Article title

Structure and Thermoelectric Transport Properties of Isoelectronically Substituted $(ZnO)_5In_2O_3$

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Running head

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Abstract for „*Chemical Abstract*" (not for paper)

We have proposed that homologous compounds of $(ZnO)_mIn_2O_3$ with layer structures can become candidate materials for high-temperature thermoelectric conversion due to their low thermal conductivity and high electron mobility. Crystal structures can be modified by the isoelectronic substitution of either divalent or trivalent metal ions for Zn or In ions, respectively. The substitution of Mg^{2+}, Co^{2+} and Y^{3+} gave rise to the shrinkage of c-axis and the elongation of a-axis of a hexagonal unit cell. Rietveld structure refinement indicated that Mg^{2+} and Co^{2+} ions occupy both 3a and 6c sites, while Y^{3+} occupy only 3a sites. An optimum amount of substitution of these cations increased electron mobility and hence the thermoelectric efficiency $Z=\sigma\alpha^2/\kappa$ (σ-electrical conductivity, α-Seebeck coefficient, κ-thermal conductivity). Z values coupled with lowered thermal conductivity, which was possibly caused by suitable modification of the electronic structure associated with distortion of the crystal structure. For instance, the figure of merit of $(ZnO)_5(In_{0.97}Y_{0.03})_2O_3$ was $Z = 1.3\times10^{-4}$ K^{-1}.

Keywords

crystal structure, Rietveld refinement, thermoelectric properties, Zinc oxide, Indium oxide, homologous series

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ABSTRACT

We have proposed that homologous compounds of $(ZnO)_mIn_2O_3$ with layer structures can become candidate materials for high-temperature thermoelectric conversion due to their low thermal conductivity and high electron mobility. Crystal structures can be modified by the isoelectronic substitution of either divalent or trivalent metal ions for Zn or In ions, respectively. The substitution of Mg^{2+}, Co^{2+} and Y^{3+} gave rise to the shrinkage of c-axis and the elongation of a-axis of a hexagonal unit cell. Rietveld structure refinement indicated that Mg^{2+} and Co^{2+} ions occupy both 3a and 6c sites, while Y^{3+} occupy only 3a sites. An optimum amount of substitution of these cations increased electron mobility and hence the thermoelectric efficiency $Z=\sigma\alpha^2/\kappa$ (σ-electrical conductivity, α-Seebeck coefficient, κ-thermal conductivity). Z values coupled with lowered thermal conductivity, which was possibly caused by suitable modification of the electronic structure associated with distortion of the crystal structure. For instance, substitution of 3% Y for In realized about one order of magnitude increase in Z up to $\sim 1.3\times10^{-4}\,K^{-1}$ at 1200 K. Substitution of small trivalent ions (Fe^{3+} for In^{3+}) shrank both c- and a-axis and deteriorated the properties.

INTRODUCTION

The homologous compounds $(ZnO)_mIn_2O_3$ (m = integer) show interesting properties suitable for specialized applications as a result of changes in the physical properties obtained by controlling the composition of materials composed of binary compounds. Minami *et al.* (1,2) and the present authors (3) reported that ZnO-In_2O_3 films prepared by means of r.f. magnetron sputtering are promising as transparent electrodes for solar cells and flat panel displays. Because of their high thermal stability and rather high electrical conductivity they should be advantageous for high-temperature thermoelectric applications (4,5). Kazeoka *et al.* (6) tried to improve the thermoelectric transport properties of $(ZnO)_5In_2O_3$ by partially substituting Y for In, and observed unusual behaviors of the thermoelectric transport properties : carrier density showed its minimum at x=0.03 in $(ZnO)_5(In_{1-x}Y_x)_2O_3$, while Seebeck coefficient and Hall mobility showed their maximum values. This was considered to be closely associated with the crystal structure of the compound.

Kasper (7) originally prepared $(ZnO)_mIn_2O_3$ (m = 2-5, and 7) and characterized it by recording X-ray powder diffraction patterns. Cannard and Tilley (8) analyzed $(ZnO)_mIn_2O_3$ (m = 4-5, 9, and 11) by high-resolution electron microscopy, and concluded that their structures were composed of metal-oxygen layers stacked perpendicular to the c-axis of the hexagonal crystal system having the space group of R3m for m = odd or $P6/_3$ mmc for m = even. Kimizuka *et al.* (9) synthesized single-crystals of $(ZnO)_mIn_2O_3$ (m = 3, 4, and 5) and took their Weissenberg photographs. They concluded $(ZnO)_mIn_2O_3$ to be isostructural with $(ZnO)_mLuFeO_3$ whose crystal structure had been determined by Isobe *et al.* (10) for m = 1, 4, 5, and 6 using a single-crystal X-ray diffraction technique.

We (11) already investigated the structures of $(ZnO)_5In_2O_3$ and $(ZnO)_5(In_{0.8}Y_{0.2})_2O_3$ using the Rietveld refinement technique on the basis of the space group $R\bar{3}m$. The basic structure was found to consist of InO_2^- and $(InZn_5)O_6^+$ layers alternately stacked along the c-axis. Y^{3+} ions were determined to occupy 3a-sites substituting for In^{3+} ions. Appropriate lattice distortion introduced by the elemental substitution was thought to cause a great change in the electronic structure and hence the conduction behavior. We tried to improve thermoelectric transport properties of $(ZnO)_5In_2O_3$ by substituting Mg or Co ions for Zn ions, and Fe or Y ions for In ions. We further studied their crystal structures using a Rietveld method to clarify the relationship between their thermoelectric properties and crystal structure.

EXPERIMENTAL SECTION

Sample Preparation

Starting powders of ZnO, In_2O_3, Y_2O_3, Fe_2O_3 (all 99.99% pure), and CoO and MgO (99.9% pure) were weighed in specific proportions to obtain the compositions given in Table 1 and were mixed in a ball mill for 24 h using zirconia balls and ethanol. The mixed powders were dried and heated at 1423 K for 6h in air. After having been cooled, they were crushed in the ball mill again for 24 h. The powders were dried and pressed into compacts under the isostatic pressure of 196 MPa, and then sintered at 1823 K for 2 h in air.

