We investigated crack generation and methods for preventing it in glass ceramics when Cu-glass paste and glass ceramics were co-fired. Cu-glass paste was used to fill the through holes of a glass-ceramic green sheet consisting of borosilicate glass/Al2O3/cordierite by screen-printing. Cracks are generated in the glass-ceramic portion that surrounds the through holes parallel to the circumference. These cracks occur when the tensile stress generated at the interface between the conductor in the through hole and the glass ceramic as a result of a mismatch in the coefficients of thermal expansion (CTEs) between Cu and glass ceramic exceeds the mechanical strength of the glass ceramic. The magnitude of the tensile stress was calculated by performing stress analysis using a model based on a thick multilayer cylinder. These cracks can be prevented by either greatly reducing the CTE of Cu conductor by adding a large amount glass or by reducing the Young’s modulus of the Cu conductor and without adding additives to the Cu paste for promoting sintering (e.g., glass), which increase the density of the Cu conductor.

Key-words: Copper conductor, Glass-ceramics, Co-fire, Crack, Young’s modulus, Coefficient of thermal expansion, Hardness
laminate produced was cut to a size of 30 × 30 mm. A substrate with through holes was obtained by burning out the binder of the laminate at 850 °C for 10 h in N₂ + 0.4 atm H₂O and sintering the laminate at 925 °C for 1 h in N₂. The heating rate was 100 °C/h, and the cooling rate was 200 °C/h. A Cu-glass sintered compact was obtained using the following procedure. The prescribed amount of Cu powder and glass powder with ethyl acetate and Al₂O₃ balls were mixed by ball milling. The resulting mixture was dried and the dry cake was granulated to a ~32 mesh powder and uniaxially pressed into a 10 × 10 × 60 mm green compact having a relative density of about 45% that was equal to the volume fraction of the inorganic ingredient in the Cu paste. A Cu-paste-based sintered compact was obtained by burning out the binder of the compact at 850 °C for 10 h in N₂ + 0.4 atm H₂O and sintering the compact at 925 °C for 1 h in N₂. The heating rate was 100 °C/h, and the cooling rate was 200 °C/h.

The microstructures of the samples were characterized using a scanning electron microscope (SEM S-570, Hitachi). Since the samples were insulating, they were coated with Au and Pd prior to SEM characterization. The CTEs were measured using a double-pass Michelson-interferometry dilatometer (LIX-1, ULVAC-RIKO, Inc.) at a heating rate of 3 °C/min (from RT to 200 °C) in 0.26 atm of helium. The test samples for the CTE measurements were prepared by cutting capsule-shaped samples that were about 6 mm in diameter and about 12 mm in length. The hardness was measured using a micro Vickers Sclerometer (Fisherscope HCU, Fisher Scientific Inc, USA) at a load of 0.245 N and a creep time of 25 s. Seven points were measured; the maximum and minimum values were discarded and the remaining five measurements were averaged. The Young’s modulus and Poisson’s ratio were measured by the rectangular parallelepiped resonance method. The test pieces were prepared by cutting into cubes of about 4 mm in length. The Young’s modulus and Poisson’s ratio of selected samples were also measured at a high temperature by the same method.

### 3. Results and discussion

#### 3.1 Crack generation around through holes in Cu/glass co-fired substrates

**Table 1** shows the compositions of the Cu pastes used for the through hole conductors and the occurrence of crack generation around the through holes of Cu/glass ceramics co-fired substrates when these pastes were used. The measured CTEs of the Cu paste sintered compacts are also shown in Table 1. The inorganic components of the Cu paste were only Cu powder and cordierite glass powder. We varied the fraction of glass in the range 0–50.9 vol%. Figure 1 shows the relationship between the fraction of glass and the CTE of the Cu paste sintered compacts. Additional data besides that given in Table 1 is plotted in Fig. 1. The solid line is what approximated by the minimum mean square method as for the plotted data. The CTE decreases as the proportion of cordierite glass increases. The actual measured values lie between the simple mixture rule (Eq. (1)) and Turner and Kerners’ equation (Eq. (2)).

