AN EXPERIMENTAL STUDY OF SiO₂ SOLUBILITY IN HAUSMANNITE

by

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(with 3 text-figures and 3 tables)

Abstract

Solid solubility of SiO₂ component in hausmannite has been experimentally determined. The solid solubility of hausmannite coexisting with rhodonite in air at 1200°C determined by microprobe analyses is the atomic ratio Si/(Mn+Si) of 0.015(2). Reaction between hausmannite and quartz at 900°C under hematite-magnetite buffer was not attained in equilibrium. Metastable Mn₅O₄-SiO₂ solid solutions have been synthesized in air at 60°C by a coprecipitation method. The atomic ratio Si/(Mn+Si) is achieved to about 0.025 by this way. It is indicated that the increase of Si content in hausmannite decreases the lattice parameter c and increases a slightly. Concentrations of constituent ions and cation vacancy in hausmannite have been calculated as a function of P₀₂ and temperature by using a defect chemical equilibrium relations. Possibility to finding the natural hausmannite which is supersaturated with SiO₂ is suggested.

Introduction

Hausmannite Mn₅O₄ is found in low-grade metamorphosed manganese ores. Although such a hausmannite is associated with braunite, Mn-pyroxens and quartz (e.g. Roy, 1981), the most hausmannite has nearly the ideal composition and contains only a little silica. According to the phase diagram of Mn₅O₄-SiO₂ studied by Muan (1959a, 1959b), no solid solubility is found along the join even over 1000°C in air and at various levels of oxygen partial pressures. It is well known that the substitution of cation in M₂⁺M³⁺₂O₄-type cubic spinel by tetra-valent cation (such as Si, Ti) causes metal vacancy in the structure. Since the hausmannite has a tetragonally distorted spinel structure, it may be possible to form a solid solution with SiO₂ by the same manner, even if its amount is small.

Precise measurement of the change of lattice parameters is an useful technique to determine the limit of solid-solubility and to estimate the valence state of constituent ions. A defect thermodynamic calculation together with the above technique was successful for estimation of the valence state of cations and vacancies in the system SnO₂-Sb₂O₃ system (Kikuchi & Umehara, 1985). The equilibrium concentrations of cations and cation vacancy of the solid solutions in the system Mn₃ O₅-MnFe₂O₄ were estimated by the same manner (Osawa et. al. 1992). They showed that the lattice parameters of the solid solution at a certain metal ratio
Mn/Fe are changeable with temperature and P₀₂.
In some cases, coprecipitation with a successive heat treatment at a suitable
temperature causes a metastable formation of solid solution, of which chemical
composition is beyond the solubility limit. Catalyzers in the system SnO₂–Sb₂O₅
have been prepared by a such method (Herrmann et al. 1979). We aimed also to
synthesize metastable hausmannite solid solutions which are supersaturated by sil­
ica. This may be relevant to the formation process of hausmannite under low-
grade metamorphism.

**Experimental procedure**

Hausmannite as a staring material was synthesized from a reagent grade MnO₂
at 1100°C for 3 hours in air. A mixture, hausmannite+quartz in 4:1 molar ratio,
was then prepared by mixing the hausmannite and a reagent grade SiO₂ (quartz).
The mixture was ground in alcohol and dried. Starting materials for the experi­
ments in air and under Fe₃O₄–Fe₂O₃ buffer were the same.

Experimental procedure under Fe₃O₄–Fe₂O₃ buffer were as follows. The Fe₃
O₄–Fe₂O₃ buffer was put at the lower part of a silica tube and a small amount of
silica-glass wool was stuffed. Then hausmannite or the mixture was put at the
upper part of the tube and vacuum-sealed. The tube was heated at 900°C for 6
days.

Metastable hausmannite solid solutions were synthesized from coprecipitates as
follows. Reagent grade MnCl₂·4H₂O and Na₂SiO₃ were measured off to the sev­
eral Mn:Si ratios and dissolved in water separately. The sodium hydroxide solu­
tion was added to the Na₂SiO₃ solution. Then the two solutions were mixed. The
silica content in coprecipitate was adjusted according to the x of the following
equation,

\[3MnCl₂ + (6−2x)NaOH + xNa₂SiO₃ + xH₂O = 3Mn(OH)₂·xSiO₂ + 6NaCl\]

The coprecipitates were washed with distilled water and dried at 60°C in air for 3
days. The solid solutions of hausmannite with SiO₂ were formed during the succes­
sive oxidation and dehydration. The exact compositions of coprecipitate were not
determined.

