เรียทเวลด์ของผงสังกะสีออกไซด์เจือด้วยโคบอลต์

Rietveld Refinement of Co-doped ZnO Powders

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บทคัดย่อ

สังกะสีออกไซด์ที่เจือด้วยโคบอลต์เตรียมขึ้นโดยวิธีบดย่อย ด้วยการผสมกันระหว่างผงสังกะสีออกไซด์กับโคบอลต์ออกไซด์ สารตัวอย่างที่เตรียมได้ถูกบดในอากาศ 24 ชั่วโมง โดยใช้ส่วนผสม $Zn_{1-x}Co_xO$ (x = 0, 0.01, 0.10, และ 0.20) ผลของโคบอลต์ในโครงสร้างของสังกะสีออกไซด์ที่เจือด้วยโคบอลต์นำไปศึกษาโดยใช้วิธีแบบเรียทเวลด์ ผลการวิเคราะห์แสดงให้เห็นว่า Co^{2+} เข้าไปแทนที่ Zn^{2+} ในโครงสร้าง wurtzite ของสังกะสีออกไซด์ แลตทิซพารามิเตอร์ลดลงเมื่อปริมาณโคบอลต์เพิ่มขึ้น สารตัวอย่างมีโครงสร้างเป็นแบบ wurtzite เฟสเดียวที่ปริมาณการเจือโคบอลต์ต่ำ (x = 0.01) และมีโครงสร้างที่สองแบบลูกบาศก์เกิดขึ้นที่ปริมาณการเจือโคบอลต์สูง (x = 0.1 and 0.2)

คำสำคัญ : เรียทเวลด์ เอกซ์เรย์ดิฟแฟรกชัน โครงสร้างผลึก สังกะสีออกไซด์เจือด้วยโคบอลต์

ABSTRACT

Co-doped ZnO powders were synthesized by the mechanical milling method with the mixture of ZnO and CoO powders. The mixed powder was milled in air for 24 hours to obtain the chemical composition of $Zn_{1-x}Co_xO$ (x = 0, 0.01, 0.10, and 0.20). The cobalt effect on the structure of Co-doped ZnO powders was investigated by the Rietveld refinement method. It was found that Co^{2+} ions substituted Zn^{2+} ions in the wurtzite-like ZnO structure. In addition, the lattice parameter was decreased with increasing the Co content. This may be attributed to the different radius between the ionic Co and Zn cations. The structure analysis showed that the low-doped sample (x = 0.01) was single phase of wurtzite-like ZnO structure whereas the high-doped sample (x = 0.1 and 0.2) showed the secondary phase CoO with cubic structure.

Keywords : Rietveld refinement, X-ray diffraction, Crystal structure, Co-doped ZnO

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INTRODUCTION

Zinc oxide is n-type semiconductor with a wide band gap of about 3.37 eV. The stable crystal structure of ZnO is wurtzite, in which each atom of zinc is surrounded by four atoms of oxygen in tetrahedral coordination. ZnO is a unique position among semiconducting oxide because of its transparent conducting properties and dilute magnetic properties. Semiconductors in which cations are partially replaced by transition metal ions are called dilute magnetic semiconductors (DMS). Recent theories predicted that the transition metal (i.e. Mn, Co, V, and Fe) doped ZnO diluted magnetic semiconductors exhibited ferromagnetic properties at room temperature. For example, Ueda et al. reported that the Co-doped ZnO film prepared by a pulsed laser deposition exhibited ferromagnetic behavior with a Curie temperature at the room temperature. Moreover, Lee et al. improved the Curie temperature of this material which grown by sol-gel method up to 350K. However, some reports failed to find ferromagnetism in ZnO-based semiconductors doped with ferromagnetic transition metal. The exact roles of cobalt in zinc oxide semiconductors and how it can improve dilute magnetic properties have not yet been clarified. Therefore, it seems very interesting to elaborate ZnO:Co in bulk form to better understand the origin of magnetism in these materials.

The Rietveld refinement is the well-known method of structure determination of polycrystalline materials. There are plenty of papers describing the theory and practical aspects of that method, applications of that procedure in structure determination, quantitative phase analysis, crystallite size and lattice strain determination and so on. In general, the Rietveld method uses the least-squares refinement for the receiving the best fit between the experimental data and the calculated pattern based on the simultaneously refined models for the crystal structure, diffraction optics effects, instrumental factors and others specimen characteristics which can be modeled.

The calculated intensities y_{ci} are determined by summing the contributions from neighbouring Bragg reflections plus the background:

$$y_{ci} = s\sum_{k} L_k |F_k|^2 \varphi(2\theta_i - 2\theta_k) P_k A + y_{bi}$$

where s is the scale factor, k represents the Miller indices, h, k, l for the Bragg reflection, L_k contains the Lorentz, polarization and multiplicity factors, φ the reflection profile function, P_k the preferred orientation parameter, A an absorption factor, F_k the structure factor for the kth Bragg reflection and y_{bi} is the background intensity at the ith step.

