Interface reactions between manganese zinc ferrite single crystals and SiO2PbOZnO ternary systems
Hae June Je, Do Kyung Kim, Chong Hee Kim, Kug Sun Hong, Byeong Won Park et al.

Citation: J. Appl. Phys. 78, 7045 (1995); doi: 10.1063/1.360408
View online: http://dx.doi.org/10.1063/1.360408
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v78/i12
Published by the American Institute of Physics.

Related Articles
Enhancement of perpendicular magnetic anisotropy through reduction of Co-Pt interdiffusion in (Co/Pt) multilayers
Organic salts as super-high rate capability materials for lithium-ion batteries
A unified interdiffusivity model and model verification for tensile and relaxed SiGe interdiffusion over the full germanium content range
Insulation and diffusion barrier characteristics of spin-on-glass layer on a stainless steel substrate
J. Renewable Sustainable Energy 4, 011603 (2012)
How do InAs quantum dots relax when the InAs growth thickness exceeds the dislocation-induced critical thickness?

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT
Interface reactions between manganese zinc ferrite single crystals and SiO$_2$-PbO-ZnO ternary systems

Hae June Jeo, Do Kyung Kim, and Chong Hee Kim
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taegon 305 701, Korea

Kug Sun Hong
Department of Inorganic Materials Engineering, Seoul National University, Seoul 151-742, Korea

Byeong Won Park and Sung Do Jang
Division of Ceramics, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

(Received 26 May 1995; accepted for publication 9 September 1995)

Interface reactions between Mn-Zn ferrite single crystals and SiO$_2$-PbO-ZnO ternary systems were investigated using scanning electron microscope, electron probe microanalyzer, and x-ray diffractometer. The addition of ZnO in a SiO$_2$-PbO glass resulted in inhibition of formation of the intermediate phase and suppression of dissolution of the ferrite. The interface morphology became a dendrite structure with increase of ZnO concentration in the glass. Appearance of the anomalous concentration profile of Zn and Mn at the ferrite adjacent to the interface was investigated in terms of the dissolved quantity of Mn and Zn ion. It was found that Zn ion has dissolved from the ferrite into the glass melt during the reaction and Mn ion in the ferrite dissolved into the glass melt more than Zn ion, resulting in changing the undissolved ferrite adjacent to the interface into a Zn-rich Mn-Zn ferrite, Mn$_{0.10}$Zn$_{0.35}$Fe$_2$O$_4$, after reaction with 57SiO$_2$-38PbO-5ZnO (in mol %) glass. It was considered that the source of the hump of Zn concentration at the ferrite adjacent to the interface would be the undissolved, remaining Zn ions. A microscopic model was suggested. © 1995 American Institute of Physics.

I. INTRODUCTION

The unique magnetic properties and the outstanding wear resistance of manganese zinc ferrite (Mn-Zn ferrite) single crystals have promoted their use as a material for VCR heads. The track part of the magnetic heads for VCR interchanging magnetic signals with magnetic tapes is composed of the very thin (~30 μm) ferrite single crystal surrounded by a bonding glass. The magnetic properties of the ferrites surrounded by the glass are degraded by the residual stress due to thermal expansion mismatch and by the chemical reaction between them. Therefore, it is important to reveal interface reactions between ferrites and glasses thoroughly. Only a few studies on interface reactions between polycrystalline ferrites and glasses have been reported.

Previously, Tanigawa et al. found that PbO·2Fe$_2$O$_3$ crystal was formed in mixtures of Mn-Zn ferrite and lead silicate glasses heat treated in air. It was reported that the grain boundary diffusion of the glass was dominant at the ferrite adjacent to the interface during the reaction and the magnetic properties of the diffusion layer were abruptly degraded.

