# New Glass Ceramics for Hard Disk Substrates with Improved Surface Flatness

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New glass ceramics were investigated for the application as substrates to be used in hard disk devices. The glass system to precipitate lithium di-silicate was studied so as to optimize the composition to realize very high surface flatness. The addition of small amount of several metal oxides with high valences had very drastic effects on the microstructure, because they played a role of crystallization agents, and consequently it determined surface flatness even after the polishing process. The possible mechanism changes of crystal growth due to the addition of metal oxides were discussed in relation to the final micro-texture development. The glass ceramics with very high surface flatness (Ra=7.1 Å) was obtained by the addition of the mixture of $P_2O_5$ and $MoO_3$ as crystallization agents.

*Key words:* Hard disk substrate, Glass ceramics, Crystallization agent, Lithium disilicate

## I. Introduction

A magnetic memory disk using a glass-ceramic plate as a substrate is being developed for compact hard disk drive units.[1-3] Since a glass-ceramic disk is greatly superior to an aluminum counter part in several aspects such as mechanical properties such as abrasion resistance, the ultimate rotation speed of the disk can be much higher. If a hard disk with a disk using a glass-ceramic substrate should achieve a higher bit density, the flatness of the polished surface is the most important factor. A flat substrate is required in order to realize a device with a higher bit density due to reduction of a flying height of an MR and GMR head. In this work, the glass system to precipitate lithium di-silicate as a primary phase was investigated so as to optimize the composition in order to realize very high surface flatness, because a fine-grained microstructure reduces the surface roughness of a glass-ceramic substrate.[2-4] The influence of the addition of small amount of several metal oxides with high valences as a nucleating agent was examined. The possible mechanism changes of crystal growth due to the addition of the metal oxides will be discussed in relation to the final micro-texture development.

## II. Experimental Procedure

The glasses of molar composition, $20Li_2O \cdot 2K_2O \cdot 3Al_2O_3 \cdot 75SiO_2$, to which 1.9 wt% $P_2O_5$ and 4.2 wt% another metal oxide was added as a nucleating agent, were prepared. The oxides chosen as the secondary nucleating agent were $TiO_2$, $V_2O_5$, $MnO_2$, $CoO$, $ZrO_2$, $MoO_3$, $Ta_2O_5$, and $WO_3$. The well-mixed powder containing appropriate amount of carbonate ($Li_2CO_3$, $K_2CO_3$, $MnCO_3$, $CoCO_3$) and oxide ($Al_2O_3$, $SiO_2$, $TiO_2$, $V_2O_5$, $ZrO_2$, $MoO_3$, $Ta_2O_5$, $WO_3$) and $NH_4H_2PO_4$ was melted in a Pt-Rh crucible for 2 h at 1450°C and quenched in air onto a steel mold. The obtained glass sample was heat treated for 2 h at 520°C and for 4 h at 760°C for nucleation and crystallization.

The powdered glass sample was examined by differential thermal analysis (Model Thermo Plus, Rigaku, Japan). The crystalline phases in glass-ceramic samples were identified with X-ray diffraction (Model Rint2100, Rigaku, Japan) using nickel-filtered Cu-Kα radiation. Scanning electron microscope (SEM) observations (Model S4500, Hitachi co., Japan) were made on polished glass-ceramic samples after etched (5 vol% HF solution, 3 min) and then coated with a Pt thin film. The surface roughness of the polished glass-ceramic samples was determined by a moving needle probe.

