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Effect of Some Metal Oxides on the Specific Resistivities of Magnesium Oxide

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The specific resistivities of magnesium oxide prepared by igniting magnesium hydroxide at about 1700°C were investigated in the temperature range 200—1200°C. The magnesium oxide was found to have a *p*-type character by the thermoelectric power method. Ignition at 1000°C in an oxygen stream brought about a small increase in specific resistivities, whereas ignition in a vacuum of 10^{-3} mmHg caused no appreciable change. The sample including univalent-metal oxides such as Na_2O or Li_2O showed a distinct decrease in specific resistivities and was converted from a *p*-type to an *n*-type semiconductor. Addition of tervalent-metal oxides such as γ-alumina or B_2O_3 to the magnesium oxide, however, raised the resistivities but gave no change in type.

Magnesium oxide is widely used as an excellent insulator since a long time ago.[1] Goodwin and Mailey found that the electrical conductivity increases rapidly with temperature.[2] A recent study showed that the activation energy for electrical conductivity through single crystals of magnesium oxide is 2.8±0.1 eV in 400—1800°C.[3]

Although the electrical resistivity of magnesium oxide was thought to decrease in the presence of a small amount of impurities,[4] it was found lately that some impurities raise the resistivity. It has already been reported that the addition of 0.25 mol % of TiO_2 sharply increases the electrical resistivity of magnesium oxide, while the addition of TiO_2 more than 2.5 mol % does not give any effective change in the temperature range 1200—1800°C.[5]

In this study we will discuss the electrical resistivity of magnesium oxide from the viewpoint of semiconductor. Change of the specific resistivity of magnesium oxide with temperature was measured, and classification of magnesium oxide into either *n*- or *p*-type semiconductor was decided by means of the thermoelectric power method.

On the basis of these results, considerations on the change of specific resistivities were made, and the effect of metallic oxides contained as impurities on the electrical resistivity was investigated in the temperature range 200—1200°C.

Experimental

Magnesium Oxide. Magnesium oxide was prepared by igniting magnesium hydroxide at 1700°C and by crushing it to 100—200 meshes.

Analytical results: MgO, 99.81; SiO_2, 0.06; Al_2O_3, 0.03; Fe_2O_3, 0.04; CaO, 0.06%.

Preparation of Specimen for Specific Resistivity Measurements. The resistivity measurement for the samples was carried out with the specimen as shown in Fig. 1-a. The sample powder was packed between the inner and the outer electodes. As described in Fig. 1-b, MgO powder was packed under the desired pressure by means of an oil-press. In the preliminary experiments, it was found that the effect of the packing density on the specific resistivities was not recognized within the range 2.0—3.0 g/cm³. When the density exceeded the upper limit (3.0 g/cm³), the outer electrode was broken. 2.3 g/cm³ was chosen as the optimum packing density for all the measurements. A Pt-PtRh thermocouple was spot-welded on the surface of outer electrode for temperature measurements, and leading wires for the resistivity measurements were also spot-welded as shown in Fig. 1-a.

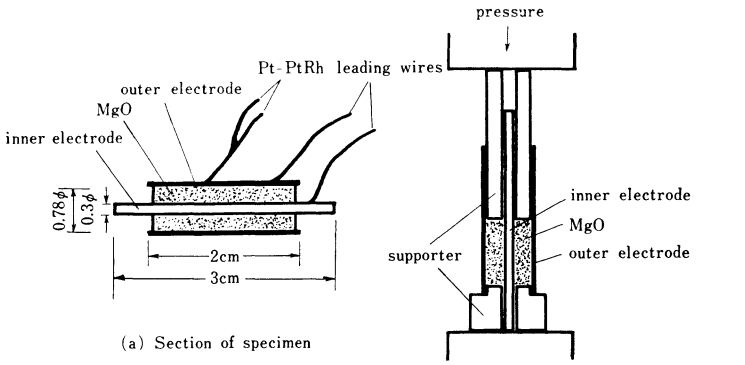
Measurement of Specific Resistivity. Resistivity was measured by the potential drop method with a Yokogawa Teraohmmeter RM-21C. The heating rate was 5°C/min. The values of specific resistivity (R) were calculated from the equation

$$R_s = \frac{2\pi hR}{2.303 \log \frac{r_2}{r_1}} \quad (\Omega\text{-cm})$$

where h is the height of MgO layer packed in specimen, R, observed resistivity, r_1, diameter of inner electrode, and r_2 is diameter of outer electrode.

Determination of *n*- or *p*-Type. The thermoelectric power method was used to decide the type of magnesium oxide (*n* or *p*) as semiconductor. Decision was made from the direction of the thermoelectric power detected by a Yokogawa Galvanometer D-2L.