Microprobe analysis of the synthesized hausmannite solid solution (grains
about 5–10 μm in diameter) was made using a JEOL JCMA-733, at 15 kV operat­
ing voltage and 2 μm beam diameter. ZAF corrections were made based on the
formula Mn₃O₄ using the reduction program of Yui (1992).

Identification of run product was made by X-ray powder diffraction technique
with a diffractometer using graphite monochromated CuKα radiation. Lattice
parameters of hausmannite and hausmannite solid solution were determined with
scanning speed 1/4'min⁻¹. Silicon powder was used as an internal standard. The
parameters were refined by the least-squares method.
Experimental results

Syntheses in air at high temperatures and by Fe$_2$O$_4$–Fe$_3$O$_4$ buffer

Experimental data are given in Table 1. A mineral assemblage, braunite +

<table>
<thead>
<tr>
<th>run No.</th>
<th>HA</th>
<th>1A</th>
<th>2A</th>
<th>HB</th>
<th>1B</th>
</tr>
</thead>
<tbody>
<tr>
<td>starting material</td>
<td>Mn$_3$O$_4$</td>
<td>4Mn$_3$O$_4$+SiO$_2$</td>
<td>4Mn$_3$O$_4$+SiO$_2$</td>
<td>Mn$_3$O$_4$</td>
<td>4Mn$_3$O$_4$+SiO$_2$</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>1200</td>
<td>1200</td>
<td>940</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>duration (days)</td>
<td>6</td>
<td>8</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>condition</td>
<td>air</td>
<td>air</td>
<td>air</td>
<td>buffer</td>
<td>buffer</td>
</tr>
<tr>
<td>associated phase</td>
<td>braunite</td>
<td>rhodonite</td>
<td>quartz</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hausmannite was obtained from the mixture at 1100°C and an assemblage, hausmannite and rhodonite at 1200°C. These results agreed well with those by Abs-Wurmbach et al. (1983). The pure hausmannite transforms to a cubic spinel structure at 1160°C and this transformation is unquenchable (Van Hook and Keith, 1958). The hausmannite solid solution formed at 1200°C appeared to be polysynthetic twins. Microprobe analysis (average of 11) gave Mn$_3$O$_4$ 99.8(5), SiO$_2$ 0.44(6), sum 100.3(5)wt%, yielding an atomic ratio Si/(Mn+Si) = 0.015(2). It is however impossible to show the chemical formula due to the lack of analysis data for oxygen. The value indicates that the solubility limit at lower temperatures will be a negligibly small. The lattice parameters refined are listed in Table 2. It is indicated that the value of parameter $c$ decreases clearly with the addition of SiO$_2$ and $a$ increases slightly.

The mineral assemblage obtained after the run at 900°C under Fe$_2$O$_4$–Fe$_3$O$_4$ buffer condition were hausmannite and quartz. It is indicated that the equilibrium between the quartz and the hausmannite is not attained. Lattice parameters of the hausmannite are almost the same with those of pure Mn$_3$O$_4$ obtained under the same condition (Table 2).

<table>
<thead>
<tr>
<th>run No.</th>
<th>ratio</th>
<th>temperature (°C)</th>
<th>condition</th>
<th>lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si/(Mn+Si)</td>
<td></td>
<td></td>
<td>a (Å)</td>
</tr>
<tr>
<td>2A</td>
<td>0.015(2)</td>
<td>1200</td>
<td>air</td>
<td>5.7688(8)</td>
</tr>
<tr>
<td>HA</td>
<td>0.00</td>
<td>1200</td>
<td>air</td>
<td>5.7643(4)</td>
</tr>
<tr>
<td>HB</td>
<td>0.00</td>
<td>940</td>
<td>buffer</td>
<td>5.7630(1)</td>
</tr>
<tr>
<td>1B</td>
<td>n. d.</td>
<td>900</td>
<td>buffer</td>
<td>5.763(1)</td>
</tr>
</tbody>
</table>

Syntheses by coprecipitation

Compositions and lattice parameters of hausmannite solid solution are listed in Table 3. The relationship between cell parameters and silica content are shown in
Table 3 Starting compositions and the lattice parameters of hausmannite-SiO₂ solid solution synthesized by coprecipitation method.