## III. Results

### 1. Differential Thermal Analysis (DTA)

A typical DTA curve of the glass samples has two exothermic peaks associated with the crystallization of the present glass as shown in Fig. 1. The first peak (T=650°C) corresponds to the crystallization of lithium di-silicate,
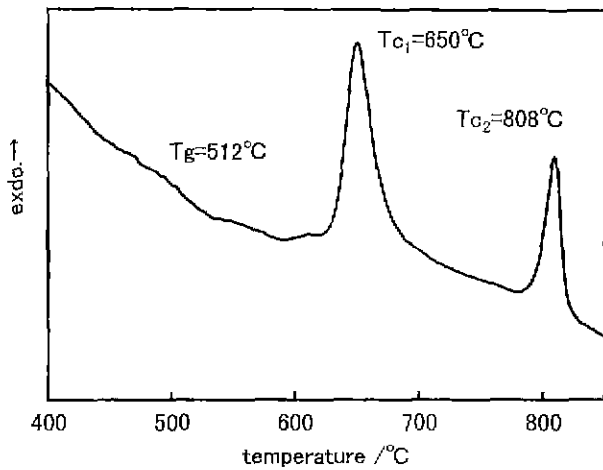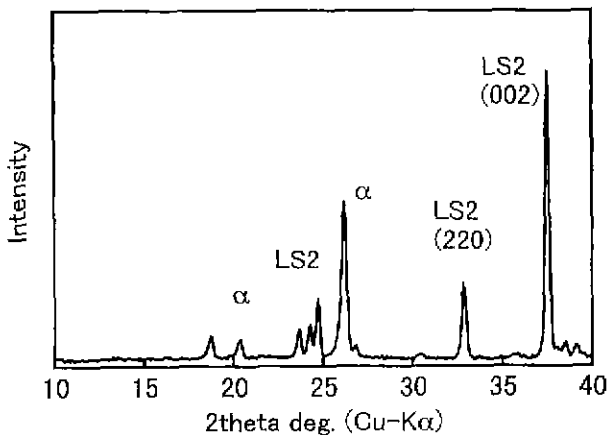
Fig. 1. A typical DTA curve of the powdered glass sample.



Fig. 3. XRD pattern of the glass-ceramic samples without $P_2O_5$ and a different metal oxide: LS2=lithium di-silicate; $\alpha$=$\alpha$-quartz solid solution.



and the second (T=808°C) corresponds to that of cristo-

Fig. 2. XRD pattern of the glass-ceramic sample without $P_2O_5$: LS2=lithium di-silicate; $\alpha$=$\alpha$-quartz solid solution.



Fig. 4. XRD pattern of the glass-ceramic samples without $P_2O_5$ and a different metal oxide: LS2=lithium di-silicate; Cri=cristobalite.

balite or $\alpha$-quartz solid solution. The glass transition temperature (Tg) ranged from 485 to 515°C.

## 2. X-ray Diffraction (XRD)

### 2.1 without $P_2O_5$

Fig. 2 shows the typical XRD patterns of the glass-ceramic samples without the addition of $P_2O_5$ after heat-treatment at 760°C. The lithium di-silicate and $\alpha$-quartz solid solution phase were identified, and it was observed that the lithium di-silicate had (002) preferred orientation due to surface crystallization mechanism.[4]