1) F. Beijerinck, *Neves Jahrb. Min. B. B.*, **11**, 448 (1897).
2) H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, **23**, 1 (1906).
3) T. J. Lewis and A. J. Weight, *Brit. J. Appl. Phys.*, **1**, 441 (1968).
4) G. H. Fetterley, *Electrochem. Soc.*, **83**, 191 (1943).
5) D. M. Shakhtin, E. V. Levintovich, T. L. Pivovar and G. G. Eliseeva, *Teplofiz. Vys. Temp.*, **5**, 510 (1967).



(a) Section of specimen

(b) Procedure for packing of MgO powder

Fig. 1. Specimen for the resistivity measurement.

Addition of Oxide Impurities. B_2O_3 and γ-Al_2O_3 of special grade reagents were used as tervalent-metal oxides, and Na_2CO_3 and Li_2CO_3, as univalent-metal oxides. All the compounds were added to magnesium oxide in an amount corresponding to the desired fraction, and were fully triturated in an agate mortar. The resulting mixture was ignited at 1000°C for 10 hr, and then pulverized to 100—200 meshes.

Results and Discussion

Specific Resistivity of MgO. Figure 2 shows the curves of R_s (specific resistivity) *vs.* $1/T$ (reciprocal of absolute temperature) for magnesium oxide and for the same oxide ignited in an oxygen stream for 3 hours. The resistivity of MgO itself was $\sim 10^7$ Ω-cm at 1000°K.

The specific resistivity can also be given by the equation

$$R_s = Ae^{E/kT}$$

where E is activation energy, k, Boltzmann's constant (8.63×10^{-5} eV deg^{-1}), T, absolute temperature, and A is frequency factor.

Thus, the activation energy could be estimated from the slope of R_s-$1/T$ curve as 2.68 eV. This value is close to but somewhat smaller than that of 2.8±0.1 eV estimated by Lewis and Weight with a single crystal.[3] From the study on the light absorption of magnesium oxide the intrinsic activation energy for resistivity might be 7.3 eV.[6,7] From these values the specific resistivity seems to be affected by the presence of impurities or lattice defects.

It is well known that the over-all conductivities are the sum of conductivities in donor and acceptor; *viz.*, $\sigma=\sigma_n+\sigma_p=e(N\mu_n+N\mu_p)$, where σ_n is conductivity in donor, σ_p conductivity in acceptor, e, electronic charge, N, donor concentration, P, acceptor concentration, μ_n, donor mobility, and μ_p is acceptor mobility.

The MgO prepared at high temperature was expected to be deficient in oxygen atom and to be of n-type. However, it was found to be of p-type by thermoelectric power (Sample I in Table 1). That the MgO is of p-type suggests that $N=0$ or $P>N$. Thus it can be assumed that the content of oxygen atoms in the MgO is, stoichiometrically, slightly greater than that of magnesium atoms. The magnesium oxide was ignited in a vacuum of 10^{-3} mmHg for 3 hr, but no change was found in type and resistivity. The sample ignited in an oxygen stream for 3 hr was expected to show the decrease of resistivity. However, increase was observed as shown in Fig. 2. The reason for these discrepancies is not clear, but they might be due to the change of conductivity caused by the presence of other impurities.

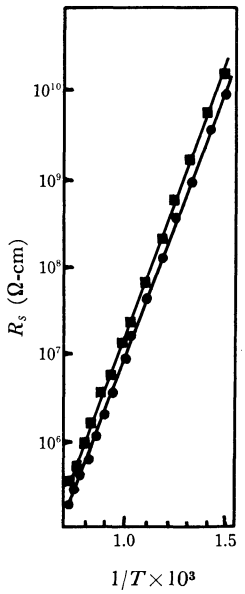


Fig. 2. R_s-$1/T$ curves for MgO (●—●) and MgO ignited in an O_2 stream (■—■).

6) P. D. Johnson, *Phys. Rev.*, **94**, 845 (1954).
7) H. Weber, *Z. Phys.*, **130**, 392 (1951).

The color of the sample ignited in an oxygen stream changed to very faint brown, while the sample ignited in a vacuum, to very faint bluish green. Though these phenomena may be ascribed to the color center related to the lattice defects, the substitution of a part of atoms and/or to the interstition of other atoms in crystal structures,[8,9] further investigations were not carried out in the present study.

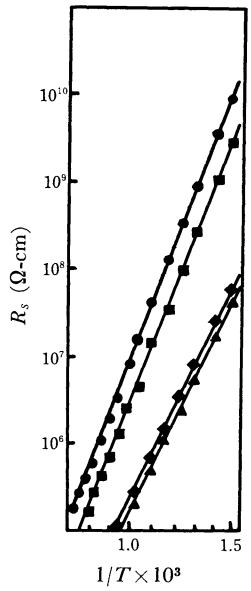


Fig. 3. R_s-$1/T$ curves for MgO (●—●), MgO+0.1%Na_2O (◆—◆), MgO+0.1%Li_2O (▲—▲), and MgO+0.1%Li_2O+10%Al_2O_3 (■—■).