<table>
<thead>
<tr>
<th>run No</th>
<th>ratio Si/(Mn+Si)</th>
<th>lattice parameters a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr1</td>
<td>0.0</td>
<td>5.7739 (2)</td>
<td>9.4543 (8)</td>
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<tr>
<td>Pr2</td>
<td>0.005</td>
<td>5.777 (2)</td>
<td>9.43 (1)</td>
</tr>
<tr>
<td>Pr3</td>
<td>0.010</td>
<td>5.778 (1)</td>
<td>9.38 (1)</td>
</tr>
<tr>
<td>Pr4</td>
<td>0.024</td>
<td>5.781 (1)</td>
<td>9.29 (1)</td>
</tr>
<tr>
<td>Pr5</td>
<td>0.048</td>
<td>5.780 (2)</td>
<td>9.30 (1)</td>
</tr>
<tr>
<td>Pr6</td>
<td>0.200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

amorphous phase

Text-fig. 1 Plots of lattice parameters as a function of the ratio Si/(Mn+Si). Solid lines are for the samples by coprecipitation method and dashed lines are for the samples by heating in air at 1200°C.

Text-fig. 1. It is shown that the parameter a slightly increases whereas the parameter c remarkably decreases, with increasing silica content up to the ratio Si/(Mn+Si) = 0.025. The both parameters then remains at constant above this value. It is indicated that the solubility limit by this method is about the ratio 0.025. Two phases, hausmannite solid solution and an amorphous substance, are coexisted above this ratio.
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Discussion

The formation of Mn₃O₄—SiO₂ solid solution can be expressed by a fundamental reaction for four oxygen ions,

\[(1-x/2)\text{Mn}^{3+}\text{Mn}^{2+}_x\text{O}_4+x\text{SiO}_2=\text{Mn}^{2+}_{1-x/2}\text{Mn}^{3+}_{x/2}\text{Si}_x\text{V}_{x/2}\text{O}_4\]  

where \(V\) denotes cation vacancy in the structure. The above reaction indicates that the addition of SiO₂ component decreases the numbers of Mn³⁺ and Mn²⁺ ions and creates cation vacancies. However, these concentrations is simultaneously also related to oxygen partial pressure \(P_{O_2}\) as shown by an oxidation reaction for pure hausmannite,

\[2\text{Mn}^{3+}+1/2\text{O}_2=(9/4)\text{Mn}^{3+}_{9/8}\text{V}_{1/8}\text{O}_4\]  

For Mn₃O₄—SiO₂ solid solution, the corresponding reaction will be written as

\[2\text{Mn}^{2+}_{1-x/2}\text{Mn}^{3+}_{x/2-x}\text{Si}_x\text{V}_{x/2}\text{O}_4+\{(2-x)/4\}\text{O}_2=\{(18-x)/8\}\text{Mn}^{3+}_{(48-2x)/(18-x)}\text{Si}_{(6x)/(18-x)}\text{V}_{(6+5x)/(18-x)}\text{O}_4\]  

Applying a defect thermodynamic approach which has been used similarly for the system Mn₃O₄—MnFe₂O₄ (Osawa et. al., 1992), the elemental equilibrium reaction for eqn. (3) can be expressed with

\[2\text{Mn}^{2+}+1/2\text{O}_2=2\text{Mn}^{3+}+\text{O}^2-+3/4\text{V}\]  

We should expect an equilibrium to be attained which satisfy the condition

\[[\text{Mn}^{3+}]^2[\text{O}^2-][\text{V}]^{3/4}=kP_{O_2}^{1/2}[\text{Mn}^{2+}]^2\]  

where \(k\) is the equilibrium constant at the temperature. The following relations among the ionic fractions of the above chemical species are holded.

\[[\text{Mn}^{2+}] + [\text{Mn}^{3+}] + [\text{Si}^{4+}] + [\text{V}] + [\text{O}^2-]=1\]  

where \([\text{O}^2-]\) is constant at 4/7 due to the formula.

For a given ratio of Si to Mn (\(=\alpha\)),

\[[\text{Si}^{4+}]=\alpha\{[\text{Mn}^{2+}] + [\text{Mn}^{3+}]\}\]  

where \(\alpha\) is equal to \(2x/(6-3x)\) in eqn. (3). For charge balance,

\[2[\text{O}^2-]=2[\text{Mn}^{2+}] + 3[\text{Mn}^{3+}] + 4[\text{Si}^{4+}]\]  

