often modify the CTE in polycrystals. Three STO bicrystals including $\Sigma 5$ (misorientation angle=36.87°), $\Sigma 13$ (22.6°) and 45° GBs were studied by STEM-EELS. About 1.6 times larger volume expansion is found near $\Sigma 5$ GB, while 45° GB, with micro-faceted morphology, shows a similar expansion behavior as bulk. Linear CTE of GB region can be obtained by considering the constraints of thermal strain normal and parallel to GB plane. In $\Sigma 5$ GB, CTE normal to GB plane is 3 times larger than that parallel to GB plane. By contrast, CTE of 45° GB remains isotropic in two directions. Furthermore, $\Sigma 13$ GB possesses a smaller CTE in the direction normal to GB plane, which is about half than bulk value. While the underlying mechanism for CTE enhancement or decline near GBs is not yet clear, this finding has an implication that CTE of polycrystalline ceramics might be tuned by the careful control of GB structure.

In Chapter 5, the general conclusion of the dissertation is given.

In summary, the dissertation is focused on two essential topics in materials characterization – structural analysis of amorphous solid as well as real-space mapping of physical quantity. By using advanced EELS techniques, both topics were achieved in ceramic materials with a nm-scale spatial resolution. In particular, we succeeded to resolve the local network structure in a phase-separated glass and measure the local thermal expansion in bulk ceramics and GBs. More importantly, the dissertation has demonstrated advanced EELS techniques possess the capability to build local structure-to-properties relationship in an atomic-scale regime, which has the potential to reshape, reform and rebuild our conceptions about matters fundamentally.