\begin{equation}
\alpha = \frac{\alpha_1 V_1 + \alpha_2 V_2}{V_1 + V_2} \quad (1)
\end{equation}

\begin{equation}
\alpha = \frac{\alpha_1 E_1 V_1 + \alpha_2 E_2 V_2}{E_1 V_1 + E_2 V_2} \quad (2)
\end{equation}

In Eqs. (1) and (2), \(\alpha\) is the CTE, \(E\) is Young’s modulus and \(V\) is the volume fraction. When the amount of the glass addition is a little, the CTE of Cu paste sintered compact nearly equals to the CTE of the frame of Cu. The CTE of compact lowers when the amount of the glass addition becomes more than a value. Cracks were observed in the substrates made using the Cu paste whose glass fraction was in the range 16.5–32.4 vol%. No cracks were observed in the substrates made using the Cu paste whose glass fraction was in the range 35.2–50.9 vol%. When the fraction of glass in the Cu conductor increases, the CTE of the Cu conductor decreases (Table 1, Fig. 1) and the difference between the CTEs of the Cu conductor and the glass ceramic becomes small (Table 1). This is the reason why cracks were not observed in the glass ceramic portion around Cu conductors having a high fraction of glass. On the other hand, no crack generation was observed in the substrate made using pure Cu paste without glass. Figure 2 shows an example of a crack that was generated in the glass ceramic portion around a through hole parallel to the circumference. The tensile stress and the compression stress were generated in right-angled to the tangent direction and in the tangent direction, respective-
Fig. 2. Example of crack generation in glass ceramic near through hole Cu-glass conductor. (Cu-glass paste No.: T2, sintering conditions: 925°C, 2 h).

Table 2. Various Properties of Cu-glass Sintered Compacts having the Same Compositions as the Cu-glass Pastes Used for the Through Hole Conductor

<table>
<thead>
<tr>
<th>Paste No.</th>
<th>(a^\ddagger) (10^6{\text{K}}^{-1})</th>
<th>(H^\ddagger)</th>
<th>(E^\ddagger) (GPa)</th>
<th>(\nu^\ddagger)</th>
<th>(\text{RD}^\ddagger) (_yaw)</th>
<th>(H_{\text{GC}}^\ddagger)</th>
<th>(E_{\text{GC}}^\ddagger) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>16.5</td>
<td>62</td>
<td>8.7</td>
<td>0.282</td>
<td>-</td>
<td>48</td>
<td>6.4</td>
</tr>
<tr>
<td>T2</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>112</td>
<td>16.5</td>
</tr>
<tr>
<td>T3</td>
<td>14.6</td>
<td>146</td>
<td>33.9</td>
<td>0.315</td>
<td>64.1</td>
<td>143</td>
<td>28.7</td>
</tr>
<tr>
<td>T4</td>
<td>11.1</td>
<td>138</td>
<td>26.6</td>
<td>0.336</td>
<td>59.7</td>
<td>163</td>
<td>40.3</td>
</tr>
<tr>
<td>T5</td>
<td>10.0</td>
<td>110</td>
<td>17.6</td>
<td>0.317</td>
<td>53.8</td>
<td>104</td>
<td>16.7</td>
</tr>
<tr>
<td>T6</td>
<td>8.2</td>
<td>157</td>
<td>25.4</td>
<td>0.334</td>
<td>58.7</td>
<td>183</td>
<td>62.0</td>
</tr>
<tr>
<td>T7</td>
<td>7.1</td>
<td>128</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>136</td>
<td>26.0</td>
</tr>
</tbody>
</table>

\(^\ddagger\): RT - 200°C  \(^\ddagger\): Micro Vickers hardness \(^\ddagger\): Young’s modulus
\(^\ddagger\): Poisson’s ratio \(^\ddagger\): Relative density \(^\ddagger\): Glass ceramic

Fig. 3. Relationship between relative density and Young’s modulus of Cu-glass sintered compact.