Recently, some systematic studies to reveal interface reactions have been performed by Nitta et al. They reported that the intermediate layers, mixtures of Pb$_2$Fe$_2$SiO$_4$ and Pb$_2$(Mn,Fe)Si$_2$O$_3$ crystals, were formed at the interface between the Mn-Zn ferrite and the glass such as SiO$_2$-PbO binary system, and SiO$_2$-PbO-MnO or SiO$_2$-PbO-Fe$_2$O$_3$ ternary system. However, no intermediate layers were observed at the interface between the Mn-Zn ferrite and the SiO$_2$-PbO-ZnO ternary system and between the Ni-Zn ferrite and the SiO$_2$-PbO-NiO ternary system. In these cases, they found an anomalous concentration profile that the concentrations of the transition elements (Zn, Ni ion) contained in the glass increased sharply at the ferrite adjacent to the interface. The reason of the hump of Zn or Ni concentration was thought that Zn or Ni ion in the glass has diffused into the ferrite even though Zn or Ni ion concentration in the glass was lower than that in the ferrite. They considered that the diffusion was caused not by the difference in concentration but by the difference in chemical potential. There was, however, no evidence that the chemical potential of Zn or Ni ion in the glass is higher than that in the ferrite.

The purpose of this article is to investigate thoroughly the interface reactions between the Mn-Zn ferrite and the SiO$_2$-PbO-ZnO ternary systems and the mechanism of the chemical reaction. The effect of the interface reactions on the morphology of the ferrite at the interface can also be investigated using the Mn-Zn ferrite single crystal instead of the polycrystalline ferrite.

II. EXPERIMENTAL PROCEDURE

A Mn-Zn ferrite single crystal used in this study was grown by composition-controlled Bridgman technique to obtain crystal with a uniform composition. The chemical composition of the Mn-Zn ferrite was Mn$_{0.55}$Zn$_{0.37}$Fe$_{0.08}$O$_{4.04}$. The (100) plane of the Mn-Zn ferrite single crystal was reacted with glasses as the case of the practical magnetic head for VCR. The glass compositions used in this study were shown in Table I. The amount of ZnO...
in glasses was varied from 0 to 12 mol % and those glasses were expressed hereafter as 0, 0.5, 5, and 12Z. The molar ratio of SiO₂ to PbO was fixed as 60:40 in all glass compositions. The concentration of ZnO was controlled within 12 mol % because the glass containing more than 12 mol % ZnO was devitrified after heat treatment. The raw materials of glass were reagent-grade SiO₂, PbO, and ZnO. After dry mixing the powders for 12 h, batches of glass were placed in platinum crucibles and melted at 1350 °C for 4 h in air. The melts were cast onto a steel mold.

A mirror-polished ferrite crystal with dimension of 6X4X1 mm was sandwiched by glass specimens with dimension of 8X6X3 mm. They were heat treated at 700, 800, 900, and 1000 °C in a platinum crucible. After heat treatment, ferrite crystals were surrounded by the glass. The heating and cooling rate was 5 °C/min. All specimens were heat treated under nitrogen atmosphere using a high-purity N₂ gas (>99.999%) in order to prevent the oxidation of ferrite crystals. Heat treatment implies the same meaning as the chemical reaction in this study.

Morphology of the interface between the ferrite crystal and glass was observed by scanning electron microscope (SEM). The chemical composition at the interface was analyzed by electron probe microanalyzer (EPMA) with a wavelength dispersive x-ray spectroscopy (WDX). The intermediate phases formed at the interface of ferrite crystal and the glass were analyzed by x-ray powder diffractometer (XRD). In order to analyze the intermediate phases more clearly, the crushed powders of the ferrite crystal and the glasses were mixed at the same weight ratio. The mixtures were heat treated under the same conditions.

The sizes of the ferrite crystal before and after heat treatment were measured precisely using micrometer and SEM. The dissolution length was calculated from the size diminution during the reaction. When the ferrite crystal was locally corroded the base line of the dissolution length was the tip of convex, undissolved ferrite.

III. RESULTS
A. Effect of ZnO concentration

Figure 1 shows SEM micrographs and the lines traced by a WDX of the interface between the Mn-Zn ferrite single crystals and 0, 0.5, 5, and 12Z glasses heat treated at 900 °C for 1 h. The intermediate layer is observed at the interface between the ferrite and OZ glass but not observed in the case of the glasses containing ZnO. With the increase of ZnO concentration in the glass, the interface morphology becomes a dendrite structure due to the local corrosion of the ferrite.