X-ray Diffraction Measurements

For the X-ray diffraction measurements the samples were pulverized in an agate mortar and pestle. Measurements were carried out by means of a Philips goniometer PW1820 equipped with a sample spinner, secondary graphite monochromator, and automatic divergence slit using Co-Kα radiation, and Cu-Kα radiation for the Co-substituted compounds. X-ray diffraction diagrams were recorded in Bragg-Brentano geometry from 4°(2Θ) to 130°(2Θ) with steps of 0.03°(2Θ). Measuring time was 10 s per step. Polycrystalline silicon was used for instrumental calibration. Observed diffraction patterns differed from that of the undoped compound, $(ZnO)_5In_2O_3$ (11) in reflection positions and intensities. They were proved to consist of a single phase only.

Rietveld Refinement

For the Rietveld structure refinement we used the PC-RIETVELD PLUS program (Philips) (12). The refinement was started using the structure data of the undoped compound $(ZnO)_5In_2O_3$ (11). Afterwards the Me-ions were located at Zn^{2+} and In^{3+} sites, respectively, with Me = Y, Mg, Co, Fe. The pseudo-Voigt function was used for the simulation of the peak shapes (13). Intensities within five times of the full width at half of maximum (FWHM) were considered to contribute to the reflection. Peaks below 42.5°(2Θ) were corrected for asymmetry effects after Rietveld (14). The analysis of powder patterns resulted in small preferred orientation effect along [001], which was corrected using the March model (15). The background was modelled by linear interpolation between 29 operator-selected points. At the first step, scaling factor, lattice constants, profile parameters, preferred orientation parameter and atomic coordinates were refined. The diffraction patterns of metal-substituted compounds differed only slightly from that of an undoped compound. As a result, the occupation numbers of Me-atoms allowed large standard deviations. For that reason the chemical composition was used as a constant in the refinement procedure. As observed in earlier studies (11) the occupation numbers of metal atoms correlate strongly making their independent refinement impossible. Consequently, they were located arbitrarily at the metal-sites M(1), M(2), M(3), and M(4), and the composition based on the resulting R-values permitted to determine the arrangement of atoms in the unit cell.

Table 2 gives the site occupancies and the resulting R-values for $(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$. From this we can conclude the arrangement of the atoms with the same occupancies at all the three 6c sites, which was proved to be realized for the other investigated compounds also. Due to a small atomic scattering factor of oxide ions in comparison with the metal ions, refinement of oxygen occupation numbers has produced different solutions. Therefore, they were fixed without assuming any vacancies. Further details and the refined structure parameters are given in Tables 3-A, 3-B and 4.

Thermoelectric Properties Measurements

The specimens for thermoelectric measurements were cut out of the sintered bodies into rectangular bars of 5 mm×5 mm×15 mm with a diamond saw. Heads of the two Pt-Pt 13% Rh thermocouples were embedded in the drilled holes at the ends of a specimen and they were fixed with platinum wires. Electrical conductivity was measured at 773-1123 K by a dc four-probe technique using each Pt leg of the thermocouple as a current lead. Two more Pt leads wound around the specimen were used to measure the voltage drop. For thermopower measurement, the temperature gradient in the specimen was generated by passing cool air in an alumina protection tube placed near the one end of the specimen. The temperature difference between the two ends was controlled to be 2-15 K by varying the flow rate of air. Thermopower measured as a function of temperature difference gave a straight line and the Seebeck coefficient was calculated from its slope. Carrier density and Hall mobility as functions of substituted ions, x, were obtained from the Hall effect measurement (van der Pauw method) carried out at room temperature. The temperature dependence of thermal conductivity for the sintered samples were measured by usual laser flash method (4).

RESULTS AND DISCUSSION

Figure 1 gives the rhombohedral unit cell of $(ZnO)_5In_2O_3$ which has been shown to be the basic structure of the investigated compounds with Me-ions (Me = Mg, Co, Fe, and Y) to be located at the metal sites M(1), M(2), M(3), and M(4), respectively (see Table 5). Mg^{2+} and Co^{2+} -ions were determined to be arranged at the 3a (M(1))-site and 6c (M(2), M(3), and M(4))-sites substituting for Zn^{2+}-ions, while Y^{3+}-and Fe^{3+}-ions occupy 3a-sites only substituting for In^{3+}-ions. In the case of Mg- and Co-doped compounds site occupancies at M(1) are almost fixed even if fractions of substituted ions are changed, but those of M(2), M(3), and M(4) vary a lot with the change in the substituted fraction. Mg and Co-ions are considered to easily occupy M(1) compared with other sites. Besides, M(2), M(3), and M(4) will be occupied after these ions cannot enter M(1) anymore. The M(1) site occupancies of Co-substituted compounds are slightly larger than that of Mg-substituted compounds. Obviously Co-ions are easier to occupy M(1) than Mg-ions. Fe-substituted compounds have been characterized by a larger quantity of Fe-ions to be arranged at 3a (M(1))-site possibly caused by the smaller ionic radius of Fe^{3+}-ions (550pm) compared with those of Co^{2+} (650pm), Mg^{2+} (720pm), Zn^{2+} (740pm), In^{3+} (810pm), and Y^{3+} (920pm) (18).

Figures 2 and 3 give the lattice constants and the unit cell volume as derived from Rietveld refinement. Fe-substituted specimen shrank in both a-axis and c-axis directions with an increasing amount of substituted Fe because of its small ionic radius. In contrast, partial substitution of Mg, Co, and Y all showed a common tendency that a-axis expanded and c-axis shrank. The unit cell volume of the Mg-, Co-, and Fe-substituted compounds were found to be smaller than that of the undoped compound because of their small ionic radii. In Table 5 are listed the distances between the metal oxide layers perpendicular to the c-axis of the unit cell calculated on the basis of the atomic positions (see Table 3). As previously supposed by Kazeoka *et al.* (6) for the Y-substituted compounds, octahedral voids of InO_2^- layers expand and tetrahedrons of $(InZn_5)O_6^+$ layers shrink along c-axis. By contrast in the Co-, Mg-, and Fe- substituted compounds voids of InO_2^- layers shrink whereas the interior tetrahedrons of $(InZn_5)O_6^+$ layers slightly expand.

