Tetragonal-to-Cubic Transformation of Hausmannite

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The tetragonal-to-cubic transformation of hausmannite, Mn_3O_4, was studied by high-temperature X-ray analysis. The transformation exhibits properties characteristic of diffusionless processes, i.e., coexistence of regions of tetragonal and cubic phases, and hysteresis. The position of the coexistence region with regard to temperature depends on the oxygen stoichiometry and/or concentration of Mn^{3+} ions.

Introduction

The presence of Mn^{3+} ions in sufficient concentration in a crystal lattice leads below a certain temperature, as a consequence of the cooperative Jahn–Teller effect, to a macroscopic deformation of the crystal structure, e.g., to the tetragonal distortion of the cubic spinel lattice. This transformation was recently studied (*1*, *2*) in the manganese chromite spinels of general formula $Mn_xCr_{3-x}O_4$. The high-temperature X-ray analysis revealed existence of temperature ranges where cubic and tetragonal phases coexist.

To explain the origin of the two-phase region we have carried out a study of the course of the transition in pure hausmannite, Mn_3O_4, where the presence of only manganese ions excludes possible influence of concentration fluctuations.

The transformation of Mn_3O_4 was studied by several authors but their results are contradictory or incomplete. Hook and Keith (*3*) found a tetragonal–cubic coexistence region. They indicated first cubic reflections at 1162°C on heating and tetragonal reflections at 1144°C on cooling, but they do not give more information about the course of the transformation. Irani *et al.* (*4*) measured the temperature dependence of the lattice parameters up to 750°C only and then determined the lattice constant of the cubic phase at 1172°C. McMurdie *et al.* (*5*) report that, contrary to manganese-rich ferrites $Mn_xFe_{3-x}O_4$, no two-phase region exists in pure hausmannite.

A hysteresis in the temperature dependence of the electrical resistivity of hausmannite due to its transformation within the temperature range 1009–1172°C was observed by Romeijn (*6*).

Experimental

Two different samples of hausmannite were prepared from "Baker Analyzed" manganese carbonate (content of metallic ion impurities less than 0.025%) by heating in air for 24 hr at 1320 and 1190 K, respectively.

The compositions of the prepared sam-

ples calculated from the total oxygen stoi-
chiometry determined by chemical analysis
are given by the formulas

$$Mn^{2+}_{1.077}Mn^{3+}_{1.949}O_4, \quad T = 1320 \text{ K};$$

$$Mn^{2+}_{1.042}Mn^{3+}_{1.972}O_4, \quad T = 1190 \text{ K}.$$
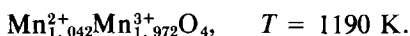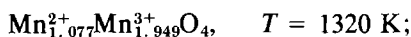
The high-temperature X-ray analysis was
done by means of a DRON-1 diffractometer
(USSR) using $CrK\alpha$ radiation with a vana-
dium filter. A high-temperature chamber of
the same manufacture was used. A Pt–PtRh
10% thermocouple placed on the surface of
the studied sample was used for measure-
ment and control of the temperature, which
was maintained constant within ±3 K. The
calibration of the temperature axis was
realized by comparing the used and stan-
dard thermocouples directly in the X-ray
furnace. The latter was calibrated on a
Netzsch DTA apparatus using ICTA stan-
dards and the method described elsewhere
(7).

The positions of 113_{tetr}, 311_{tetr}, and 311_{cub}
Bragg lines were measured. The tempera-
ture was increased and decreased stepwise
and the investigation of the transformation
kinetics showed no changes in the positions
and intensities of the measured lines in
dependence on the annealing time.

To prevent changes of the oxidation state
and/or segregation of Mn_2O_3 or MnO, the
measurements were carried out up to about
1120 K under an inert atmosphere and in
the temperature range 1120–1450 K in air.
No traces of MnO or Mn_2O_3 were detected
in the measured samples at any tempera-
ture and repeated chemical analysis after
the measurements revealed no changes of
the oxidation state.

Results and Discussion

The course of the tetragonal–cubic tran-
sition was studied on two samples of differ-
ent oxygen stoichiometry. No observable
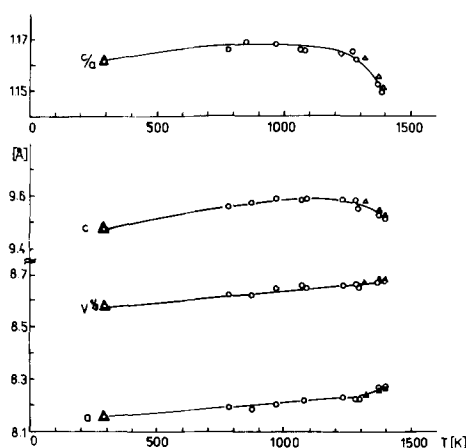influence was found on the lattice parame-

FIG. 1. The dependence of the lattice parameters on
the temperature of the tetragonal phase within the
temperature range 293–1400 K. O, $Mn^{2+}_{1.042}Mn^{3+}_{1.972}O_4$;
△, $Mn^{2+}_{1.077}Mn^{3+}_{1.949}O_4$ compositions.