As shown in Fig. 1, the composition of Mn-Zn ferrite reacted with the glasses containing ZnO changes from inside to the interface. The Zn concentration near to the interface increases sharply, while the Mn concentration decreases symmetrically, and the Fe concentration decreases slightly. These anomalous concentration profiles, i.e., the hump of the Zn concentration at the ferrite adjacent to the interface appears even though the glass contains only 0.5 mol % ZnO. The height and width of the Zn hump increase with increase of the ZnO concentration in the glass.

In Fig. 2 shows x-ray diffraction patterns of the powder mixtures of Mn-Zn ferrite and 0, 0.5, 5, and 12Z glasses heat treated at 900 °C for 1 h. The intermediate phase in Fig. 1(a) is identified to be the same solid solution mixture, [Pb₂(Mn,Fe)₅Si₃O₁₉ and Pb₈(Mn,Fe)₃Si₃O₁₉], as that of the previous study. With increase of the ZnO concentration in the glass, the amount of these crystals decreases and they finally disappear. This result indicates that the Zn ions in the glass inhibit the formation of the intermediate phase at the interface. It is noticeable, however, that no second phase is formed but only spinel phase is detected even though the quantity of Zn ion increases at the ferrite adjacent to the interface, as shown in Fig. 1(d).

Figure 3 shows the effect of the ZnO concentration in the glass on the dissolution length of the Mn-Zn ferrite heat treated at 900 °C for 1 h. It decreases exponentially with the increase of the ZnO concentration. The dissolution length of
FIG. 2. X-ray diffraction patterns of powder mixtures of Mn-Zn ferrite and (a) OZ, (b) 05Z, (c) 5Z, and (d) 12Z glasses heat treated at 900 °C for 1 h.

the ferrite reacted with the OZ glass is about 27 μm whereas that with the 12Z glass is only 10 μm. This result indicates that the Zn ions in the glass suppress the dissolution of the ferrite.

B. Effect of reaction temperature

Figure 4 shows SEM micrographs and the lines traced by WDX of the interface between the Mn-Zn ferrite single crystal and the 5Z glass heat treated at 700, 800, 900, and 1000 °C for 1 h. At 700 °C, the interface maintains the original flat morphology, which indicates that the ferrite hardly dissolves at this temperature. At 800 °C, a dendrite morphology appears. With increasing the reaction temperature, however, the interface has a planar morphology. As shown in Fig. 4, the hump of the Zn concentration at the ferrite adjacent to the interface appears clearly above 800 °C and stays at similar height above 900 °C. The width of the hump increases with increasing temperature.

SEM micrograph and the lines traced by WDX of the interface between the Mn-Zn ferrite and the OZ glass heat treated at 1000 °C for 1 h are shown in Fig. 5. As compared with the result at 900 °C [Fig. 1(a)], the intermediate layer disappears, which coincides with the previous work.10 It is noticeable that the Zn concentration at the ferrite adjacent to the interface increases very little and the Mn concentration decreases slightly. It indicates that the anomalous concentration profile appears in the case of the interface reaction between the Mn-Zn ferrite and the ZnO free glass.

In order to thoroughly investigate the diffusion behaviors of the components of the Mn-Zn ferrite (ZnO, MnO, Fe2O3) at the interface during reaction, their concentrations in 0 and 5Z glasses were quantitatively analyzed by WDX before and after reaction at 1000 °C for 1 h. The analyzed zones were the inner parts of glass about 200 μm off the interface in Figs. 4(d) and 5. As shown in Table II, the concentrations of ferrite components in the glass increase after reaction due to the dissolution of the ferrite whether the glass contains Zn ion or not. It is noteworthy that the ZnO concentration in the 5Z glass increases slightly after reaction. This result indicates that the Zn ions in the ferrite dissolve into the glass during interface reaction even though the quantity of the Zn ion increases at the ferrite adjacent to the interface, which contradicts the previous work.12

Figure 6 shows x-ray diffraction patterns of the powder mixtures of the Mn-Zn ferrite and the 5Z glass heat treated at 700, 800, 900, and 1000 °C for 1 h. The mixture heat treated.
at 700 °C has a small quantity of a second phase that is identified as Pb₅(Mn,Fe)₃Si₂O₈. This phase disappears and only spinel phase is detected above 800 °C.

