7C, 12C/2002G267

Local structure around Ga in $MgIn_2O_4$:Ga by XAFS

Kei-ichiro MURAI, Hirotaka OHNO, Yoshinori MIKI, Ichiro NAKABAYASHI, and Toshihiro MORIGA*
Department of Chemical Science & Technology, Faculty of Engineering,
The University of Tokushima, Tokushima 770-8506, Japan

Introduction

The inverse-spinel type $MgIn_2O_4$ is well known as one of the promising transparent conducting oxide materials. The substitution of In^{3+} by Ga^{3+} in $MgIn_2O_4$ decreases its conductivity rapidly but enhances its optical band gap and transparency in visible region. Though $MgGa_2O_4$ also takes the inverse-spinel type structure, the $MgIn_2O_4$–$MgGa_2O_4$ binary does not always form solid solutions in the whole compositional range. $MgInGaO_4$ appears at around [Ga]/([In]+[Ga]) =0.5, where In^{3+} and Ga^{3+} ions occupy the octahedral and trigonal bipyramidal sites, respectively. This phenomenon is due to the fact that ionic radius of In^{3+} is larger than that of Ga^{3+}. In the system so diluted that Ga cations are not adjacent to the other ones through oxygens, it would be interesting to clarify the coordination states of Ga.

In this study, we have analyzed the local structure of Ga in $MgIn_2O_4$:Ga by fluorescent XAFS technique.

Experimental

The preparation procedure of $MgIn_2O_4$:Ga was essentially identical to that described earlier [1]. The amounts of doped Ga x varied from 0.01 to 0.1 in $MgIn_{2-x}Ga_xO_4$. The results of X-ray diffraction indicated that all the specimens had the inverse-spinel type structure free from impurities. The XAFS measurement was performed at BL–7C and BL–12C blanch lines with a Si(111) double crystal monochromator. The Ga K-edge EXAFS spectra were collected in a fluorescent mode using a Lytle-type detector. The programs *XAFS93* and *MBF93* were employed for the data analysis to determine local structure parameters [2].

Results and Discussion

Figure 1 shows compositional dependence of Ga–O bond length in $MgIn_{2-x}Ga_xO_4$. In the low x region (x=0.01 and 0.02), the bond length kept at the ideal 6-fold distance which can be calculated from the effective ionic radii determined by Shannon [3]. This phenomenon that Ga^{3+} ion would have a 6-fold coordination in the low x region gives a surprising impression because the larger In^{3+} ion have both octahedral 6-fold and tetrahedral 4-fold coordinations in the inverse-spinel type $MgIn_2O_4$. If Ga^{3+} ions will be distributed into the 6- and 4-fold sites homogeneously, the distance should be equal with hypothetical 5-fold distance of 1.94Å by XAFS.

However, it seemed that the bond length tend to shrink with an increase of Ga content, even though the

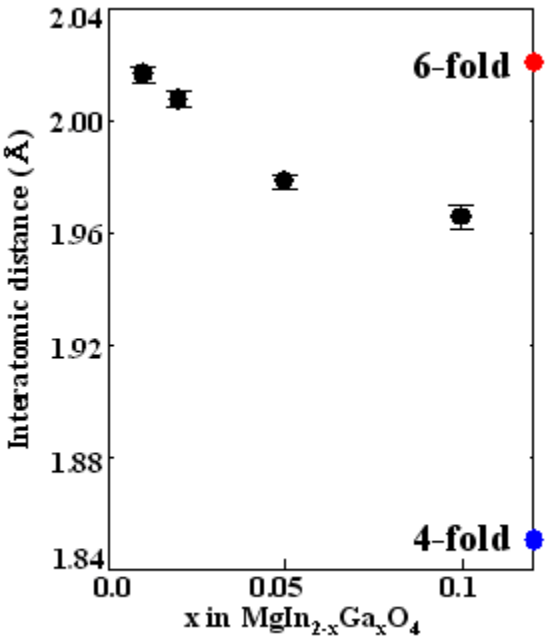

Fig. 1 The Ga–O distance in $MgIn_{2-x}Ga_xO_4$

coordination number of Ga by oxygen would be 6 or less. This shrinkage of the distance would result from two reasons. One is occupation of the tetrahedral 4-fold sites by Ga. The other is localization of oxygen vacancies around the octahedral Ga site. The transparent conductor $MgIn_{2-x}Ga_xO_4$ is an n-type semiconductor and intrinsic oxygen vacancies which will serve native electron carriers exist to some extent. As mentioned in the Introduction, Ga^{3+} ion is so small that oxygen vacancies will be located preferentially between two Ga^{3+} ion, that is Ga^{3+}–O^{2-}–Ga^{3+} pairs. As long as the concentration of Ga is dilute (*e.g.*, x=0.01 and 0.02), the Ga^{3+}–O^{2-}–Ga^{3+} pairs would be hardly formed.

References

[1] T. Moriga et al., J. Solid State Chem. 142, 206 (1999).
[2] H. Maeda, J. Phys. Soc. Jpn. 56, 2777 (1987).
[3] R.D. Shannon, Acta Cryst. A32, 751 (1976).

* moriga@chem.tokushima-u.ac.jp