

The valence of Co ions doped in In_2O_3 Ikuko Nakai^{1,*}, Ryohei Hisamatsu¹ and Yingjie Li²¹Department of Electrical and Electronic Engineering, Tottori University, Tottori, 680-8552, Japan²Inner Mongolia Normal University, Hohhot, 010022, China

We have made x-ray diffraction and XANES measurements to investigate the solubility of Co cations in a bixbyite type In_2O_3 . The solid state reaction at 1400 °C substitutes Co ions up to 7 mol% for trivalent In cations. Approximately half of doped Co cations are divalent and the other half are trivalent.

1 Introduction

Indium oxide In_2O_3 has a bixbyite type structure (space group $Im-3$), which is one of key materials for electronic applications such as thin film transistors [1] and gas sensing [2]. In these applications it is important to understand the states of the solid solution of In_2O_3 with the transition metal elements [3]. This motivates us to investigate the solubility of Co cations in In_2O_3 . In the report we focus on the effect of calcination temperature on the Co solubility from the view point of the valence state of Co ions doped in In_2O_3 as well as the crystallographic structure.

2 Experiment

We attempted to dope Co cations up to 20 mol% Co in In_2O_3 . Raw materials were powder oxides of In_2O_3 with the purity of 4N and 3N Co_3O_4 . They were mixed for 5 hours in a ball milling apparatus. We calcined the mixture at three temperatures such as 1000 °C, 1200 °C and 1400 °C for 40 hours in air. The sample thus obtained is referred to as $(\text{In}_{1-x}\text{Co}_x)_2\text{O}_3$. The reference compound CoO was made from calcination of Co_3O_4 at 1300 °C for 10 hours in air. Another reference YCoO_3 was synthesized using 4N Y_2O_3 and 3N Co_3O_4 by milling and subsequent firing at 900 °C for 40 hours in air. X-ray powder diffraction with a bright X-ray generator with rotating Cu anticathode and XANES measurements were carried out at room temperature to determine the crystallographic structure and the electronic states of $(\text{In}_{1-x}\text{Co}_x)_2\text{O}_3$.

3 Results and Discussion

X-ray powder diffraction shows as follows. The reference CoO has a NaCl-type structure (space group $Fm-3m$) and YCoO_3 shows a GdFeO_3 -type structure (space group $Pnma$). All the specimens of $(\text{In}_{1-x}\text{Co}_x)_2\text{O}_3$ ($0.03 \leq x \leq 0.20$) annealed at 1000 °C include some amounts of Co_3O_4 with the spinel structure (space group $Fd-3m$); in 1200 °C annealing the spinel reduces abruptly but still exists in a subtle amount. Co_3O_4 disappears completely by the oxidative calcination at 1400 °C, while CoO grows in the samples with Co more than 10 mol%. In other words, purely bixbyite type $(\text{In}_{1-x}\text{Co}_x)_2\text{O}_3$ with $0.03 \leq x \leq 0.07$ are synthesized by calcination at 1400 °C. The Rietveld analysis by FULLPROF [4] shows that the lattice parameter decreases with increasing Co content. This may come from substitution of a smaller Co ion for an In cation with a larger ionic radius.

Figure 1 shows XANES spectra near the Co K edge for $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ at different calcination temperatures. The Co cations in the reference CoO is in a divalent state while YCoO_3 possesses a trivalent Co ion. Co_3O_4 has both of Co^{2+} and Co^{3+} in the ratio of 1 to 2. The spectrum of $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ at 1000 °C is quite similar in shape to that of Co_3O_4 . This indicates that a firing temperature of 1000 °C is too low to dope Co cations in In_2O_3 . XANES of $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ at 1200 °C shifts to a lower energy side. This shows that some amounts of Co ions are substituted for In cations. As mentioned above, all the Co cations in $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ at 1400 °C are situated at the In sites. The energy of absorption edge for $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ at 1400 °C is located approximately halfway between that of CoO and YCoO_3 , which suggests that about half of Co cations substituted for In ions are divalent and the other half are trivalent.

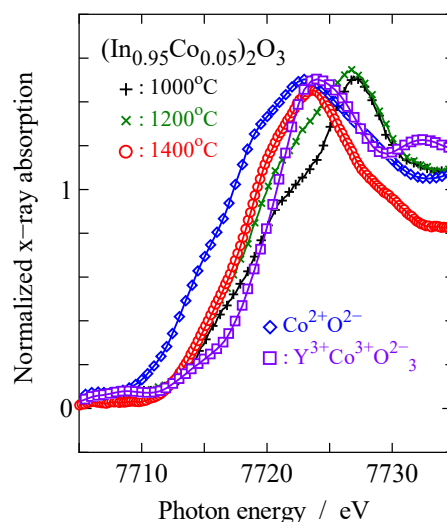


Fig. 1: Co K XANES of $(\text{In}_{0.95}\text{Co}_{0.05})_2\text{O}_3$ annealed at 1000 °C, 1200 °C and 1400 °C. The references CoO and YCoO_3 are also shown in comparison.

References

- [1] Z. J. Yuan *et al.*, *Thin Solid Films* **519**, 3254 (2011).
- [2] Y. F. Sun *et al.*, *Sensors* **12**, 2610 (2012).
- [3] C. Sena *et al.*, *J. Magn. Magn. Mater.* **387**, 165 (2015).
- [4] J. Rodriguez-Carvaja, *Physica* **B192**, 55 (1993).

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