In this article, we investigated the crystal structure of $Zn_{1-x}Co_xO$ (x = 0, 0.01, 0.10, and 0.20) at room temperature. The sample was synthesized by the mechanical milling method and then characterized by X-ray diffraction. Rietveld refinement was also used to refine its structure, phase and lattice parameters.

MATERIALS AND METHODS

Sample preparation

The $Zn_{1-x}Co_xO$ samples (x = 0, 0.01, 0.10, and 0.20) were fabricated by the mechanical milling method. Zinc oxide powder (ZnO, 99.9% Aldrich), and cobalt oxide powder (CoO, 99% Aldrich) were used as starting materials. The powder mixture was milled in a polyethylene bottle with zirconia grinding media in ethanol for 24 h and then drying and sieving that reported by S. Sujinnapram et al.

X-ray data collection

The step-scanned diffraction data were measured on a Philips diffractometer using Cu-Kα radiation (λ = 1.5406 Å) operating at 40kV and 30mA. The divergence slit size was 1 mm and the receiving slit was 0.1 mm. The pattern was collected in the 20° < 2θ < 70° range with a step size of 0.02° and counting time of 1 seconds per step.

Structure solution and refinement

Automatic indexing of conventional X-ray powder diffraction data using the WinPlotr and TREOR90 programs suggested hexagonal cells with parameters *a* ~ 3.25 Å and *c* ~ 5.20 Å. Simulated X-ray powder patterns using the atomic coordinates of the Co-doped ZnO (space group $P6_3mc$) were very similar to the experimental patterns, and so this structure model was used for subsequent calculations. Rietveld refinement was performed using FULLPROF. In the refining process, wurtzite ZnO structure was selected as starting model structure. Co ions were assumed to incorporate into the ZnO lattice and occupy the Zn^{2+} cites. An experimentally determined $K\alpha_2/K\alpha_1$ ratio of 0.5 for the monochromator polarization correction and a Pseudo-Voigt profile shape function were used. The background was refined with a polynomial function. In the final cycles of the least squares refinements, the refined positional parameters and isotropic thermal parameters for the atoms were allowed to vary while the occupancy parameters for the atoms were held constant.

RESULTS AND DISCUSSION

The Rietveld refinement analysis of XRD data of Co-doped ZnO samples for different compositions are presented in Fig. 1. It was found that Co-doped ZnO samples were single phase with a wurtzite-like structure (space group $P6_3mc$) at low-doped sample (x = 0.01). The high-doped sample (x = 0.1 and 0.2) showed the secondary phase CoO with cubic structure. The crystal structure was obviously shown as x was between 0 and 0.01. This is because the Zn+2 ion site is

replaced by Co+2 ions. As x was above 0.01, the CoO peaks started to show up and became dominant as x was equal to or greater than 0.10. The "*c*" parameter was decreased with the increasing of the x composition. The same behavior was also observed in the "*a*" parameter. The increase in the x lattice parameter to 0.01 indicated that the sample was a homogeneous solid solution. This means that Co^{2+} replaces the Zn^{2+} by occupying the 2b crystallographic site. As x became greater than 0.01, the lattice parameters remained the same because of over solubility.