ters in the whole region investigated (see
Figs. 1 and 2). Starting from room tempera-
ture one can observe an increase of the
volume due to the thermal expansion of the
crystal lattice. The dependences of a, c,
and c/a indicate a slightly anisotropic char-
acter of this expansion corresponding to the
deformation tendency of octahedra in con-
sequence of the Jahn–Teller effect. The
increase of temperature leads simultane-
ously to the randomization of octahedra
consonantly oriented at low temperatures.
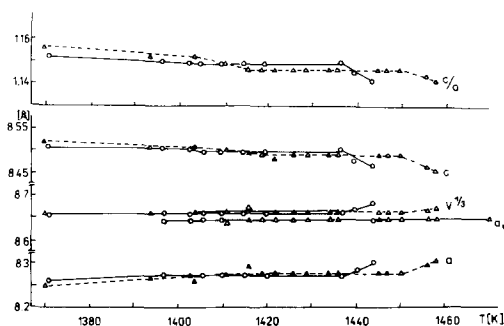This tendency appears above 1050 K,

FIG. 2. The dependence of the lattice parameters on
the temperature of the tetragonal and cubic phases
within the temperature range 1370–1470 K; see Fig. 1
for explanation of symbols.

where the macrosocpic distortion diminishes progressively as the degree of disorder becomes sufficient for the formation of the cubic phase coexisting with the tetragonal phase. The coexistence region exhibits properties typical for two-phase systems, i.e., the lattice parameters remain constant (see Fig. 2) and the amounts of the phases present change continuously as is demonstrated in Fig. 3, where the temperature dependences of the intensity ratio $I_{113_{tetr}}/I_{311_{cub}}$ are given. The oxygen stoichiometry does not influence the width of the coexistence region, but there is an obvious effect on the position of this region due to the stabilizing influence of Mn^{3+} ions on the existence of the tetragonal phase. The coexistence region is determined at "heating run" within the temperature range 1395–1446 K for the composition $Mn^{2+}_{1.077}$ $Mn^{3+}_{1.949}O_4$ and within the range 1409–1460 K for the composition $Mn^{2+}_{1.042}Mn^{3+}_{1.972}O_4$. The transformation exhibits an extremely large hysteresis as is apparent from comparison of the heating and cooling experiments.

The described behavior, i.e., the coexistence region and its hysteresis, is characteristic of diffusionless processes and consists of the tendency of the system to attain the equilibrium state at a given temperature, i.e., to minimize its free enthalpy. The free enthalpy change associated with the transition is given by the formula

$$\Delta G = \Delta H - T\Delta S + \Delta E_{surface} + \Delta E_{strains},$$

where ΔH is the enthalpy change, $T\Delta S$ the entropy contribution, $\Delta E_{surface}$ the change of the interphase surface energy, and $\Delta E_{strains}$ the energy change necessary to overcome the mechanical stresses due to volume changes (dilatation contraction, and reorientation of crystal domains).

The course of the transition is controlled simultaneously by contributions of the enthalpy change leading to formation of a new phase and of the strains term which acts against them and cuts off the growth of emerging crystal domains. The continuation of the transformation requires change of the equilibrium condition, i.e., an increase or decrease of the temperature in the dependence on the direction of the process. The influence of the remaining terms is probably less significant, given the character of this transition, which is diffusionless, accompanied by slight changes of the atomic positions only, resulting in mutually coherent phases. This explanation seems to be in agreement with the observation that both transformations—tetragonal to cubic and vice versa at increasing and decreasing temperatures, respectively—commence at the same temperature and, consequently, the coexistence region lies above this temperature in the former case and below it in the latter.

The obtained results are in qualitative agreement with those reported by Hook and Keith (3). The discrepancies found in the starting transformation temperatures can have several reasons: lower sensitivity of the Hook and Keith apparatus, influence of the oxygen stoichiometry, and calibration of the temperature, which is generally a delicate problem.
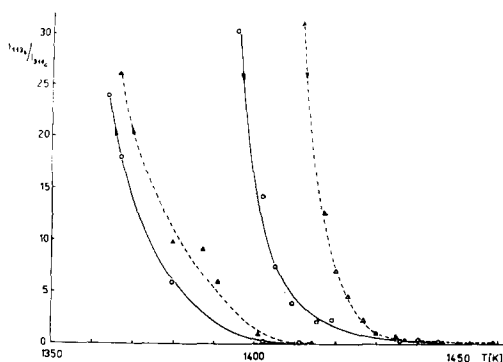

FIG. 3. The temperature dependences of the intensity ratio $I_{113_{tetr}}/I_{311_{cub}}$; see Fig. 1 for explanation of symbols.

From this point of view, it seems to be suitable to emphasize that the aim of the present work was to study the transformation process and not to determine the exact transition temperature which has no real meaning with respect to the described nature of the transition.

Acknowledgment

References

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