Fig. 4. Relationship between micro Vickers hardness and Young’s modulus of Cu-glass sintered compact.

ly at the glass ceramic portion near the interface between Cu and the glass ceramic of the substrate. The former caused the crack as the temperature decreased from the softening point of glass to room temperature during the post-sintering cooling process due to the mismatch of CTEs of Cu (high CTE) and that of glass ceramic (low CTE). It is thought that this tensile stress produced the crack shown in Fig. 2. The details of tensile stress are described in section 3.3.

3.2 Properties of Cu paste sintered compact

Table 2 shows various properties of the Cu paste sintered compacts that have the same compositions as the Cu pastes mentioned in section 3.1. Figure 3 shows the relationship between the relative densities and Young’s modulus of the Cu paste sintered compacts. The theoretical densities were calculated from the Cu/glass fraction by assuming that the Cu powder did not react with the glass powder. The data of Table 2 together with additional data and the Young’s modulus of Cu bulk are plotted in Fig. 3. There is a high correlation between the Young’s modulus and the relative density of the Cu paste sintered compacts. The Young’s modulus reaches about 130 GPa, which is almost the same as that of Cu bulk, when the relative density is 100%. The Young’s modulus increased monotonously with the relative density. The Young’s modulus becomes near 0 when becoming 50% or less in a relative density. This relative density almost equals to that of molding body. The Young’s modulus of molding body is almost 0, because only necking occurs in it. Figure 4 shows the relationship between the micro Vickers hardness and the Young’s modulus of the Cu paste sintered compacts. Additional data besides that shown in Table 2 is also included in Fig. 4. The lines are quadratic curve what approximated by the minimum mean square method as for the plotted data. There is a high correlation between the micro Vickers hardness and the Young’s modulus of the compacts. The Young’s modulus increased monotonously with the micro Vickers hardness. Though the Young’s modulus has only the correlation with the inclination of the load displacement curve in measurement of hardness, there is no theoretical direct correlation between them. However, it is reported that the hardness is four or five times of the Young’s modulus in the same material series.17 The hatching area shows this range in Fig. 4. The plotted data is almost corresponding to the range reported.17 Figure 5.
shows an example of measuring the temperature dependence of Young’s modulus and Poisson’s ratio of the Cu paste sintered compact. The lines are what approximated by the minimum mean square method as for the plotted data. It shows that Young’s modulus and Poisson’s ratio vary little with temperature between room temperature and 700 °C. It is important to note that the properties of the Cu paste sintered compact investigated in this study are not the properties of the through hole conductor, but only the properties that are simulated for the through hole conductor. In particular, the Young’s modulus of the through hole conductor does not necessarily correspond to that of the sintered compact; this is because the degree that the paste fills the through hole and the sintering shrinkage of the glass ceramic greatly influence the relative density, consequently the Young’s modulus of the through hole conductor. The relative density of the through hole conductor can’t be measured directly. However, there is a high correlation between the Young’s modulus of the through hole conductor and the correlation in Fig. 4. The stress generated at the interface of the through hole conductor and glass ceramic greatly influence the relative density, consequently the Young’s modulus of the through hole conductor. The relative density of the through hole conductor can’t be measured directly. The stress generated at the interface of the through hole conductor and glass ceramic is expressed by Eq. (3). The stress is generated at the interface between the through hole conductor and the glass ceramic during the cooling stage after co-firing of the Cu/glass ceramic substrate by the mismatch in the CTEs of the Cu conductor and the glass ceramic.

\[
P_m = \frac{\Delta T (\alpha_1 - \alpha_2)}{E_1 + \frac{1}{E_2} + \frac{2}{E_2 b^2 - c^2}}
\]

