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INFLUENCE OF PROCESSING PARAMETERS ON THE ELECTRICAL PROPERTIES OF $\text{Zn}_{1-x}\text{Co}_x\text{O}$ CERAMICS ($0 \leq x \leq 0.10$)

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Résumé - L'influence de la concentration en cobalt et de la durée du frittage sur la conductivité électrique de céramiques de la solution solide $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.10$), mesurée entre 400 et 1300 K, a été étudiée. L'interprétation des résultats obtenus associe la dissolution du cobalt dans la structure wurtzite de l'oxyde de zinc à la formation de deux niveaux d'énergie dans la bande interdite.

Abstract - The electrical conductivity of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ solid solution has been studied as a function of composition ($0 \leq x \leq 0.10$) and of sintering time. The behavior observed is probably due to the appearance of two energy levels in the forbidden band.

I - INTRODUCTION

Zinc oxide is a n-type semiconductor with a large energy gap (≈ 3.2 eV). This is generally attributed to the presence of an excess of metal in the wurtzite structure /1/. The electrical properties are thus controlled by the departure from stoichiometry which depends itself of the elaboration process /2/. They may also be influenced by the dissolution of small amounts of transition metals able to create energy levels in the forbidden band /3/. Such effects are particularly important in the case of cobalt-doped zinc oxide, which is the major phase in varistor materials /4/. In order to understand the influence of their processing parameters on the final properties, we have undertaken the study of the electrical conductivity of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ceramics as a function of sintering time and of composition ($0 \leq x \leq 0.10$).

II - EXPERIMENTAL

Ceramics samples were prepared from mixtures of reagent-grade ZnO and cobaltous carbonate. The powders were suspended in ethanol and stirred for 4 h. in an agate jar mill. After drying, they were ground and bound with polyvinyl alcohol, then pressed under 200 MPa. The pellets obtained were set in an alumina boat and fired at 1300°C in pure oxygen for the times selected. In all cases the heating and cooling rates were 600°C h⁻¹.

The ceramic microstructures were examined on polished samples by scanning electron microscopy. X-ray dispersive energy analysis does not show the existence of cobalt oxide precipitates.

The electrical conductivity was measured in the 1300-400 K range in air using the four-probe method /5/. For electrical contacts, platinum wires and paint were used. For each temperature the equilibrium value reported is the ordinate of the horizontal asymptote to the $\log \sigma = f(\text{time})$ curve.

III - RESULTS

1 - Influence of the sintering time on the electrical properties of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ solid solution.

This study was performed on ceramics having the same composition, but sintered at 1300°C for various times from 3 up to 63 hours.

Figure 1a) illustrates the temperature dependence of the electrical conductivity of the samples studied. All the curves $\log \sigma = f(10^3 T^{-1})$ show two linear parts separated by a transition temperature T_{tr} determined with an accuracy of 30 K. To each linear part can be associated an activation energy E

Fig.1 - Temperature dependence of the electrical conductivity of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ceramics sintered at 1300°C in air.

- a) influence of the sintering time (composition of sample : $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$) b) influence of the composition (sintering time : 24 h.)

calculated from the expression $\sigma = \sigma_0 \exp(-E/kT)$. The activation energy values, calculated at low and high temperature - E_{lt} and E_{ht} respectively - are listed in Table I.

TABLE I

Evolution of T_{tr} , E_{lt} and E_{ht} parameters with sintering time

Sintering time (h)	$T_{tr} \pm 30$ K	E_{lt} (eV)	E_{ht} (eV)
3	805	0.22	0.50
6	805	0.18	0.43
13	860	0.20	0.34
22	925	0.21	0.26
63	780	0.20	0.31

From these results it appears that the electrical conductivity and the transition temperature both increase with the sintering time. The opposite behavior is observed for the high temperature activation energy E_{ht} whereas the low temperature activation energy E_{lt} seems to be insensitive to the sintering time. The peculiar case of the sample sintered for 63 h will be justified later (see Discussion).

2 - Influence of the cobalt concentration on the electrical conductivity of the $Zn_{1-x}Co_xO$ solid solution ($0 \leq x \leq 0.10$).

The study was performed on samples of various cobalt content ($0 \leq x \leq 0.10$) all sintered in the same conditions (24 h. at 1300°C in a stream of pure oxygen). The temperature dependence of the electrical conductivity of the samples studied is represented on Figure 1b. As in the previous study it appears that all the curves $\log \sigma = f(10^3/T)$ consist of two linear parts, separated by a transition temperature T_{tr} . The values of T_{tr} and of the activation energies E_{ht} and E_{lt} are listed for every composition in Table II.

From these results it appears that the electrical conductivity of $Zn_{1-x}Co_xO$ ceramics decreases when the fraction of cobalt oxide is increased. The peculiar behavior observed for the solid solution of composition $x = 0.005$ will be discussed later.

TABLE II

Evolution of T_{tr} , E_{lt} and E_{ht} parameters with composition

Cobalt concentration x	$T_{tr} \pm 30$ K	E_{lt} (eV)	E_{ht} (eV)
0.005	625	0.10	0.20
0.010	900	0.21	0.26
0.020	890	0.22	0.31
0.025	780	0.24	0.47
0.030	680	0.23	0.64
0.040	680	0.40	0.74
0.100	680	0.62	0.78

IV - DISCUSSION

For all the samples studied, the electrical conductivity was

independent on the applied voltage which indicates that no effective potential barrier is localized at the grain boundaries in the 1300 - 400 K temperature range.

Comparing Figure 1a) and 1b) shows that the electrical conductivity can be lowered by either increasing the cobalt content of the solution or decreasing the sintering time. This can mean that the diffusion of cobalt ions in the matrix is a rather slow process. Then, for short sintering times, the distribution of cobalt is not even, its concentration being the highest in the outer core of the zinc oxide grains. Indeed, if such a similar configuration exists in a sample sintered for a long time -due to the evaporation of zinc oxide from the outer core of the grains for instance- then it would explain the lowering of the electrical conductivity observed for the sample sintered for 63 h.

At low temperature and for $x < 0.04$ the activation energy E_{lt} does not depend on the cobalt concentration and is close to that of pure ZnO. The low temperature conductivity must then be controlled mainly by the oxide own donor states which lie 0.3 eV below the conduction band /6/. The decrease in the conductivity observed when x is increased could then be the result of a lowered carriers mobility (Fig. 1b).

On the opposite, the high temperature activation energy E_{ht} , observed when $x < 0.10$, and consequently the Fermi level, depends on the cobalt concentration. The lowering of the transition temperature T_{tr} when x increases (Table II) could be due to a decrease in the ZnO level concentrations, and to a contribution of deeper levels created by the introduction of Co^{2+} ions in the wurtzite structure which would lie 1.6 eV below the conduction band (7).

The increase of the electrical conductivity observed when $x = 0.005$ is associated with a sharp increase in density /7/. The dissolution could then involve the formation of interstitial zinc and of donor levels according to :

As the concentration of cobalt is increased, the evolution of the density suggests that a substitutional mechanism would take over the previous one, i.e. :

which would involve the existence of deep energy levels.

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