The effect of the reaction temperature on the dissolution length of the ferrite with various ZnO concentrations in the glass is shown in Fig. 7. With increasing the reaction temperature the dissolution lengths increase exponentially. When the reaction temperature is raised above 900 °C the dissolution lengths show a large difference upon the ZnO concentration. The dissolution length of the ferrite reacted with the OZ glass at 1000 °C is about 72 µm and that with the 12Z glass is about 37 µm. These results mean that the effect of ZnO addition in the glass becomes evident with increasing the dissolution rate of the ferrite. The dissolution lengths of the ferrite in Fig. 7 are shorter than those of the previous study, the reason of which is thought to be the difference in mass transport behavior between the polycrystalline and single-crystal ferrite. Generally, the polycrystalline ceramics would dissolve more rapidly into the glass melt than the single crystals due to the grain boundary diffusion.

### Table II. Concentration of Mn-Zn ferrite components contained in OZ and 5Z glasses before and after reaction at 1000 °C. (Analysis error: ±2% of the analyzed.)

<table>
<thead>
<tr>
<th>Z</th>
<th>ZnO (mol %)</th>
<th>MnO (mol %)</th>
<th>Fe₂O₃ (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Before</td>
<td>1.54</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>6.19</td>
<td>1.71</td>
</tr>
<tr>
<td>5</td>
<td>Before</td>
<td>5.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>6.19</td>
<td>1.71</td>
</tr>
</tbody>
</table>

**C. Effect of reaction time**

Figure 8 shows SEM micrograph and lines traced by WDX of the interface between the Mn-Zn ferrite single crystal and the 5Z glass heat treated at 900 °C for 10 h. The dendrite structure grows with increasing the reaction time due to the development of local corrosion of the ferrite. X-ray diffraction patterns of the powder mixtures of the ferrite and the 5Z glass heat-treated 900 °C for 1 and 10 h are shown in Fig. 9. It is also found that no second phase is formed even though the quantity of Zn ion increases at the ferrite adjacent to the interface.

The chemical composition of the undissolved ferrite adjacent to the interface indicated by A in Fig. 3 and of the inner ferrite that has no influence of the interface reactions are quantitatively analyzed by WDX and shown in Table III. It is found that the undissolved ferrite adjacent to the interface changes into a Zn-rich Mn-Zn ferrite, M₀.₁₅Zn₀.₈₅Fe₂O₄, which is the stoichiometric spinel (AB₂O₄) as a result of dissolving of the excess Fe ions. Even...
under the consideration of the analysis errors, it is obvious that the undissolved ferrite reacted with the SZ glass changes from a Mn-rich to a Zn-rich Mn-Zn ferrite and near the stoichiometric spinel as a result of dissolving of the excess Fe ions. As shown in Table III, Pb and Si ions in the glass hardly diffuse into the ferrite. This result indicates that the hump of Zn concentration is independent of the diffusion behaviors of them.

<table>
<thead>
<tr>
<th></th>
<th>ZnO (mol %)</th>
<th>MnO (mol %)</th>
<th>Fe₂O₃ (mol %)</th>
<th>PbO (mol %)</th>
<th>SiO₂ (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted</td>
<td>19.31</td>
<td>27.42</td>
<td>53.27</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Reacted</td>
<td>42.17</td>
<td>7.47</td>
<td>49.62</td>
<td>0.74</td>
<td>...</td>
</tr>
</tbody>
</table>

IV. DISCUSSION

A. Phase formation

From Figs. 1(a) and 2 the intermediate phase is formed at the interface between the Mn-Zn ferrite and the ZnO-free glass heat treated at 900 °C for 1 h and identified to be the solid solution mixture, [Pb₂(Mn,Fe)₂SiO₅ and Pb₈(Mn, Fe)₆Si₄O₁₆]. As shown in Fig. 5, these crystals disappear when the temperature is raised to 1000 °C. These results are in good agreement with the previous work by Nitta et al. However, the amount of these crystals decreases and finally disappears with the increase of ZnO concentration in the glass. It indicates that the Zn ions in the glass inhibit their formation. It is suggested that the Zn ions would diffuse into the intermediate crystals and make them a glass phase with the increase of ZnO concentration in the glass. As shown in Fig. 6, the powder mixture of Mn-Zn ferrite and 5Z glass heat treated at 700 °C has a small quantity of a second phase that is identified as Pb₈(Mn,Fe)₆Si₂O₁₉. However, it is not observed at the interface in Fig. 4(a), which means its thickness would be very thin. It is suggested that its formation is caused by the accumulation of the dissolved ferrite components near the interface that is resulted from the low diffusivities of them in the glass melt due to high viscosity of the melt. Therefore, it disappears with increasing the temperature above 800 °C.