Temperature dependences of both electrical conductivity and Seebeck coefficient were observed to be all similar for the substituted specimens, thougth their absolute values differed greatly depending on the kind of substituted ions. Figure 4 shows the Seebeck coefficient and the electrical conductivity measured at 1073 K as a function of substituted ions, x. For all samples with $x > 0.05$ the electrical conducivity decreased gradually with increasing amount of substituted ions for all the invesigated cases, which is obviously caused by electron scattering on an increasing with number of defects in crystal structure. Seebeck coefficients were always negative hinting the investigated compounds were *n*-type semiconductors. Seebeck coefficient of Mg- and Co-substituted compounds showed a maximum at x=0.005 and that of Y-substituted compound at x=0.03. On the other hand, Fe substitution gave rise to a decrease in the Seebeck coefficient with a minimum at x=0.01. Accordingly, power factor ($\sigma \ \alpha^2$) showed an extremum at corresponding x-values (Figure 5). Site occupancies of Mg and Co at M(1) become maximum (0.08) when a fraction of substituted ions is x=0.016, and a falling gradient of power factor becomes gentle at this point (x=0.016). Furthermore, power factor becomes maximum, when metal ions occupy M(1) position only and when they occupy about one third of the maximum site occupancy of metal atoms at M(1). In the case of Y- and Co-substituted compounds the carrier density decreases with increasing amount of substituted ions showing an absolute minimum which coincides with the composition to give the largest power factor at high temperatures (Figure 6). At the same time Hall mobility showed a maximum, which is the case for the Mg-doped compounds also. For the Fe-substituted compounds inverted behavior was observed. In general, the unusual behavior of thermoelectric transport properties is supposed to be caused by the site occupancy of metal ions at M(1)-site and the changes in structure, namely distortion of crystal lattice giving rise to changed electronic structure and scattering behavior of carriers. However, fundamental understanding of structure-property relations requires calculation of the electronic structure which would be useful also for the purpose of further improving the thermoelectric properties in this system through certain effective and appropriate partial substitutions. Figure 7 shows the temperature dependence of thermal conductivity for the sintered samples with the compositions $(ZnO)_5In_2O_3$, $(Zn_{0.995}Mg_{0.005}O)_5In_2O_3$, and $(ZnO)_5(In_{0.97}Y_{0.03})_2O_3$. As a result of structural disorder caused by substitution of Mg- and Y-ions the corresponding compounds showed ~ 60 % and ~30 % lower thermal conductivity than that of an undoped compound. Consequently, the largest figure of merit obtained in this system was Z = 1.3×10^{-4} K^{-1} for $(ZnO)_5(In_{0.97}Y_{0.03})_2O_3$ (6). This value is substantially large compared to other *n*-type oxide materials. This system is considered to be one of the promising materials for the purpose of thermoelectric energy conversion (19). Hence for the purpose of improving the thermoelectric properties further in this system through certain effective and appropriate partial substitutions (i.e. expand to a-axis and shrink to c-axis), it is necessary to analyze the electronic structure–property relations associated with the site occupancies of substituted ions in the crystal lattice.

CONCLUSIONS

The crystal structure of isoelectronically substituted $(ZnO)_5In_2O_3$ compounds was analyzed using the Rietveld method. In addition the thermoelectric transport properties were measured as a function of fraction of substituted ions. The elemental substitution introduces an appropriate lattice distortion leading to a great change in the conduction behavior. The unusual behavior of thermoelectric transport properties is supposed to be caused by the site occupancy of metal ions at M(1)-site. However, detailed discussion of structure-property correlations in $(ZnO)_5In_2O_3$ requires calculation of the electronic structure.

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Figure captions

FIG. 1. Crystal structure of $(ZnO)_5In_2O_3$ as derived from Rietveld refinement (space group R$\bar{3}$m).

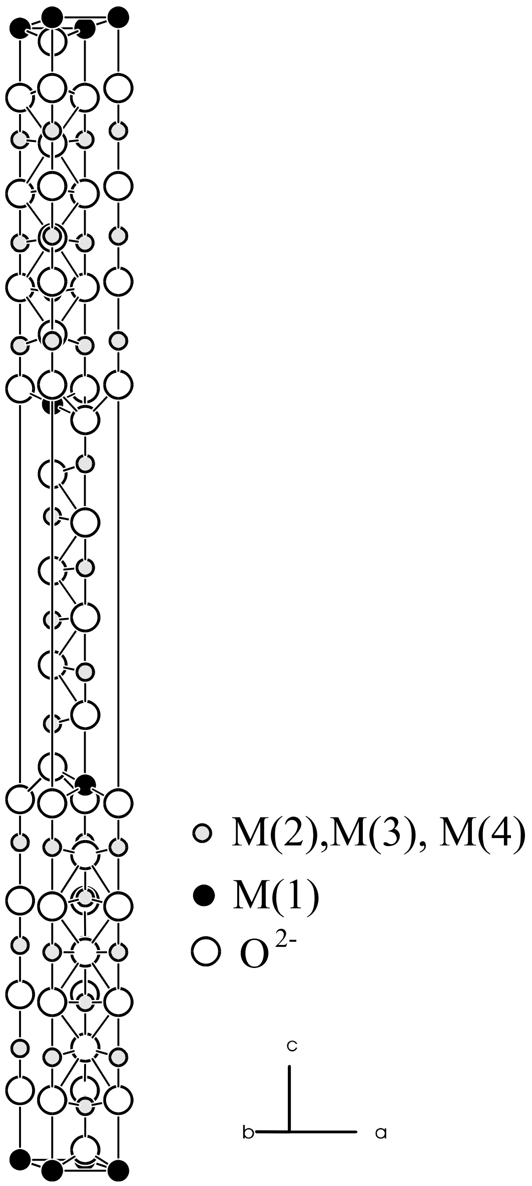


FIG. 2. The relationship between lattice constant and x for $(ZnO)_5(In_{1-X}Y_X)_2O_3$, $(Zn_{1-X}Mg_X)_5In_2O_3$, $(Zn_{1-X}Co_X)_5In_2O_3$, $(ZnO)_5(In_{1-X}Fe_X)_2O_3$, $(Zn_{0.9}Mg_{0.1})_5(In_{1-X}Y_X)_2O_3$, and $(Zn_{0.9}Co_{0.1})_5(In_{1-X}Y_X)_2O_3$.