### 2.2 with $P_2O_5$

Samples containing both $P_2O_5$ and another oxide as the secondary nucleating agent were heat treated at 760°C. All the crystalline phases shown as Figs 3 and 4 were almost randomly oriented in comparison with JCPDS Files No. 40-376 (lithium di-silicate), No. 39-1425 (cristobalite) and No. 46-1046 (a-quartz), it was concluded that the volume crystallization occurred. Two types of the crys-
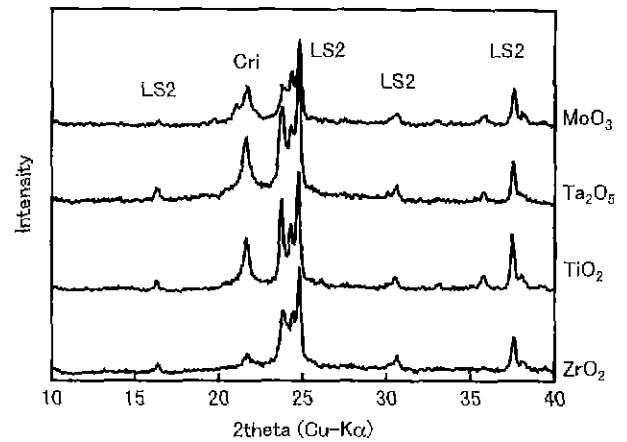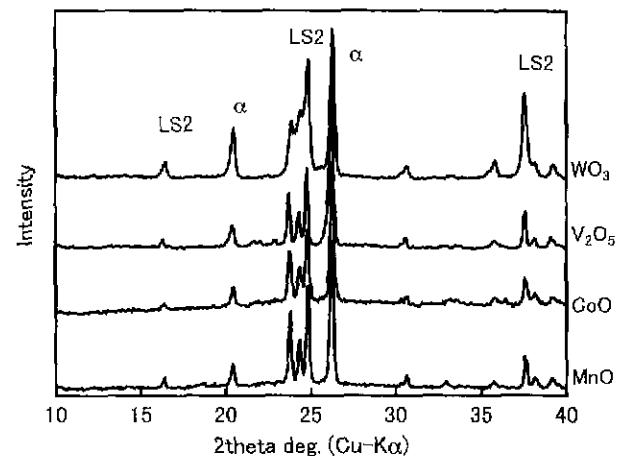
tallization were observed depending on the kinds of the additional oxides. In the case of $TiO_2$, $ZrO_2$, $MoO_3$ and $Ta_2O_5$, the crystal phases of lithium di-silicate and cristobalite were precipitated as shown in Fig. 3. In the case of $V_2O_5$, $MnO_2$, CoO and $WO_3$, the phases of lithium di-silicate and $\alpha$-quartz solid solution appeared (Fig. 4).