From eqns. (6)~(8) we obtain

\[ [\text{Mn}^{3+}] = \frac{4}{7+14\alpha} \frac{3+4\alpha}{2+4\alpha} [\text{Mn}^{3+}] \]  

\[ [\text{V}] = \frac{3}{7} \frac{4+4\alpha}{7+14\alpha} + \frac{1+\alpha}{2+4\alpha} [\text{Mn}^{3+}] \]  

\[ [\text{Si}^{4+}] = \frac{4\alpha}{7+14\alpha} - \frac{\alpha}{2+4\alpha} [\text{Mn}^{3+}] \]  

Substituting of eqns. (9)~(11) in eqn. (5), \([\text{Mn}^{3+}]\) is expressed in terms of equilibrium constant \(k\), \(P_{O_2}\), and \(\alpha\). By giving a numerical value to the product \(kP_{O_2}^{1/2}\), one can calculate \([\text{Mn}^{3+}]\) for a given \(\alpha\). Subsequently, the other concentrations are calculated by eqns. (9)~(11). The number of each cation and that of vacancy in Mn₃O₄—SiO₂ solid solution as a function of \(kP_{O_2}^{1/2}\) for \(\alpha=0\) and for \(\alpha=0.05\) (\(x=0.14\)) are shown in Text—fig. 2. The figure demonstrates the following features.
Text-fig. 2 Number of cations and cation vacancy per formula as a function of log \( (kP_0^1/2) \). Solid lines are for pure MnO, and dashed lines are for hausmannite solid solution of 0.05 of the ratio Si/(Mn+Si).

(i) Under low \( P_0 \) and at low temperatures \( (kP_0^{1/2} < 10^{-1.5}) \)

Cation vacancies are nothing and \([\text{Mn}^{2+}]\) exceeds 1. This indicates some \( \text{Mn}^{2+} \) ions must occupy the octahedral sites in the structure. The excess \( \text{Mn}^{2+} \) and the excess \( \text{Si} \) make the component \( \text{Mn}^{2+} [\text{Mn}^{2+} \text{Si}]_4 \), of which formula is just the same as tephroite. Abs-Wurmbach et. al. (1983) found the stable assemblage of tephroite and hausmannite under \( P_0 < 10^{-10} \) at 600°C and at total pressure 4 kb. Actually, \( \text{SiO}_2 \) may be therefore less soluble in this case.

(ii) Under relatively high \( P_0 \) and at high temperatures \( (kP_0^{1/2} > 10^{-1.5}) \)

The number of \( \text{Mn}^{3+} \) increases with increasing \( P_0 \) and decreases with increasing \( \text{SiO}_2 \) content.

All the present experimental results except one obtained by hematite–magnetite buffer should be explained by the case (ii). The reaction between \( \text{SiO}_2 \) and \( \text{Mn}_3\text{O}_4 \) is not occurred at the 900°C by hematite–magnetite buffer. But the starting \( \text{Mn}_3\text{O}_4 \) is thought to be reached at equilibrium with \( P_0 \) because the \( a \) and \( c \) parameters agreed well with those of \( \text{Mn}_3\text{O}_4 \) studied under the same condition. The \( \text{Mn}_3\text{O}_4 \) thus obtained should be nearly stoichiometric because the product \( kP_0 \) has been small.

The deviation from the cubic symmetry of the tetragonal spinel \( \text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4 \),
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Text-fig. 3 Dependence of distortion ratio $c/\sqrt{2}a$ against the ratio $\text{Si}/(\text{Mn}+\text{Si})$. Solid lines are for the samples by coprecipitation method and dashed lines are for the samples by heating in air at 1200°C.

has been explained by a cooperative phenomenon of Jahn Teller effect of the distorted Mn$^{3+}$O$_6$ octahedra in its structure (Kanamori, 1960). It is therefore expected that the decrease of Mn$^{3+}$ in the structure decreases the parameter $c$ of which direction corresponds to one of $O^{2-}$—Mn$^{3+}$—$O^{2-}$ direction of Mn$^{3+}$O$_6$ octahedra. It is indicated by the structural relation of hausmannite to the cubic spinel that the axis of the pseudo-cubic cell is related to $\sqrt{2}a$. The distortion ratio of hausmannite is therefore expressed by $c/\sqrt{2}a$. The dependence of the distortion ratio to the ratio $\text{Si}/(\text{Mn}+\text{Si})$ is shown in Text-fig. 3. The solid line is by the coprecipitation method and the dashed line by the experiment in air. The difference between two lines will be due to the difference of oxidation state.

We have inferred that hausmannites altered at low temperatures after braunite or other Mn-minerals may have contained a considerable amount of SiO$_2$ at the initial stage.

References

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