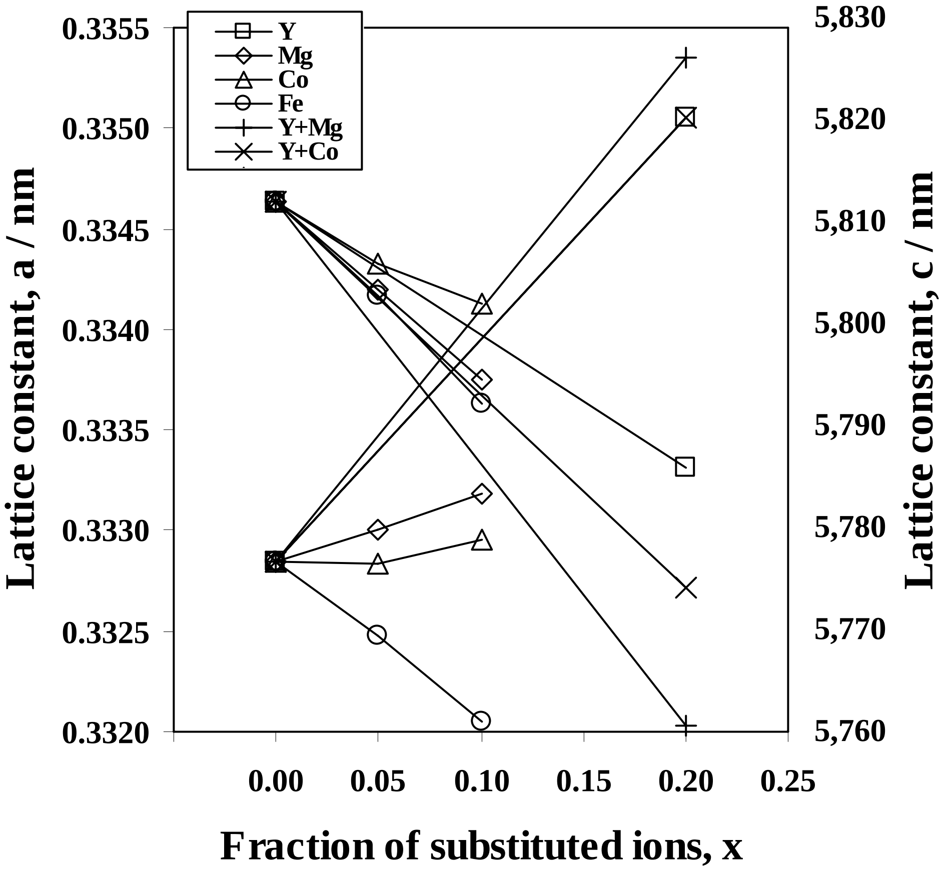
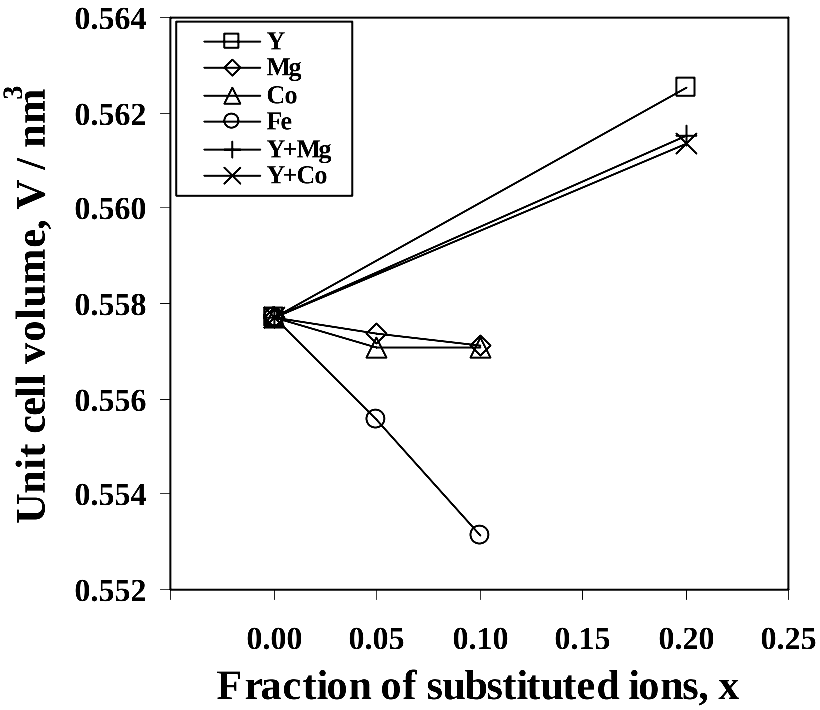


FIG. 3. The relationship between unit cell volume and x for $(ZnO)_5(In_{1-X}Y_X)_2O_3$, $(Zn_{1-X}Mg_X)_5In_2O_3$, $(Zn_{1-X}Co_X)_5In_2O_3$, $(ZnO)_5(In_{1-X}Fe_X)_2O_3$, $(Zn_{0.9}Mg_{0.1})_5(In_{1-X}Y_X)_2O_3$, and $(Zn_{0.9}Co_{0.1})_5(In_{1-X}Y_X)_2O_3$.