TABLE 1. DETERMINATION OF *n* OR *p* TYPE

	Sample	Type
I	MgO	*p*
II	MgO ignited in an O_2 stream	*p*
III	MgO ignited in vacuum of 10^{-3} mmHg	*p*
IV	MgO+0.1%Li_2O	*n*
V	MgO+1%Li_2O	*n*
VI	MgO+1%Li_2O+10%Al_2O_3	*p*
VII	MgO+0.1%Na_2O	*n*
VIII	MgO+1%Na_2O	*n*
IX	MgO+2.5%Al_2O_3	*p*
X	MgO+5%Al_2O_3	*p*
XI	MgO+10%Al_2O_3	*p*
XII	MgO+15%Al_2O_3	*p*
XIII	MgO+2.5%B_2O_3	*p*
XIV	MgO+5%B_2O_3	*p*
XV	MgO+10%B_2O_3	*p*

8) H. G. Hecht and E. D. Taylor, *J. Phys. Chem. Solids*, **28**, 1599 (1967).
9) T. M. Searle and A. M. Glass, *ibid.*, **29**, 609 (1968).

Change in Resistivity and Transformation of Types due to Mixing Impurities. It may be expected that the addition of univalent- or tervalent-metal oxides would change the resistivity of magnesium oxide and, in some cases, transform the type into a semiconductor. Figure 3 shows the R_s-1/T curves of the samples containing univalent-metal oxides, and Table 1 shows the types of various samples. We see that the resistivity is diminished to large extent, when Na_2O or Li_2O is added to magnesium oxide, and the type is converted from *p* to *n* (samples IV, V, VII and

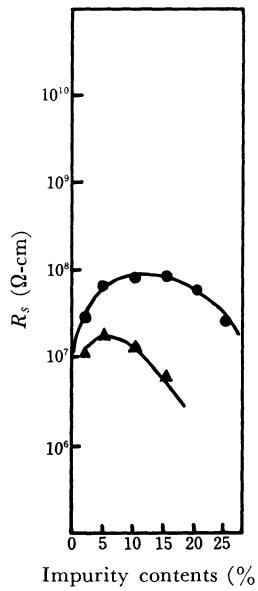


Fig. 4. R_s *vs.* impurity contents (%) curves for γ-Al_2O_3 (●—●) and B_2O_3 (▲—▲) at 1000°K.

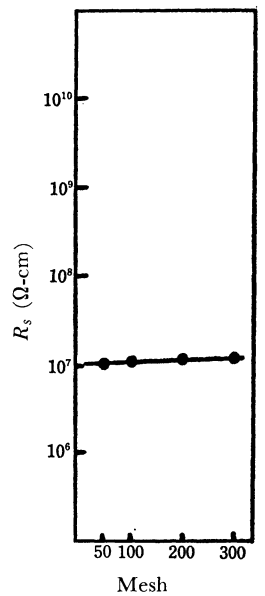


Fig. 5. R_s *vs.* grain size (mesh) curve at 1000°K.

VIII in Table 1). When γ-Al_2O_3 is added to the above samples, the resistivity is again increased (Fig. 3) and the type turned from *n* to *p* (sample VI in Table 1).

On the contrary, the addition of γ-Al_2O_3 or B_2O_3 increases the resistivity but no change is found in the type (Table 1, samples IX through XV). Figure 4 shows the curves of resistivity *vs.* the content of γ-Al_2O_3 or B_2O_3 at 1000°K. The maximum appeared at 10 % of γ-Al_2O_3 and 5 % of B_2O_3, respectively. All the samples were *p* type as shown in Table 1. Various modifications of Al_2O_3 were reported.[10-12] However, the alumina acted effectively as descrived above is γ-Al_2O_3, but not α-Al_2O_3.

10) E. Iwase, S. Nishiyama and T. Isono, This Bulletin, **29**, 147 (1956).
11) K. Funaki and Y. Shimizu, *Kogyo Kagaku Zasshi*, **56**, 53 (1953).
12) T. Sato, *ibid.*, **55**, 66 (1952).

On the activation energy for resistivity of these samples, only a small difference is found, *i.e.*, the sample containing 1 % of Li_2O showed 2.60 eV, whereas the sample containing 10 % of γ-Al_2O_3 2.72 eV.

From the principle of valency-control, it is expected that MgO containing the univalent-metal oxide should show a *p*-type character, whereas MgO with the tervalent-metal oxide, an *n*-type. The results obtained in the present work, however, can be recognized to be inconsistent with what we expected. However, the reason of this inconsistency is unknown for the present.

Grain Size and Resistivity. To observe the effect of grain size on resistivity, magnesium oxide was separated into portions 50, 100, 200 and 300 meshes with a standard sieve. Figure 5 gives the curve of the resistivity *vs.* mesh at 1000°K. The smaller the grain size, slightly larger becomes the resistivity. The resistivity hardly changes with grain size.