Identification of Ultra-Dilute Dopants in Ceramics

The properties of ceramic materials are strongly influenced by the presence of ultra-dilute impurities or dopants. The near-edge X-ray absorption fine structure (NEXAFS) method by the third-generation synchrotron can be a powerful tool for identifying impurities if a good theoretical tool for interpreting the spectra is provided. We have adopted a novel method to break the bottleneck for its wide application [1]. Local environments of a few 10 ppm levels of Ga in otherwise high-purity MgO ceramic samples were quantitatively examined by NEXAFS and the first-principles supercell calculation. Formation of Mg vacancy to compensate the extra charge of substitutional Ga at the Mg site is suggested by the analysis. It is then unambiguously confirmed by the combined study of positron lifetime measurements and plane-wave pseudopotentials calculations. The powerful combination of techniques with NEXAFS to identify the ultra-dilute dopant is fully demonstrated.

The experiments were carried out at beamline **BL01B1** with a bending magnet system with two mirrors and a fixed-exit double crystal monochromator utilizing Si (311) planes. X-ray fluorescence from the sample was detected by a 19-element Ge solid-state detector. Most of previous studies on ultra dilute samples in the literature used Si(111) planes in order to maximize photon flux. In the present study, we adopted Si(311) in order to achieve high energy resolution at the expense of reducing the photon flux. All measurements were carried out in air at room temperature.

In order to interpret NEXAFS and analyze the local environment of dilute dopants, reliable theoretical calculations of NEXAFS are necessary. It is true that a number of theoretical methods have been utilized to simulate the NEXAFS. However, there has been very little success in systematic and quantitative reproduction of NEXAFS for dilute dopants. We have adopted a novel method to break the bottleneck. In Fig. 1, experimental Ga-*K*-edge NEXAFS of β-Ga_2O_3 is compared with the theoretical spectrum obtained by an orthogonalized linear combination of atomic orbital (OLCAO) method [2] that is a first-principles band structure method. A large supercell composed of 120 atoms was used in order to minimize interactions among core holes. Since two kinds of different sites of equal numbers are present in the β-Ga_2O_3 crystal, two sets of initial and final states calculations for different

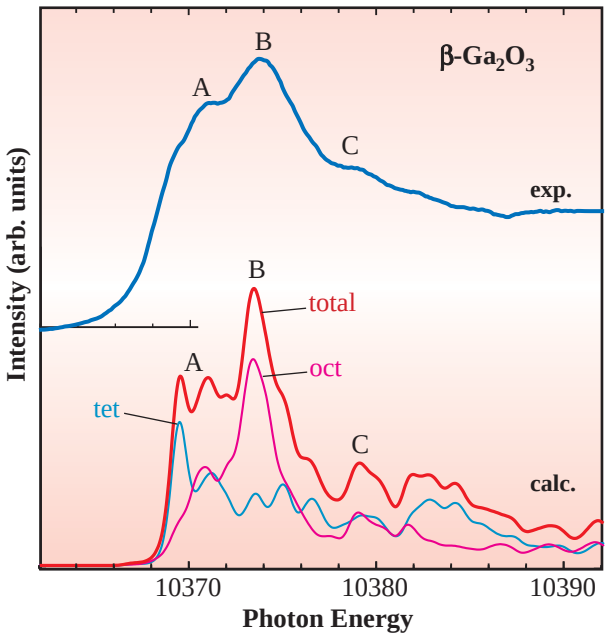

Fig. 1. Comparison of experimental and theoretical Ga-*K*-edge NEXAFS of β-Ga_2O_3. Theoretical spectra denoted by tet and oct correspond to spectra for Ga atoms at tetrahedral and octahedral sites, respectively. The sum of the two spectra is shown as total.

Ga sites were performed. The combined spectrum from the two sites shows excellent agreement with the measured one.

Local environments of 30 ppm Ga in otherwise high-purity MgO ceramic samples were identified by the combination of NEXAFS and the first-principles calculations. Three kinds of models as shown in Fig. 2 were constructed for Ga in MgO. Among them, Model 3 in which Mg vacancy is formed to compensate the extra charge of substitutional Ga at the 2nd nearest-neighbor Mg site shows best agreement with the experimental NEXAFS. The validity of the model is then confirmed by the combined study of positron lifetime measurements and plane-wave pseudopotentials (PWPP) calculations [3]. The formation energy obtained by PWPP calculation is found to be 0.05 eV per Ga atom smaller for Model 3 than that for Model 2. Model 1 shows a prohibitively high formation energy. All theoretical and experimental results show good consistency.

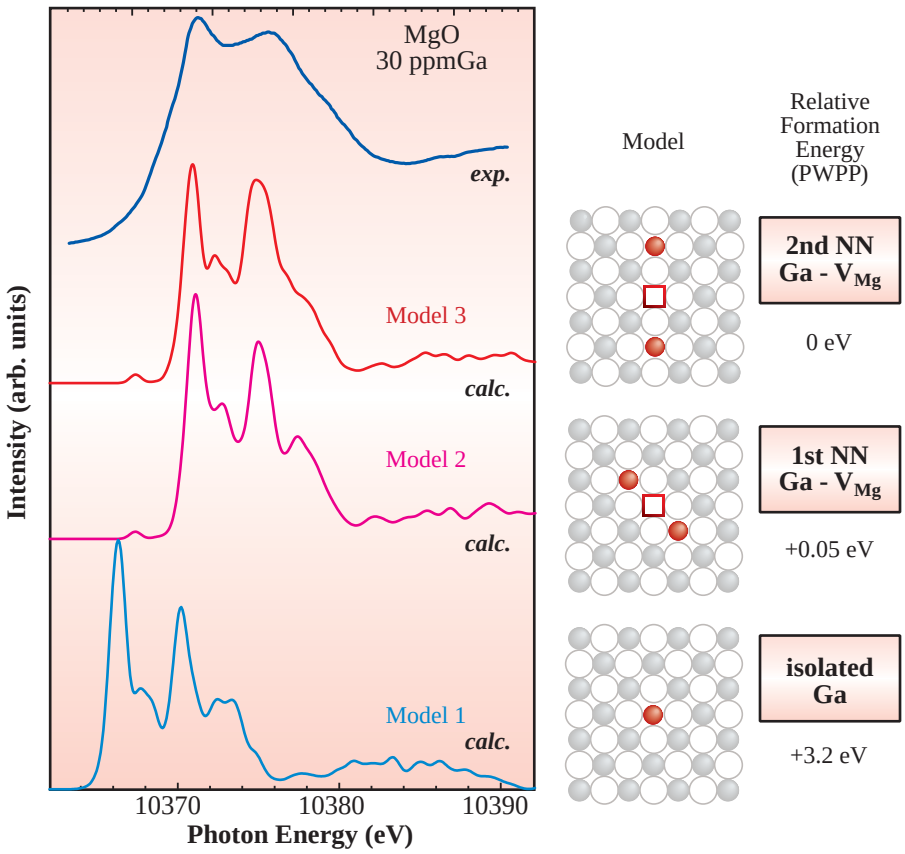

Fig. 2. Comparison of experimental and theoretical Ga-*K*-edge NEXAFS of Ga in MgO. Theoretical formation energies per Ga atom in MgO obtained by the PWPP calculations for the three models are shown together.

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