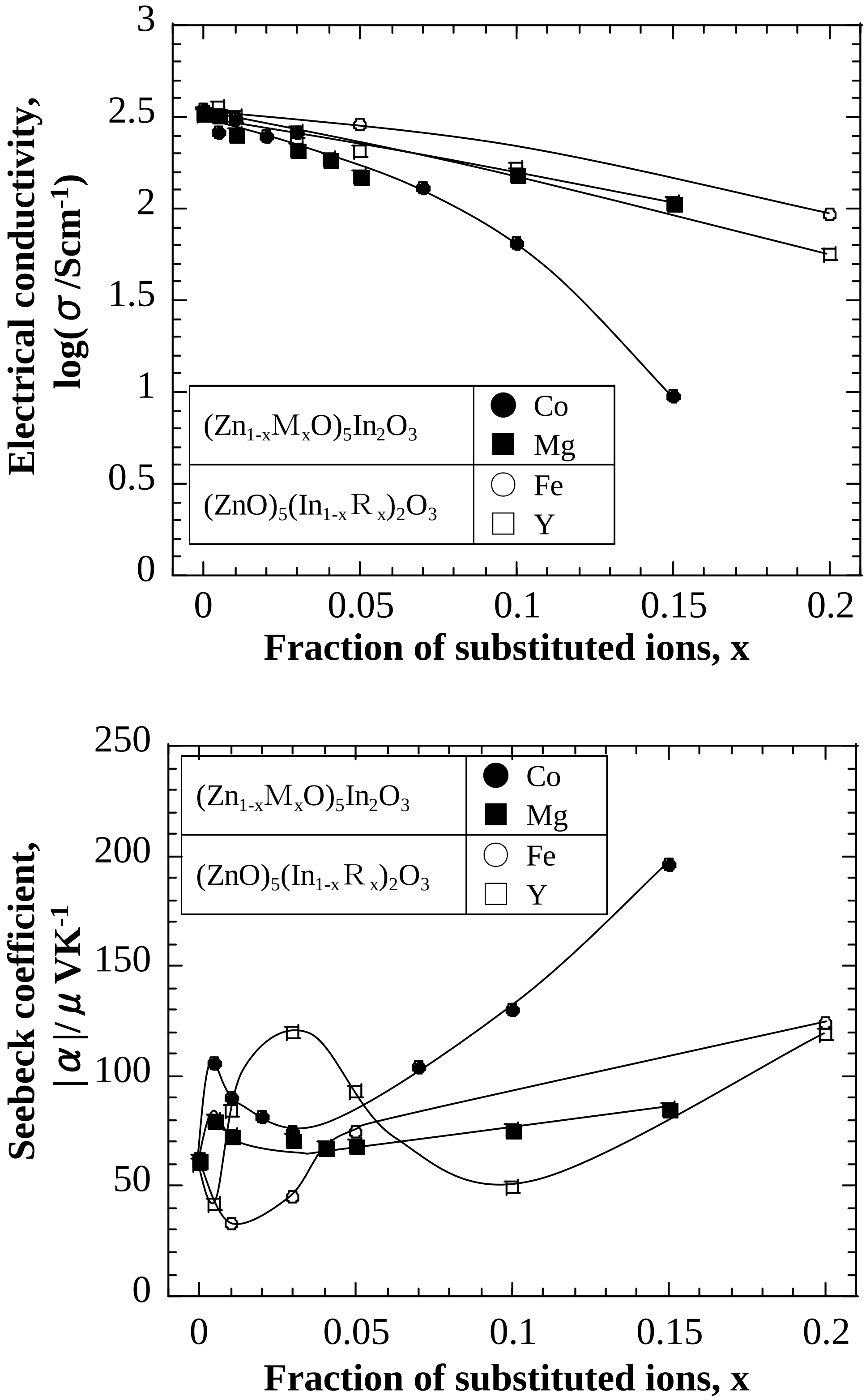


Fig. 4. Plots of electrical conductivity and Seebeck coefficient as functions of amount of substituted ions,x, at 1073K.

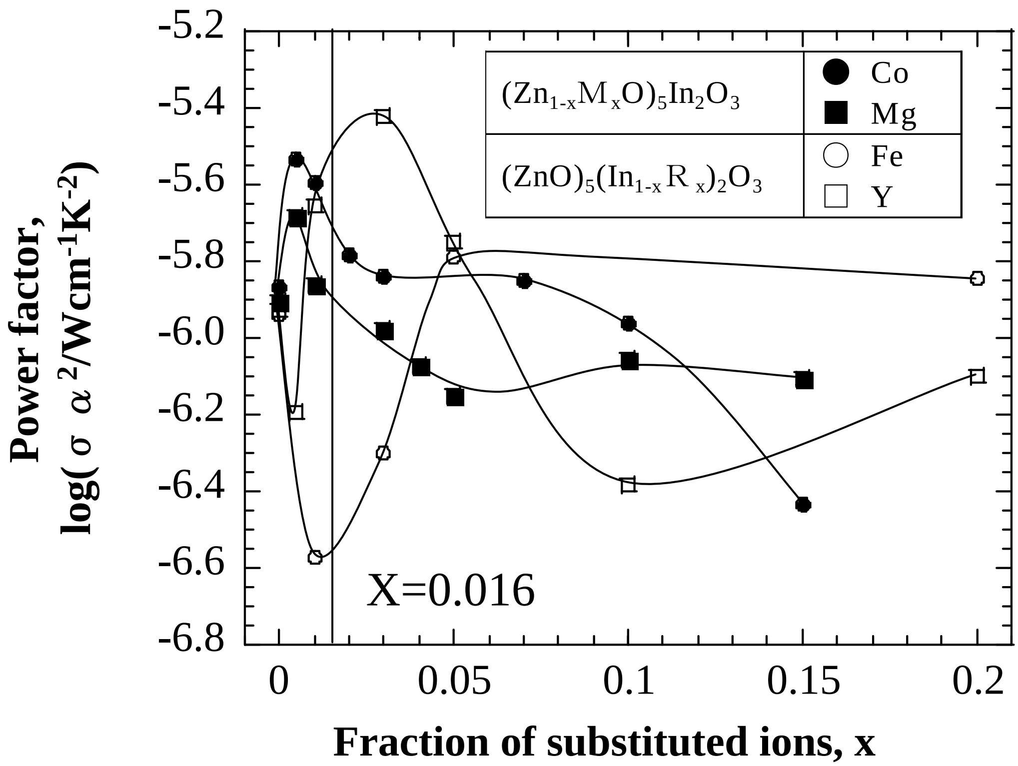


Fig. 5. The relationship between power factor and x for $(ZnO)_5(In_{1-X}Y_X)_2O_3$, $(Zn_{1-X}Mg_X)_5In_2O_3$, $(Zn_{1-X}Co_X)_5In_2O_3$, and $(ZnO)_5(In_{1-X}Fe_X)_2O_3$.

