

Local environment analysis of Fe ions in BaMgSiO₄

Junya Kase, and Tomoyuki Yamamoto*

Faculty of Science and Engineering, Waseda University, Tokyo 169-8555, Japan

1 Introduction

Photochromism is a phenomenon that the reversible color change occurs by the light irradiation with specific wave length and/or heating. Although this phenomenon has been often observed in organic materials, some of the inorganic materials also show this phenomenon. Among these inorganic photochromic materials, it was found that BaMgSiO₄ shows photochromism [1], which is strongly enhanced by Fe-doping [2]. However, the mechanism of this enhancement has not yet been understood. In the current study, local environment of doped Fe ions in BaMgSiO₄ is studied by the X-ray absorption near-edge structure (XANES) measurements with the aid of the first-principles calculation.

2 Experiment

Samples were fabricated by the conventional solid state reaction method. Reagent grade high purity powders of BaCO₃, MgO, SiO₂ and α -Fe₂O₃ were used as starting materials, which were crushed and mixed in an agate mortar. Resultant powders were pressed into a pellet form, which were sintered in a reducing atmosphere (3% H₂ + 97% Ar) at 1473 K for 4 hours.

Fe-K XANES spectra of Fe-doped BaMgSiO₄ was observed at BL-12C, KEK-PF, in a transmission mode. Incident beams were monochromatized by the Si(111) double crystal. Samples were prepared by mixing with appropriate amount of BN, which were pelletized for XANES measurements. That of α -Fe₂O₃ was also observed for comparison.

3 Results and Discussion

Color change by the UV irradiation from white to purple and by heating from purple to white were examined repeatedly (Fig. 1). This color change was also confirmed by the UV-Vis measurements which showed that this cycle does not change after 10 cycles.

Observed Fe-K XANES spectrum of Fe-doped BaMgSiO₄ is shown in Fig. 2 together with that of α -Fe₂O₃. These two spectra show different profiles, which

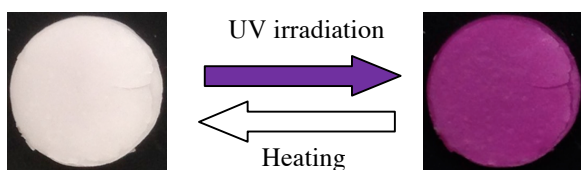


Fig. 1: Color of samples of as sintered one (left) and that after UV (254 nm) irradiation.

suggests that local environment of Fe ions is different in these two materials. However, this type of comparison does not tell us the local environment of the ions of interest, when we do not have a good fingerprint accidentally. Then the theoretical calculations are mandatory to analyze the profiles. Here we performed the first-principles DFT calculations using the full-potential augmented plane wave plus local orbital (FP-APW+lo) package, WIEN2k [3]. Three types of substitution models were constructed by replacing Ba, Mg and Si ions by Fe ion in the unit-cell of hexagonal structured BaMgSiO₄ with 42 atoms. Calculated XANES spectrum of Mg site model showed best reproduction of the experimental XANES spectrum. Hence it is concluded that the doped Fe ions are likely to substitute at Mg site.

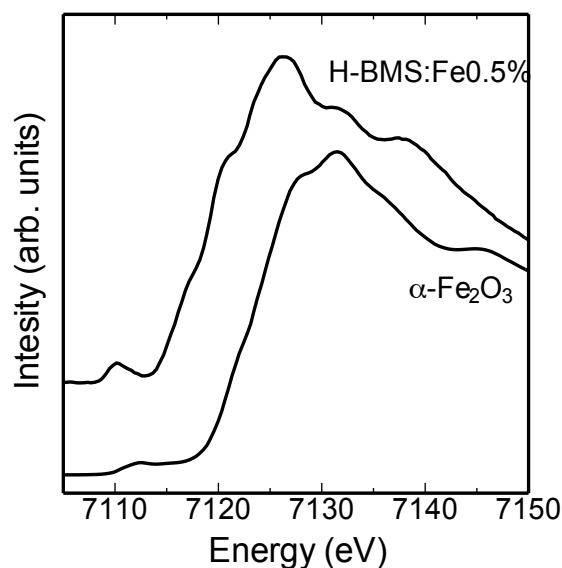


Fig. 2 Observed Fe-K XANES spectra of Fe-doped BaMgSiO₄ and α -Fe₂O₃.

References

- [1] M. Akiyama et al., J. Ceram. Soc. Jpn. 119, 105 (2011).
- [2] M. Akiyama, et al., J. Ceram. Soc. Jpn. 119, 338 (2011).
- [3] <http://www.wien2k.at>

* tymmt@waseda.jp