### 3. Microstructure

Figs. 5(a)~(h) show the microstructure of the glass-ceramics heat-treated at 760°C. Two types of the micro-structures were observed corresponding to the precipitated phases. When the specimen contained the precipitation of cristobalite and lithium di-silicate, only the crystalline particles having fine grain sizes less than 30 nm were detected. On the other hand, in the case of $\alpha$-quartz solid solution and lithium di-silicate, flowerlike, needlelike or planar crystalline particles were observed and their mean grain sizes were much larger than those
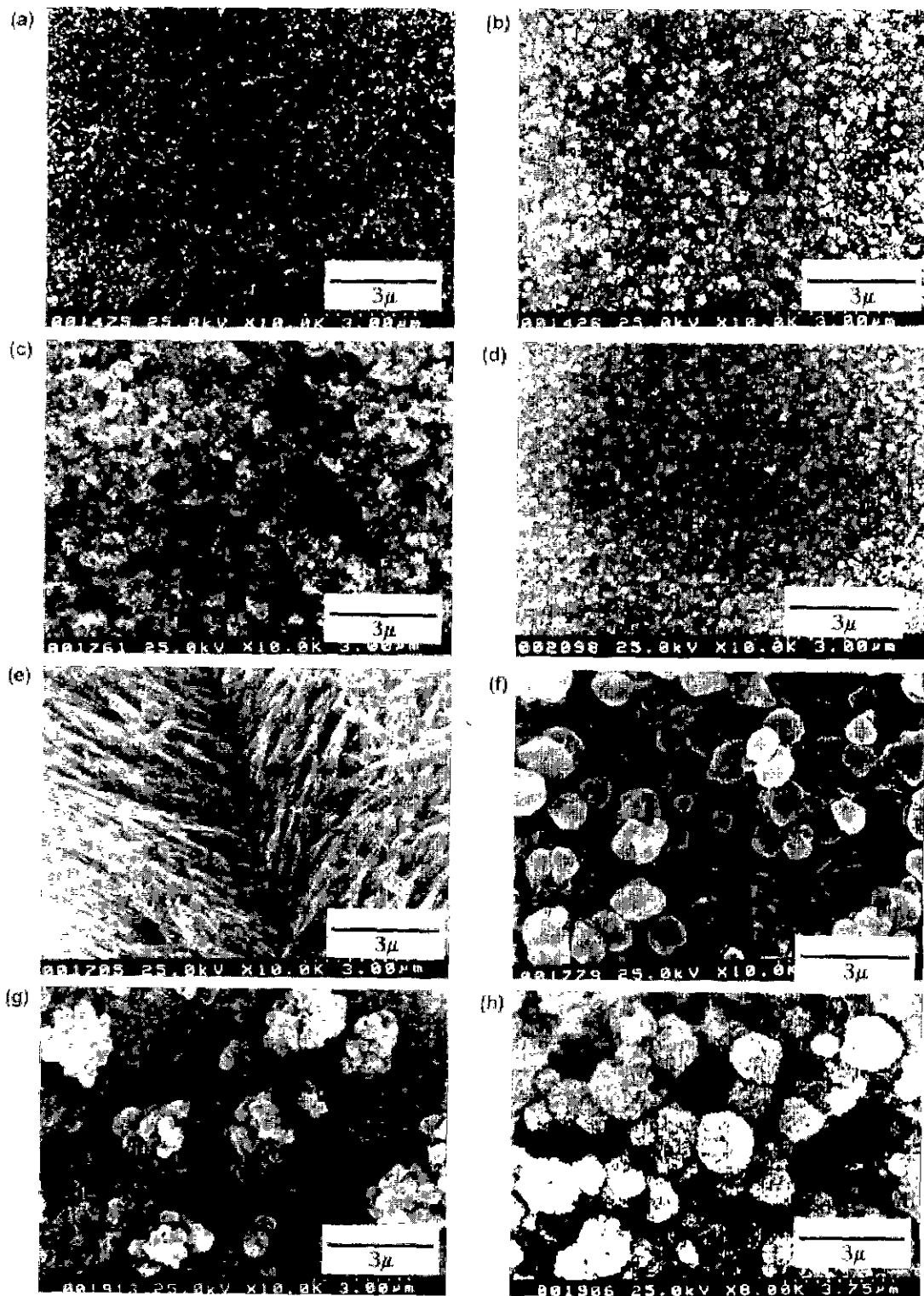
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**Fig. 5.** SEM images of polished and etched (HF solution) surface sections through the samples with $P_2O_5$ and a different metal oxide: (a) $TiO_2$, (b) $ZrO_2$, (c)$MoO_3$, (d)$Ta_2O_5$, (e) $WO_3$, (f) $V_2O_5$, (g) $MnO_2$ and (h)$CoO$.

of cristobalite.

## 4. Surface roughness

In the case of the samples without $P_2O_5$, their surfaces were not smooth due to surface crystallization, so their surface roughness was not measured. The surface roughness of the samples with α-quartz solid solution was not examined because it was considered that the degree of

**Table 1.** Surface Roughness of the Glass-ceramic Samples with $P_2O_5$ and a Different Metal Oxide

| Secondary nucleating agent | Ra(Å) |
|:---:|:---:|
| $TiO_2$ | 8.1 |
| $ZrO_2$ | 7.7 |
| $MoO_3$ | 7.1 |
| $Ta_2O_5$ | 8.2 |

surface roughness was very high due to the larger grains revealed by SEM. The values of the surface roughness (Ra) are summarized in Table 1. Very flat surface with Ra=7.1 Å was attained by the addition of both $P_2O_5$ and $MoO_3$.

# IV. Discussion

Without the addition of $P_2O_5$, lithium di-silicate and/or α-quartz solid solution was orientated due to surface crystallization as shown in Fig. 2.[4] In this case the surface was not flat because the crystal growth occurred near the surface. In general, when surface crystallization occurs, the nucleation density is so low that the crystallite size increases. In fact, the outer shape of the sample without $P_2O_5$ changed before and after the crystallization. It seems hard to achieve a high mechanical strength due to its low degree of crystallinity. Therefore, it is necessary for the present glass to add $P_2O_5$ as a nucleating agent.