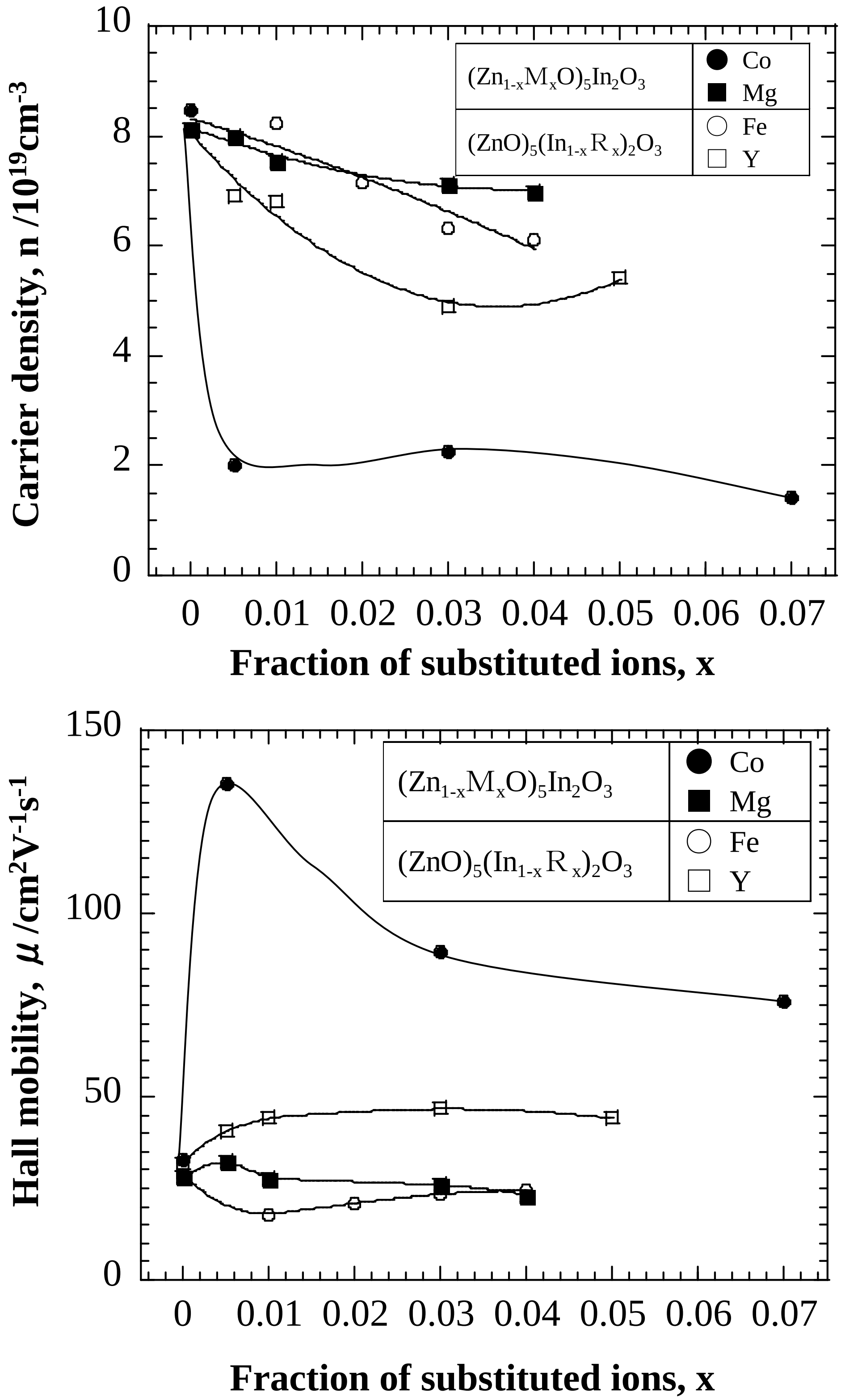


FIG. 6. Plots of carrier density and hall mobility as functions of the amount of substituted ions, x, at room temperature.

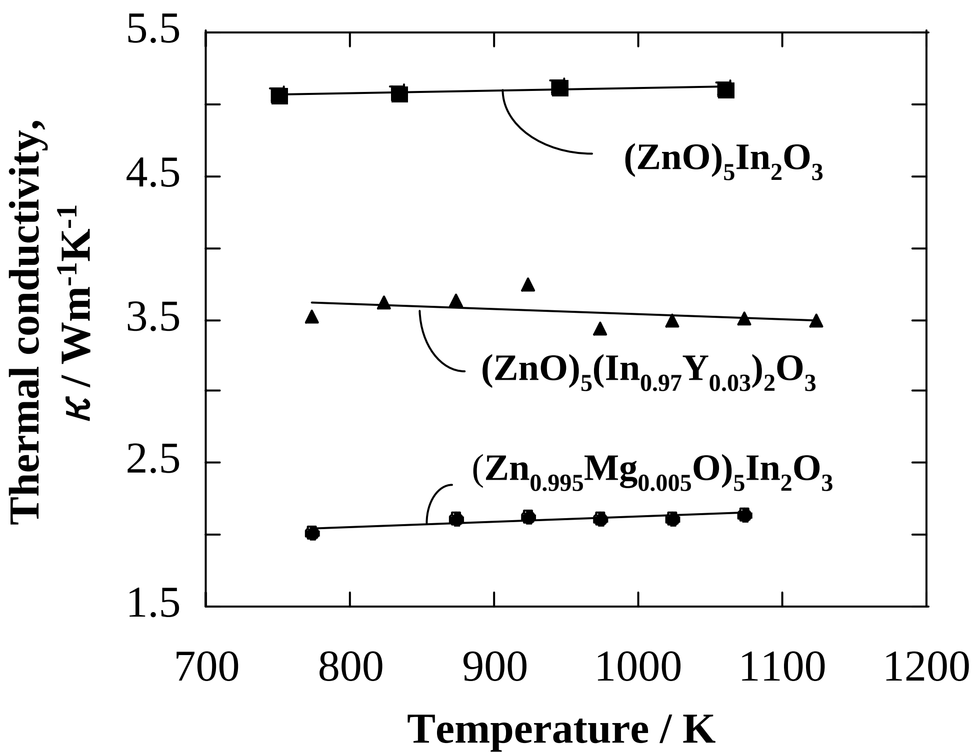


FIG. 7. Temperature dependence of Thermal conductivity, κ of the sintered samples with the compositions (Zn0.995Mg0.005O)5In2O3, (ZnO)5(In0.97Y0.03)2O3 and (ZnO)5In2O3.