In Eq. (4), \(\Delta T\) is temperature interval over which the stress is generated, \(\alpha_1\) is the CTE of the Cu conductor, \(\alpha_2\) is the CTE of the glass ceramic, \(E_1\) is Young’s modulus of the Cu conductor, \(E_2\) is Young’s modulus of the glass ceramic, \(\nu_1\) is Poisson’s ratio of the Cu conductor, \(\nu_2\) is Poisson’s ratio of the glass ceramic, \(b\) is half the pitch of the through hole, \(c\) is the radius of the through hole. In this study, \(\Delta T (799°C)\)
was taken to be the difference between the softening point of glass (824°C) and room temperature (25°C), \( b \) and \( c \) were determined from the size of the through hole after sintering and were taken to be 225 \( \mu \)m and 55 \( \mu \)m respectively, and the value of the CTE in the range 0–200°C was used for \( \alpha \). The values of Young’s modulus and Poisson’s ratio at room temperature were substituted for \( E \) and \( \nu \) respectively, since they vary little with temperature from room temperature to 700°C (see Fig. 5). Consequently, the stress \( P_m \) at the interfaces of through holes that were filled with pastes T1–T7 and then sintered were calculated and are shown in Fig. 8 together with whether cracks were generated or not. The assumed value from micro Vickers hardness given in Section 3.2 was used for the Young’s modulus of the through hole conductor. The Poisson’s ratios of some Cu conductors were not measured, but were assumed to be 0.3, since the Poisson’s ratios of all the Cu paste sintered compacts were close to 0.3. Stress analysis was performed by keeping the CTE constant, even though the CTE is temperature dependent. As a result, the relationship between the properties of the through hole conductor and the stress generated at the interface of the through hole have been clarified. Figure 8 shows that only substrates whose stresses \( P_m \) exceed 170 MPa exhibit crack generation. This value is approximately equal to the bending strength of the glass ceramic (200 MPa). The relationship between Young’s modulus and the CTE of the through hole conductor is expressed by Eq. (5) by substituting 170 MPa for \( P_m \), the properties of the glass ceramic, and 0.3 for \( \nu_1 \) in Eq. (4).

\[
\alpha_1 \times 10^{-6}/^\circ C = \frac{148.9}{E_1[\text{GPa}]} + 5.475
\]

This expression is plotted as the curve shown in Fig. 9. The region above this curve is for \( P_m > 170 \) MPa and the region
beneath the curve is for $P_m < 170 \text{MPa}$. This figure shows that cracks are not generated even for the case when a low-CTE component (e.g., glass) is not added to the Cu paste and the through hole conductor has a high CTE, provided the relative density and Young's modulus are sufficiently low. In contrast, when glass is added to the through hole conductor, the CTE decreases, but Young's modulus increases because of densification. The results show that to prevent the generation of cracks it is necessary to greatly reduce the CTE by adding a large amount of glass. In other words, we found that lowering either Young's modulus or the CTE is effective for preventing the formation of cracks. Adding a large amount of glass causes a dramatic increase in the electric resistance of conductor. Moreover, when the temperature increases the CTE increases while the increase in the electric resistance of conductor. Adding a large amount of glass causes a dramatic increase in the electric resistance of conductor. Moreover, when the temperature increases the CTE increases while the Young's modulus of the Cu conductor hardly changes (see Fig. 5). It is thought that the former technique, namely, that of reducing Young's modulus is more effective, in light of the high temperatures generated during manufacture and in applications.

4. Conclusions

The effect of the properties of Cu-glass conductor on crack generation at the glass portion near the through holes in Cu-glass conductor paste/glass ceramic green sheet co-fired substrates was investigated. The following findings were made.

1) There is a high correlation between Young's modulus and micro Vickers hardness of a Cu paste sintered compact. Thus, the Young's modulus of a through hole conductor can be estimated by measuring its micro Vickers hardness.

2) Cracks are generated in a glass ceramic near through holes parallel to the circumference due to the tensile stress generated at the interface of a through hole during post-sintering cooling stage due to a mismatch between the CTEs of Cu and glass ceramics. This stress was calculated by performing a two-dimensional stress analysis of the through hole section. Cracks are generated when this stress exceeds the strength of the glass ceramic. An expression for the plane stress based on the thick cylindrical multilayer model was used for the two-dimensional stress analysis.

3) Cracks are not generated even for the case when a low-CTE component (e.g., glass) is not added to the Cu paste and the through hole conductor has a high CTE, provided the relative density and Young's modulus are sufficiently low. In contrast, when glass is added to the through hole conductor, the CTE decreases, but Young's modulus increases because of densification. It was found that to prevent the generation of cracks it is necessary to greatly lower CTE by adding a large amount of glass.

References