$P_2O_5$ was found as an essential nuclear agent to form fine-grained lithium di-silicate crystals. By the addition of $P_2O_5$, randomly oriented XRD profiles, as shown Figs. 3 and 4, were obtained owing to the volume crystallization.[4-6] According to the DTA result in Fig. 1, α-quartz solid solution or cristobalite precipitated as secondary crystalline phase from $SiO_2$-rich residual glassy phase. It has not yet been made clear which $SiO_2$ phase precipitated by the addition of nucleating agents with $P_2O_5$. In the case of the precipitation of α-quartz solid solution as shown in Figs. 5(e)~(h), flowerlike, needlelike or planar larger crystals were observed. The surface roughness was, therefore, expected to increase due to the large particles. In the case of present glass, it seemed inevitable to suppress precipitation of α-quartz solid solution in order to improve surface roughness. By the addition of $WO_3$, the needlelike crystals, which are characteristic of the growth of lithium di-silicate crystals, were observed as illustrated in Fig. 5(e).[7,8] It was assumed that the addition of $WO_3$ caused the reduction of the efficiency of phase separation ability of $P_2O_5$, because the precipitation of the needlelike crystals was the proof of the reduction of nucleation density for lithium di-silicate. It will be a similar reason that the planar crystals were precipitated by the addition of $V_2O_5$. As discussed already, the α-quartz solid solution phase appeared in the case of the glass without $P_2O_5$, and it was concluded that the phase is observed more frequently when no effective nucleation agent is added to the

present glass. The addition of CoO or $MnO_2$ is, also, supposed to reduce the efficiency of phase separation ability of $P_2O_5$ because the flowerlike crystals, probably corresponding to α-quartz solid solution, precipitated.

In the case of the precipitation of cristobalite as the secondary phase, larger particles were not observed. Therefore, it is important to control the crystallization of both cristobalite and lithium di-silicate so as to obtain the fine-grained microstructure. The addition of the mixture of $MoO_3$ and $P_2O_5$ resulted in the lowest degree of surface roughness and the finest mean grain size. In order to discuss the relationship between the surface roughness and the crystal phases, the glass-ceramics sample containing $MoO_3$ was compared with the sample containing $Ta_2O_5$. From the comparison of the XRD peaks corresponding to cristobalite, the intensity in $Ta_2O_5$ was higher that in $MoO_3$. While the slightly large particles having the mean grain size of 20-30 nm appeared in the SEM photograph of $Ta_2O_5$ system, which they were not observed in $MoO_3$ system. The particles were, therefore, identified as cristobalite In the case of $Ta_2O_5$ system, the cristobalite crystals grew in the crystallization stage at 760°C, but on the contrary the crystal growth was not observed for $MoO_3$ system. $MoO_3$ is considered to play a role of a nucleating agent for cristobalite. This explains why the XRD peaks corresponding to cristobalite in $MoO_3$ was broadened by the reduction of particle sizes. It was assumed that the role of $MoO_3$ was an effective nucleating agent for cristobalite rather than an agent to enhance $P_2O_5$ for nucleation of lithium disilicate.

# V. Conclusion

New glass ceramics were investigated for the application as substrates to be used in hard disk devices. In the present glass, the precipitation of α-quartz solid solution phase increased the surface roughness due to the large particles. It is necessary to optimize the crystallization of both cristobalite and lithium di-silicate in order to obtain the fine-grained microstructure. The addition of the mixture of $P_2O_5$ and $MoO_3$ had very drastic effects on the microstructure, because the addition of $P_2O_5$ was efficient to form fine-grained lithium di-silicate crystals and the addition of $MoO_3$ was adequate to precipitate fine-grained cristobalite crystals. The glass ceramics with very high surface flatness (Ra=7.1 Å) was obtained.

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