Table captions

TABLE 1

Chemical compositions of the samples analyzed by the Rietveld method.

No.		Me (Mg, Co, Fe)	Y	Zn	In	O
	$(ZnO)_5\ In_2O_3$	-	-	0.333	0.133	0.533 [a]
	$(ZnO)_5\ (In_{0.8}Y_{0.2})_2O_3$	-	0.027	0.333	0.107	0.533 [a]
1	$(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$	0.033	-	0.300	0.133	0.533
2	$(Zn_{0.95}Mg_{0.05}O)_5In_2O_3$	0.017	-	0.317	0.133	0.533
3	$(Zn_{0.9}Co_{0.1}O)_5In_2O_3$	0.033	-	0.300	0.133	0.533
4	$(Zn_{0.95}Co_{0.05}O)_5In_2O_3$	0.017	-	0.317	0.133	0.533
5	$(ZnO)_5(In_{0.9}Fe_{0.1})_2O_3$	0.013	-	0.333	0.120	0.533
6	$(ZnO)_5(In_{0.95}Fe_{0.05})_2O_3$	0.007	-	0.333	0.127	0.533
7	$(Zn_{0.9}Mg_{0.1}O)_5(In_{0.8}Y_{0.2})_2O_3$	0.033	0.027	0.300	0.107	0.533
8	$(Zn_{0.9}Co_{0.1}O)_5(In_{0.8}Y_{0.2})_2O_3$	0.033	0.027	0.300	0.107	0.533

[a] See (11).

TABLE 2

Site occupancies of Mg^{2+}-ions at M(1), M(2), M(3), and M(4) sites in $(Zn_{0.9}Mg_{0.1}O)_5 In_2O_3$ and R_{wp} and R_B - values (%). In the parentheses the standard deviations are given.

M(1)	0.08 (1)	0.08 (1)	0.08 (1)	0.08 (1)
M(2)	0.07 (1)	0.21 (1)	0.00 (1)	0.00 (1)
M(3)	0.07 (1)	0.00 (1)	0.21 (1)	0.00 (1)
M(4)	0.07 (1)	0.00 (1)	0.00 (1)	0.21 (1)
R_{wp}	7.73	9.37	8.60	9.89
R_B	5.35	6.51	6.30	7.63

M(1)	0.08 (1)	0.08 (1)	0.08 (1)
M(2)	0.105 (1)	0.105 (1)	0.00 (1)
M(3)	0.105 (1)	0.00 (1)	0.105 (1)
M(4)	0.00 (1)	0.105 (1)	0.105 (1)
R_{wp}	8.44	8.21	7.93
R_B	5.94	6.14	5.81

TABLE 3–A

Rietveld refinement parameters and residuals for $(ZnO)_5In_2O_3$, $(ZnO)_5(In_{0.8}Y_{0.2})_2O_3$, $(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$, and $(Zn_{0.95}Mg_{0.05}O)_5In_2O_3$. (space group R3m, Z = 3, No. of observations : 4201, No. of reflections (α_1+α_2) : 234, No. of parameters : 24)

		$(ZnO)_5In_2O_3$ [b]		$(ZnO)_5(In_{0.8}Y_{0.2})_2O_3$ [b]		$(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$		$(Zn_{0.95}Mg_{0.05}O)_5In_2O_3$	
a (Å)		3.3285(1)		3.3505(1)		3.3318(1)		3.3300(1)	
c (Å)		58.127(2)		57.863(1)		57.950(2)		58.040(2)	
V $(Å)^3$		557.71(3)		562.53(2)		557.10(3)		557.39(3)	
d_x (g/cm^3)		6.11		5.97		5.94		6.02	
R_p (%) [a]		8.42		7.13		5.90		5.57	
R_{wp} (%)		10.52		9.05		7.73		7.30	
R_B (%)		8.56		6.94		5.35		5.06	
atom	site	z	B[Å^2]	z	B[Å^2]	z	B[Å^2]	Z	B[Å^2]
M(1)	3a	0	1.1(1)	0	1.9(2)	0	0.9(1)	0	0.7(1)
M(2)Zn	6c	0.1894(1)	1.7(2)	0.1893(1)	2.7(2)	0.1899(1)	0.9(1)	0.1899(1)	0.8(1)
M(3)Zn	6c	0.0986(1)	1.9(2)	0.0989(1)	2.7(2)	0.0978(1)	1.0(1)	0.0976(1)	0.8(2)
M(4)Zn	6c	0.2804(1)	1.7(2)	0.2798(1)	2.9(2)	0.2809(1)	1.2(1)	0.2807(2)	1.6(2)
O(1)	6c	0.1464(2)	1.7(3)	0.1456(2)	2.8(3)	0.1468(2)	1.7(1)	0.1468(2)	1.4(2)
O(2)	6c	0.2286(3)	1.7(3)	0.2301(3)	2.8(3)	0.2281(2)	1.7(1)	0.2284(2)	1.4(2)
O(3)	6c	0.0629(3)	1.7(3)	0.0614(3)	2.8(3)	0.0627(2)	1.7(1)	0.0631(2)	1.4(2)
O(4)	6c	0.3163(3)	1.7(3)	0.3169(3)	2.8(3)	0.3150(2)	1.7(1)	0.3147(2)	1.4(2)

[a] For the definition of R-values see (16,17).
[b] See (11).