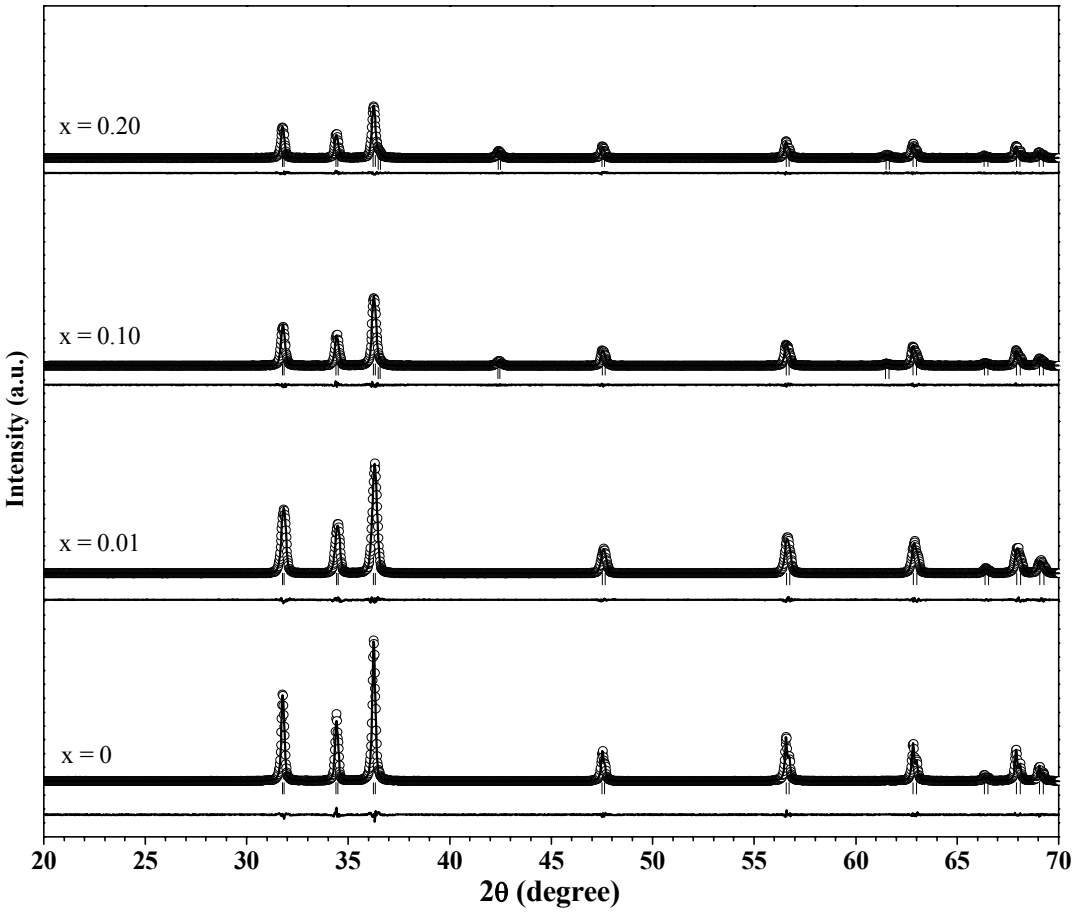

Figure 1 Experimental (o), calculated (solid line) and difference X-ray diffraction profiles for the Rietveld refinement of $Zn_{1-x}Co_xO$ (x = 0, 0.01, 0.1 and 0.2). The vertical tics below the all curve indicate that Bragg position.

Crystallographic data and details of the Rietveld refinement are given in Table 1. It was obvious that the agreement between the experimental data and the simulations was excellent since the R factor was small. Fig. 2 shows the crystal structure for $Zn_{1-x}Co_xO$ sample with the lower cobalt concentration.

Table 1 Parameters for data collection and structural refinements of $Zn_{1-x}Co_xO$ with x = 0, 0.01, 0.10, and 0.20.

	Composition			
	x = 0	x = 0.01	x = 0.10	x = 0.20
Cell parameters (Å)				
a	3.2523(5)	3.2515(1)	3.2513(4)	3.2512(6)
c	5.2107(3)	5.2093(8)	5.2088(6)	5.2088(7)
Volume ($Å^3$)	47.53(1)	47.67(2)	47.66(1)	47.69(6)
Number of reflections	22	20	20	20
Number of refined parameters	23	22	36	33
Zero point (° 2θ)	0.211(9)	0.014(4)	-0.019(2)	0.078(7)
Halfwidth parameters				
U	0.00232	0.00565	0.09404	0.02357
V	-0.04491	-0.01593	-0.11632	-0.03680
W	0.06509	0.01070	0.05322	0.02316
Rietveld reliability factors (%)				
R_p	5.46	5.84	7.53	8.29
R_{wp}	9.72	9.21	12.4	13.7
χ^2	1.45	1.77	1.31	1.26

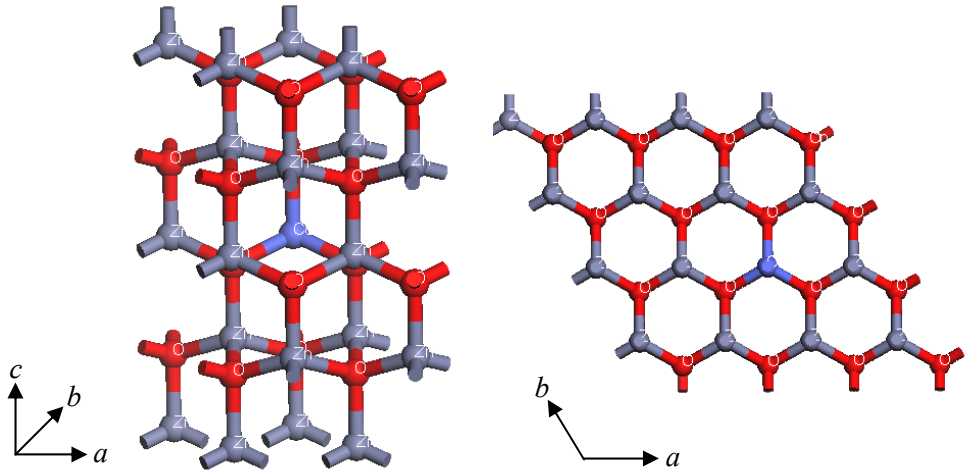

Figure 2 Crystal structure for $Zn_{1-x}Co_xO$ samples with lower cobalt concentration (x < 0.10).

CONCLUSIONS

The cobalt effect on the structure of Co-doped ZnO was investigated by the Rietveld refinement method. It was found that Co ions with a valence of +2 substituted Zn. The lattice parameter was decreased with increasing the Co content. This may be attributed to the influence of the different radius between the ionic Co and Zn cations. The structure analysis showed that the low-doped sample (x = 0.01) was single phase of wurtzite-like structure whereas the high-doped sample (x = 0.1 and 0.2) showed the secondary phase CoO with cubic structure.

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