According to the results of XRD analysis, it is found that no second phase is formed but only spinel phase is detected even though the quantity of Zn ion at the ferrite adjacent to the interface increases and that of Mn decreases. As shown in Table III, the chemical composition of the undissolved ferrite adjacent to the interface changes into a Zn-rich Mn-Zn ferrite, Mn₀.₁₅Zn₀.₈₅Fe₂O₄, after reaction with the SZ glass at 900 °C. Mn-Zn ferrite is known to be a complete solid solution of Mn ferrite (MnFe₂O₄) and Zn ferrite (ZnFe₂O₄), which means that Mn and Zn ions can be completely replaced by each other in the spinel structure. However, the increasing Zn ions would not go into the sites of dissolving Mn ions. Mn-Zn ferrite has an inverse spinel structure that the tetrahedral sites are occupied by Zn⁺ and Fe³⁺ ions and the octahedral sites by Mn²⁺ and the rest of Fe³⁺ ions. Therefore, it would be reasonable that the increasing Zn ions would go into the tetrahedral sites due to the preference for them over Fe³⁺ ions and the expelled Fe³⁺ ions on the tetrahedral sites would go into the octahedral sites of dissolving Mn ions. In conclusion, it is thought that the spinel structure is maintained by the rearrangement of Zn, and Fe ions at the
sites of the spinel structure even though a large quantity of Mn ions dissolves into the glass melt and the quantity of Zn ions increases at the undissolved ferrite adjacent to the interface.

B. Interface reaction mechanism

It is seen in Fig. 1 that the Zn concentration at the ferrite adjacent to the interface with the glasses containing ZnO is higher than that in the inside, while the Mn concentration is lower and the Fe concentration is slightly lower. These concentration profiles appear even though the glass contains only 0.5 mol % ZnO and more obviously with the increase of ZnO concentration in the glass. From a viewpoint that the concentration of ZnO in the Mn-Zn ferrite (about 19 mol %) is higher than that in the glass (at most 12 mol %), Zn ion in the ferrite would diffuse into the glass melt. On the contrary, it seems that Zn ion in the glass melt diffuses into the ferrite. At the previous work, Nitta et al. have also observed the hump of Zn concentration at the ferrite adjacent to the interface after reactions with the glasses containing 1 and 5 mol % ZnO. They interpreted this anomalous Zn concentration profile as follows. When ZnO is added in PbO-SiO2 glass the chemical potential of Zn ion in the glass might be higher than that in the Mn-Zn ferrite. Consequently, Zn ions in the glass would diffuse into the ferrite and thus the hump of Zn concentration at the ferrite adjacent to the interface has appeared. This interpretation means that Zn ions diffuse against the concentration profile of Zn because the concentration of Zn in the Mn-Zn ferrite is much higher than that in the glass. Namely, they have thought that the diffusion was caused not by the difference in concentration but by the difference in chemical potential. They have also interpreted the interface reactions between the Mn-Zn ferrite and the SiO2-PbO-MnO glass melt and between the Ni-Zn ferrite and the SiO2-PbO-NiO glass melt by the same mechanism.

There was, however, no evidence that the chemical potential of a component in the glass with its lower concentration is higher than that in the ferrite with its higher concentration.

In this study, Table II shows that the Zn concentration in 5Z glass increases after reaction with Mn-Zn ferrite even though the quantity of Zn ion increases at the ferrite adjacent to the interface. If the Zn ions in the glass diffuse into the ferrite, the Zn concentration in the glass cannot be increased. Therefore, the increase of Zn concentration in the glass after reaction means that Zn ions in the ferrite dissolve into the glass. In Fig. 5, moreover, the Zn concentration at the ferrite adjacent to the interface increases very slightly after the reaction between the Mn-Zn ferrite and the ZnO-free glass. In this case, it is impossible that the Zn ions in the glass diffuse into the ferrite. In conclusion, it is evident that the Zn ions in the glass do not diffuse into the ferrite but the Zn ions in the ferrite dissolve rather into the glass during interface reaction.

