Thermal and Compositional Dependence of Electric Conductivity of $Cu_{1-x}Zn_xAl_2O_4$ Spinels

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The preparation of compact samples of binary and mixed copper oxides suitable for investigations of their electric properties is severely hampered by the tendency of such substances to decompose by losing oxygen at elevated temperatures. The disadvantages of studying the specimens in powder form are, however, greatly reduced if the measurements are performed with ac instead of dc methods. It is then assumed that at sufficiently high frequencies the high-resistance contact between the powder grains is electrically shorted by its own capacitance and that the remaining resistance corresponds to the bulk resistivity of the particles.[1]

The experimental set-up used in the present investigation consists of a circuit magnification meter (Q meter), a 20—300 Mc/s oscillator and a specimen cell, designed and built at this Institute. The latter consists of a cylinder condenser which forms the external capacitance of the resonance circuit. The specimen can be heated to temperatures towards 900°C by means of an electrically heated resistance furnace. The whole specimen cell assembly is kept under a gas tight jacket fitted to the water cooled base of the apparatus which makes it possible to work in a controlled atmosphere. The apparatus has been tested using several semiconductor materials, *e.g.* CuO, Cu_2O and ZnO, and has given activation energy values (ΔE = 0.20, 1.02 and 2.0 eV, respectively) which are in satisfactory agreement with those reported by several previous investigators. The reproducibility of ΔE for a particular sample has been found to be better than ± 3 % in the region 0.10—0.90 eV and somewhat higher (± 5 %) for higher ΔE values. Conductivity values (σ) should be more susceptible to varying conditions of the test substance and to experimental errors. It has also been stated that empirically ΔE is a more characteristic physical constant of the material than σ.[2]

The measuring frequency used in the present experiments was 25 Mc/s and the investigations were performed in air. The heating rate of the furnace was 3°C/min. Spinel samples $Cu_{1-x}Zn_xAl_2O_4$ (x = 0.0, 0.2 . . . 1.0) were prepared by heating appropriate mixtures of the binary oxides at 1130°C for three weeks in an oxygen atmosphere. Portions of the various preparations were given an additional heat-treatment for seven days at 1000°C in oxygen. The monophasic character of the various specimens was controlled by their X-ray Guinier powder photographs and also by testing for constant weight after treatment with an aqueous solution of ammonium peroxodisulphate which dissolves unreacted cupric and zinc oxide while leaving spinel and alumina unaffected.

As indicated above, conductivity data obtained under the circumstances present in this work are likely to be of limited significance as far as absolute values are concerned. Quantitative comparisons of σ values found for different samples should

Table 1. ΔE values of $Cu_{1-x}Zn_xAl_2O_4$ spinels.

$Cu_{1-x}Zn_xAl_2O_4$ x	Heated at 1130°C for three weeks ΔE (eV)	Temp. range °C	Same samples with additional heat treatment at 1000°C (7 days) ΔE (eV)	Temp. range °C
0.0	0.31	70—240	0.29	70—140
0.2	0.38	150—300	0.30	75—170
0.4	0.44	190—320	0.32	100—190
0.6	0.54	240—400	0.35	180—250
0.8	0.62	430—690	0.59	525—720
1.0	1.02	660—860	0.80	720—880

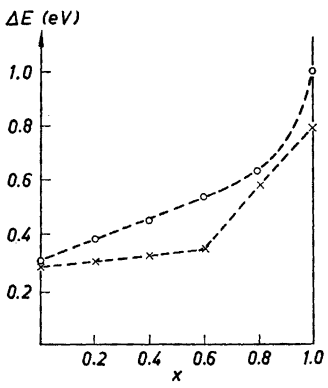

Fig. 1. ΔE values of spinels. O Samples heated at 1130°C for three weeks. × Same samples with additional heat treatment at 1000°C for seven days.

thus not be made. It may, however, be stated as indicated in the trend of the data observed that the σ values decrease with increasing contents of zinc of the samples. While $CuAl_2O_4$ has a conductivity of the order of magnitude of 10^{-4} ohm^{-1}cm^{-1} at room temperature such values are reached for $ZnAl_2O_4$ only towards 900°C.

The ΔE values of the various samples obtained by plotting ln σ *versus* $1/T$ (°K) are given in Table 1 which also indicates the temperature intervals of the linear parts of the curves attainable in the experiments. For both series of spinels there is a steady increase of ΔE with increasing contents of zinc. The curve for samples annealed at 1000°C may be approximated by two straight lines intersecting at $x \sim 0.6$ as indicated in Fig. 1. The accelerated increment of ΔE of the samples without this additional heat treatment takes place at higher x values.

The thermal prehistory of the spinel samples evidently has a considerable influence on their ΔE values. Several causes of this divergence may be imagined such as chemical inhomogeneities and structural properties including the type of metal atom distribution. The careful and protracted heat treatment of the samples is likely to have resulted in homogeneous preparations. It may be added that experiments performed on very inhomogeneous materials (incompletely reacted mixtures of the constituent binary oxides) have been found to give ΔE curves drastically different from those shown in Fig. 1.

The possibility of the metal-atom distribution influencing the ΔE value seems to be of a particular interest. The arrangement of the metal atoms on the octahedral (o) and tetrahedral (t) sites has recently been found to be temperature dependent for some spinels, *e.g.* $MgAl_2O_4$.[3] According to literature $ZnAl_2O_4$ is a normal spinel, $[Zn]_t[Al_2]_oO_4$,[4] while $CuAl_2O_4$ is partly inverse with the metal atom distribution $[Cu_{0.6}Al_{0.4}]_t[Cu_{0.4}Al_{1.6}]_oO_4$ at 1000°C.[5] (It would seem tempting to associate this with a solubility mechanism in the copper zinc aluminium oxide spinel system reflected in the appearance of the ΔE curve at the composition $Zn_{0.6}Cu_{0.4}Al_2O_4$ in the 1000°C series.) The small difference in scattering power for X-rays of copper and zinc and the close similarity of the unit cell parameters of $CuAl_2O_4$ and $ZnAl_2O_4$ obstruct X-ray investigations of the structural details in the ternary spinel system.

Further details on this work and on the apparatus used are given elsewhere.[6,7]

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