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Some Aspects of the Solid-solid Reaction Products between MgO and V_2O_3

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Synopsis. This report is concerned with the characterization of the metastably occurring reaction products with the spinel structure of a solid-solid reaction between MgO and V_2O_3 in an H_2 atmosphere. The measurements of the lattice constants and the magnetic properties suggest that the oxygen framework of the product is formed in an early stage of the reaction, followed by the ordering of the magnetic ions in the tetrahedral sites.

The present paper will deal the lattice constants and the magnetic properties of several reaction products obtained by solid-solid reactions between MgO and V_2O_3 in an H_2 atmosphere at different temperatures, the results give an insight into the characteristics of the metastably developed reaction products.

Two series of magnesio-vanadates, $MgO \cdot xV_2O_3$, with the spinel structure were prepared by firing oxide mixtures of MgO and V_2O_3 in different ratios; one of the species was fired at 1100 °C (A specimen series), and the other, at 1200 °C (B specimen series). The V^{3+} ion is stable in the $PO_2 \simeq 10^{-13}$—10^{-23} atm. region at 1100 °C—1200 °C, while the PO_2 in the H_2 atmosphere was measured to be $\sim 10^{-15}$ atm. therefore, only V^{3+} ions are supposed to be present in these materials throughout this investigation. X-Ray diffraction work was carried out in order to make precise lattice-constant measurements of the materials by the conventional method,[1] while the magnetic susceptibility was traced from 180 K to 100 K.

X-Ray diffraction patterns indicated that specimens of $1.0<x<1.13$ were monophasic, while specimens of $x>1.13$ more or less involved vanadium sesquioxide together with the host magnesio-vanadate.

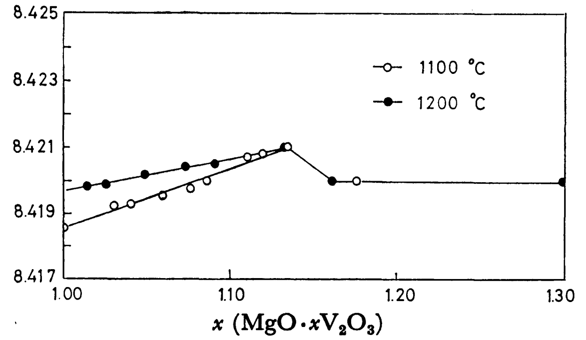

Fig. 1. Lattice constants of magnesio-vanadates with spinel structure.

Figure 1 gives the lattice constants as a function of the x value for the two series of materials. There is the general trend for the lattice constants for the two series to increase linearly with an increase in the x value up to $x=1.13$. For the materials in this range, excess vanadium ions can occupy the tetrahedral sites of the spinel lattice, and as the result, cation vacancies in these sites may form to maintain the charge neutrality. Therefore, the general trend of present interest may be connected with such configuration change in the tetrahedral sites.

Figure 1 further shows that the respective lattice constants for the two series of materials approach each other with an increase in the x value, finally coinciding at $x=1.13$. This fact suggests that materials with a larger x value have a larger number of cation vacancies and arrive at an "equilibrium structure" easily by means of the diffusion of oxygen. It is noticeable that at least two different lattice constants are possible for a fixed x value in the range of $1.0<x<1.13$. This fact strongly suggests that the A specimen series, with smaller x value, is metastable, in contrast to the B specimen series. The most probable model of the metastable structure is the Schottky-defect pairs of V_{mg}—V_o and V_v—V_o formed on the V_2O_3 side and the MgO side of the reaction product respectively, with their concentration ratio, $V_{mg}/V_v/V_o$, being always kept equal to the ratio of the constituent ions of MgV_2O_4, the number of vacancies decrease with an increase in the temperature. If this idea is correct, the lattice constant of the metastable

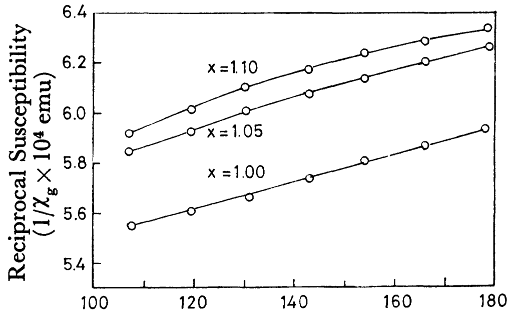

Fig. 2. The reciprocal values of the gram susceptibility ($1/\chi_g$) as a function of temperature for magnesio-vanadates fired at 1100 °C (A specimens).

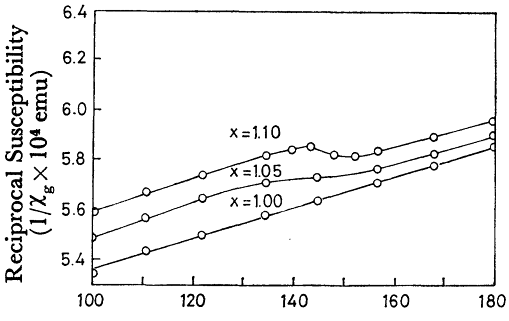

Fig. 3. The reciprocal values of the gram susceptibility ($1/\chi_g$) as a function of temperature for magnesio-vanadates fired at 1200 °C (B specimens).

structure can change by losing the respective vacancies without any change in its overall composition.

Figures 2 and 3 show the reciprocal susceptibility of A and B specimen series as a function of the temperature. The Curie-Weiss law held exactly over the entire range tested for the A specimen series, whereas deviation from the law began from the vicinity of 145 K for the $x=1.05$ and 1.10 materials in the B specimen series. It is unlikely that such anomalous magnetic behavior is associated with V^{3+} ions in the octahedral sites, which are occupied by V^{3+} in all the specimens. The deviation from the Curic-Weiss law may apear as a result of a contribution of an antiferromagnetic-like spin ordering partially occurring over the tetrahedral sites to the major paramagnetic disordering in the sites of the materials. This idea may be supported by the previous magnetic study of V_2O_3.[2] The occurrence of this anomaly, therefore, can be regarded as indirect evidence of cation ordering in the tetrahedral sites. Of the A specimen series and $MgO \cdot V_2O_3$ in the B specimen series, on the other hand, the lack of any cation order-disorder transition suggests cation disordering as well as spin disordering in the tetrahedral sites.

Figure 1 shows that the lattice constants of the two materials of $x=1.13$ fired at 1100 °C and 1200 °C respectively coincide, suggesting that the oxygen framework in the spinel lattice reached the equilibrium state in terms of structure. Nevertheless, the susceptibility versus temperature curves of the two materials are different from each other, thus, the $x=1.13$ material fired at 1200 °C can be regarded as being cation-ordered.

In summary, in the solid-solid reaction products between MgO and V_2O_3, the building of the oxygen framework takes place in an early stage of the reaction, followed by an ordering of the magnetic cations in the tetrahedral sites. A detailed study of this is in progress.

References

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2) H. Oshima, *Yogyo Kyokai Shi*, **81**, 162 (1973).