TABLE 3–B

Rietveld refinement parameters and residuals for $(Zn_{0.9}Co_{0.1}O)_5In_2O_3$, $(Zn_{0.95}Co_{0.05}O)_5In_2O_3$, $(ZnO)_5(In_{0.9}Fe_{0.1})_2O_3$, and $(ZnO)_5(In_{0.95}Fe_{0.05})_2O_3$. (space group R3m, Z = 3, No. of observations : 4201, No. of reflections ($\alpha_1+\alpha_2$) : 234, No. of parameters : 24)

		$(Zn_{0.9}Co_{0.1}O)_5In_2O_3$		$(Zn_{0.95}Co_{0.05}O)_5In_2O_3$		$(ZnO)_5(In_{0.9}Fe_{0.1})_2O_3$		$(ZnO)_5(In_{0.95}Fe_{0.05})_2O_3$	
a (Å)		3.3295(1)		3.3284(1)		3.3205(2)		3.3248(1)	
c (Å)		58.026(2)		58.066(3)		57.926(2)		58.034(2)	
V $(Å)^3$		557.07(5)		557.10(5)		553.09(4)		555.59(4)	
d_x (g/cm^3)		6.09		6.11		6.06		6.08	
R_p (%)[a]		6.48		6.61		6.41		5.98	
R_{wp} (%)		8.33		8.71		8.33		7.79	
R_B (%)		7.22		8.79		5.30		4.83	
atom	site	z	B[Å^2]	Z	B[Å^2]	z	B[Å^2]	z	B[Å^2]
M(1)	3a	0	0.5(1)	0	0.7(1)	0	1.0(1)	0	0.9(1)
M(2)Zn	6c	0.1901(1)	0.5(1)	0.1901(2)	0.8(1)	0.1901(1)	1.4(1)	0.1901(1)	0.9(2)
M(3)Zn	6c	0.0974(1)	0.4(1)	0.0972(1)	0.4(1)	0.0974(1)	0.9(1)	0.0974(1)	0.7(2)
M(4)Zn	6c	0.2814(1)	0.6(1)	0.2812(2)	1.5(1)	0.2811(2)	2.0(2)	0.2812(2)	1.5(2)
O(1)	6c	0.1466(3)	1.2(1)	0.1470(3)	1.4(1)	0.1463(2)	2.1(2)	0.1462(2)	1.9(2)
O(2)	6c	0.2285(3)	1.2(1)	0.2287(3)	1.4(1)	0.2281(2)	2.1(2)	0.2284(2)	1.9(2)
O(3)	6c	0.0624(3)	1.2(1)	0.0622(3)	1.4(1)	0.0626(2)	2.1(2)	0.0625(2)	1.9(2)
O(4)	6c	0.3159(3)	1.2(1)	0.3156(3)	1.4(1)	0.3160(2)	2.1(2)	0.3157(2)	1.9(2)

TABLE 4
Site occupancies of metal atoms as derived from Rietveld refinement

	$(ZnO)_5 In_2O_3$ [a]		$(ZnO)_5 (In_{0.8}Y_{0.2})_2O_3$ [a]		$(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$		$(Zn_{0.95}Mg_{0.05}O)_5In_2O_3$		$(Zn_{0.9}Co_{0.1}O)_5In_2O_3$		$(Zn_{0.95}Co_{0.05}O)_5In_2O_3$	
	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)
Me	-	-	0.42(1)	0.00(2)	0.08(1)	0.07(1)	0.06(1)	0.03(1)	0.08(1)	0.07(1)	0.09(1)	0.03(1)
In	1.00(1)	0.19(2)	0.58(1)	0.17(2)	0.92(1)	0.18(1)	0.94(1)	0.18(1)	0.92(1)	0.18(1)	0.91(1)	0.18(1)
Zn	0.00(1)	0.81(2)	0.00(1)	0.83(2)	0.00(1)	0.75(1)	0.00(1)	0.79(1)	0.00(1)	0.75(1)	0.00(1)	0.79(1)

	$(ZnO)_5(In_{0.9}Fe_{0.1})_2O_3$		$(ZnO)_5(In_{0.95}Fe_{0.05})_2O_3$		$(Zn_{0.9}Mg_{0.1}O)_5(In_{0.8}Y_{0.2})_2O_3$		$(Zn_{0.9}Co_{0.1}O)_5(In_{0.8}Y_{0.2})_2O_3$	
	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)	M(1)	M(2), M(3), M(4)
Me	0.15(1)	0.01(1)	0.10(1)	0.00(1)	0.04(1)	0.08(1)	0.07(1)	0.07(1)
Y	-	-	-	-	0.42(1)	0.00(1)	0.42(1)	0.00(1)
In	0.85(1)	0.17(1)	0.90(1)	0.18(1)	0.54(1)	0.17(1)	0.51(1)	0.18(1)
Zn	0.00(1)	0.82(1)	0.00(1)	0.82(1)	0.00(1)	0.75(1)	0.00(1)	0.75(1)

[a] See (11).

TABLE 5

Distances between the metal oxide layers for the compounds $(ZnO)_5In_2O_3$, $(ZnO)_5(In_{0.8}Y_{0.2})_2O_3$, $(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$, $(Zn_{0.9}Co_{0.1}O)_5In_2O_3$, and $(ZnO)_5 (In_{0.9}Fe_{0.1})_2O_3$

	$(ZnO)_5In_2O_3$	$(ZnO)_5(In_{0.8}Y_{0.2})_2O_3$	$(Zn_{0.9}Mg_{0.1}O)_5In_2O_3$	$(Zn_{0.9}Co_{0.1}O)_5In_2O_3$	$(ZnO)_5(In_{0.9}Fe_{0.1})_2O_3$
:					
$(Me(2))_2O_2$					
	2.645	2.633	2.695	2.716	2.647
$(Me(2))_2O_2$					
	2.633	2.622	2.642	2.663	2.653
$(Me(3))_2O_2$					
	2.656	2.639	2.631	2.634	2.636
$(Me(4))_2O_2$					
	3.075	3.096	3.037	3.017	3.041
$Me(1)O_2$					
:					