Then, what is the source of the hump of Zn concentration? Comparing the concentrations of the ferrite components \( C_{(Zn,Mn,Fe)} \) in at % with those increasing in 0 and 5Z glasses after reaction \( \Delta C_{(Zn,Mn,Fe)} \) in at % in Table II, the interesting results can be found as follows.

It is found that the concentrations of Mn, Fe, and Zn ion increasing in the ZnO-free glass melt after reaction \( [\Delta C_{(Zn,Mn,Fe)}] \) increase at the similar atomic ratio of those in the ferrite \( [C_{(Zn,Mn,Fe)}] \). When 5 mol % ZnO is added in the glass, the concentrations of Mn and Fe \( [\Delta C_{(Mn,Fe)}] \) increase also at the similar ratio of those in the ferrite, but the Zn concentration \( [\Delta C_{(Zn)}] \) increases at the lower ratio than that in the ferrite. These results indicate that the Zn ions contained in the glass suppress the dissolution of Zn, resulting in suppression of dissolution of the ferrite as the results of Figs. 3 and 7. These interpretations from Table II are reasonable even under the consideration of the analysis errors because the concentrations of Mn, Fe, and Zn in the glasses were analyzed under the same conditions and compared relatively. It can be thought that if the diffusion rates of Mn, Zn, and Fe ions in the glass melt are the same, the quantity of Mn ions dissolving into the glass melt would be larger by 2.9 times that of Zn ions. Anyway, it is obvious that the Mn ions in the ferrite dissolve into the glass melt more than Zn ions because the dissolution of Zn ions in the ferrite is suppressed by Zn ions in the glass melt. Therefore, the source of the hump of Zn concentration is considered to be the undissolved, remaining Zn ions at the ferrite adjacent to the interface and the concentration profiles of Mn become symmetrical with those of Zn as shown in Figs. 1, 4, and 8. With the increase of ZnO concentration in the glass, the amount of remaining Zn ions at the ferrite adjacent to the interface would be increased due to the suppression of the dissolution of Zn ions in the ferrite, resulting in the increase of the height of the Zn hump as shown in Fig. 1.

On the assumption that the composition of undissolved ferrite at the interface after reaction with 5Z glass change into MnZnOFeO and the quantity of Mn ions dissolving into the glass melt is larger by 2.9 times than that of Zn ions, a microscopic model of interface reaction between the Mn-Zn ferrite and the 5Z glass is suggested in Fig. 10. The quantity of dissolved Mn ion (a) and Zn ion (b) are calculated from the altered composition, MnZnOFeO. That of Fe ion (c) would be the sum of that of excess Fe ions (0.08) which become Fe2+ ions in spinel structure and 2 times of that of divalent ions (Mn2+,Zn2+,Fe2+) for the conservation of the spinel stoichiometry (AB2O4). This model shows that the spinel structure can be maintained in the ferrite at the interface after reaction by the rearrangement of the remaining components at the sites of the spinel structure, resulting in only the compositional change from Mn-rich to Zn-rich Mn-Zn ferrite, i.e., the appearance of the hump of Zn concentration. In Nitta's mechanism the dissolution of Mn-Zn ferrite into the glass has been neglected. In this model, however, the interface reaction is always accompanied by the dissolution of all
It was reported that the grain boundary diffusion of the ferrite elements was dominant at the polycrystalline ferrite adjacent to the interface during the reaction. It is, therefore, difficult to investigate the effect of interface reaction on the interface morphology during the reaction between the polycrystalline ferrite and glass. In this experiment, it can be thoroughly investigated using the Mn-Zn ferrite single crystal.

