

The local structure of Co-doped ZnGa₂O₄

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We have investigated the local structure of a diluted Co-doped ZnGa₂O₄ semiconductor with the Curie temperature above room temperature. All the Co cations are doped in the octahedral Ga site, half of which is divalent and the others are trivalent. The Co dopants are surrounded by a large lattice disorder including oxygen vacancies and the local distortion.

1 Introduction

Zinc gallate ZnGa₂O₄ is a blue emitting phosphor [1] with the normal spinel structure where the divalent Zn atom is located in the tetrahedral site surrounded by four oxygens and the trivalent Ga cation is situated at the octahedral site with six oxygen anions. We attempt to dope Co ions in the octahedral site preferentially to fabricate a diluted magnetic semiconductor with the Curie temperature above room temperature. In the report we concentrate on the local structure of Co-doped ZnGa₂O₄ (Zn[Ga_{0.97}Co_{0.03}]₂O₄).

2 Experiment

ZnGa₂O₄ and Zn[Ga_{0.97}Co_{0.03}]₂O₄ were synthesized from powder oxides of ZnO with the purity of 5N, 5N Ga₂O₃ and 3N Co₃O₄ by the conventional solid state reaction [2]. A mixture of them milled for 5 hours and subsequently calcined at 1200 °C for 40 hours in air. We carried out X-ray powder diffraction, XAFS and SQUID magnetometry at room temperature to investigate the crystallographic structure, local structure and magnetic properties.

3 Results and Discussion

X-ray powder diffraction demonstrates that ZnGa₂O₄ and Zn[Ga_{0.97}Co_{0.03}]₂O₄ have the spinel structure (space group *Fd-3m*). The Rietveld analysis by FULLPROF [3] evaluates the lattice parameters $a=8.3332\pm 0.0001$ Å for ZnGa₂O₄ and $a=8.3309\pm 0.0002$ Å for Zn[Ga_{0.97}Co_{0.03}]₂O₄. Zn[Ga_{0.97}Co_{0.03}]₂O₄ has a small ferromagnetic component superimposed on a large paramagnetic contribution to the magnetization at room temperature, while ZnGa₂O₄ is diamagnetic.

Figure 1 represents the radial structure function of Zn[Ga_{0.97}Co_{0.03}]₂O₄ for Co, Zn and Ga K edges. It shows the following features below 3.5 Å. The function for Zn K edge consists of two peaks near 1.6 Å and 3.1 Å, while that of the Ga K edge has a peak near 2.6 Å in addition to 1.6 Å and 3.1 Å. The function for the doped Co K edge is quite similar to that of the Ga K edge. This is a direct evidence for the Co atom not in the tetrahedral Zn site but in the octahedral Ga site. Another feature is on the neighboring distance. Three peaks for the Co K edge are located closer to the central atom than those of the Ga K edge. This is especially prominent in the oxygen peak.

EXAFS analysis using Demeter [4] shows that the

distances from the central Zn and Ga atoms to the neighboring O, Ga and Zn ions for Zn[Ga_{0.97}Co_{0.03}]₂O₄ are same as those of ZnGa₂O₄ within the statistical error of 0.02 Å. On the other hand, Zn[Ga_{0.97}Co_{0.03}]₂O₄ shrinks the distances between the central Co ion and the O, Ga and Zn neighbors as compared with those of the central Zn and Ga atoms. Co ions in the octahedral Ga site reduce the neighboring O anions in number by about one. This means existence of the oxygen vacancy around the octahedral Co ions. The XANES measurement reveals that half of the Co cations is divalent and the others are trivalent in Zn[Ga_{0.97}Co_{0.03}]₂O₄. The charge neutrality contributes to the oxygen vacancy in substitution of Co²⁺ for Ga³⁺. In conclusion we find existence of a large local disorder including oxygen vacancies and local distortions around the Co dopants in Zn[Ga_{0.97}Co_{0.03}]₂O₄ [2].

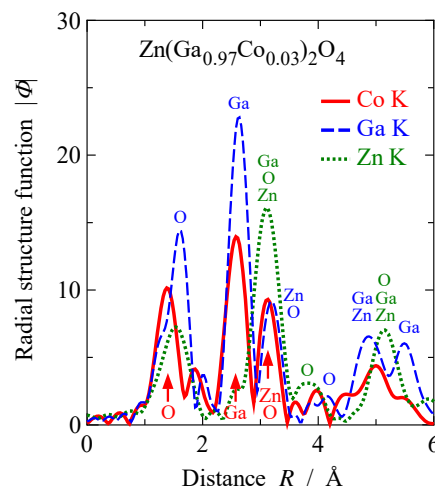


Fig. 1: Radial structure function of Zn[Ga_{0.97}Co_{0.03}]₂O₄ for each absorbing atom with assignment of scattering ions. .

References

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