In 1990 Schmalzried pointed out that a high transport capacity in the moving phase boundary tends to stabilize a planar morphology by rendering the interface to an equipotential surface. In this study, the interface morphology becomes a dendrite structure with the increase of ZnO concentration in the glass due to the suppression of the ferrite dissolution. The dendrite structure grows with increasing the reaction time due to the development of local corrosion of the ferrite. With increasing the reaction temperature, it becomes planar due to the rapid dissolution of the ferrite. These results mean that the more soluble the ferrite is, the more planar the interface, which is in agreement with Schmalzried's suggestion.

V. CONCLUSION

The interface reactions between Mn-Zn ferrite single crystals and SiO2-PbO-ZnO ternary systems were investigated and the microscopic model was suggested. The effect of the interface reactions on the interface morphology was also investigated. The intermediate phases, Pb₂(Mn,Fe)₂Si₂O₆ and Pb₂(Mn,Fe)Si₆O₁₈, were formed after interface reaction between the ferrite and the ZnO-free glass heat treated at 900 °C. With the increase of ZnO concentration in the glass, the amount of these phases decreased and finally they disappeared because Zn ions contained in the glass inhibited their formation. However, a small quantity of Pb₂(Mn,Fe)₂Si₂O₆ phase was formed at the interface between the ferrite and the SZ glass heat treated at 700 °C. Its formation was caused by the accumulation of the dissolved ferrite components near the interface due to high viscosity of the glass melt. Therefore, it has disappeared with increasing the temperature above 800 °C.

The composition of the Mn-Zn ferrite reacted with the glasses containing ZnO changed from inside to the interface. The Zn concentrations at the ferrite adjacent to the interface increased sharply, while the Mn concentrations decreased symmetrically. These anomalous concentration profiles appeared even though the glass contained only 0.5 mol % ZnO, and more obviously with the increase of ZnO concentration in the glass. It was found that the Zn ion has dissolved from the ferrite into the glass melt during reaction between the ferrite and the SZ glass heat treated at 700 °C. Its formation was caused by the accumulation of the dissolved ferrite components near the interface due to high viscosity of the glass melt. Therefore, it has disappeared with increasing the temperature above 800 °C.

The interface reactions between Mn-Zn ferrite and the SZ glass was suggested in this study. The microscopic model of interface reaction between the Mn-Zn ferrite and the SZ glass on the assumption that the quantity of dissolving Mn ions (a) is larger by 2.9 times than that of Zn ions (b).

<table>
<thead>
<tr>
<th>components of the ferrite, resulting in the dissolution of the ferrite as shown in Fig. 7.</th>
<th>It was reported that the grain boundary diffusion of the ferrite elements was dominant at the polycrystalline ferrite adjacent to the interface during the reaction. It is, therefore, difficult to investigate the effect of interface reaction on the interface morphology during the reaction between the polycrystalline ferrite and glass. In this experiment, it can be thoroughly investigated using the Mn-Zn ferrite single crystal.</th>
<th>It was reported that the grain boundary diffusion of the ferrite elements was dominant at the polycrystalline ferrite adjacent to the interface during the reaction. It is, therefore, difficult to investigate the effect of interface reaction on the interface morphology during the reaction between the polycrystalline ferrite and glass. In this experiment, it can be thoroughly investigated using the Mn-Zn ferrite single crystal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(before) Mn₅.₅₅Zn₅.₇₇Fe₂.₈₂O₄.₆₄</td>
<td>a = 2.9b = 0.516</td>
<td>a = 2.9b = 0.516</td>
</tr>
<tr>
<td>dissolution</td>
<td>h = 0.17R</td>
<td>h = 0.17R</td>
</tr>
<tr>
<td>(after) Mn₀.₃₄Zn₁₀.₉₂Fe₀.₆₉O₀.₇₉₀₄</td>
<td>c = 0.08 + 2x(a+b+0.08) = 1.626</td>
<td>c = 0.08 + 2x(a+b+0.08) = 1.626</td>
</tr>
<tr>
<td>(spinel formula) Mn₀.₁₅Zn₀.₈₅Fe₂O₄</td>
<td>d = (a+b) + 1.5x = 3.136</td>
<td>d = (a+b) + 1.5x = 3.136</td>
</tr>
</tbody>
</table>

FIG. 10. Model of interface reaction between Mn-Zn ferrite and SZ glass on the assumption that the quantity of dissolving Mn ions (a) is larger by 2.9 times than that of Zn ions (b).


