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Semiconducting Glass-Ceramics Based on the $CuAlO_2$–SiO_2 System

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SUMMARY

Glass-ceramics consisting of delafossite-type $CuAlO_2$ and cristobalite crystals were prepared by crystallising the $Cu_2O.Al_2O_3.nSiO_2$ ($n = 2 \sim 3{\cdot}5$) glasses at 950°C ~ 1000°C in air. Their electrical conductivity was between 10^{-3} and 10^{-5} S cm^{-1} at room temperature, depending on the amount of $CuAlO_2$, and behaved as p*-type semiconductors. They were stable up to about 700°C in air, but transformed to glass-ceramics containing spinel-type $CuAl_2O_4$ at higher temperature. It is proposed that the precipitated delafossite-type crystals are deficient in copper as $Cu_{1-x}AlO_2$ ($x = 0{\cdot}7 \sim 0{\cdot}8$).*

1 INTRODUCTION

The $Cu_2O.Al_2O_3.nSiO_2$ glasses have been known to show thermal expansion coefficients as low as about 10×10^{-7}/°C.[1] It has been reported by Matusita *et al.*[2] that the glass-ceramics obtained from the $Cu_2O.Al_2O_3.nSiO_2$ glasses by heating around 900°C are composed of crystals isostructural with β-spodumene, $Li_2O.Al_2O_3.4SiO_2$, and also

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show low, even slightly negative thermal expansion. In that work, the authors have noticed that the β-spodumene-type $Cu_2O.Al_2O_3.nSiO_2$ crystal is decomposed to $CuAlO_2$ and SiO_2 around 1000°C.[2] The $CuAlO_2$ is known to be isostructural with $CuFeO_2$ (delafossite) and a *p*-type semiconductor.[3-5]

In general, crystallisation of glasses to form glass-ceramics has been one of the important ceramic processes. This technique has the following advantages over the sintering process: (1) forming of the product can be easily performed because it is done in the glassy or viscous state, (2) highly dense ceramic products can be obtained at relatively low temperatures, and (3) ceramics with useful physical and chemical properties are easily obtained by selecting the composition of the starting glasses and crystalline species precipitated in the glasses. Among them, the $PbO–ZnO–B_2O_3$ glasses containing powdered Ag or Ag_2O have been developed as crystallising solder glasses to form electricity conducting glass-ceramics.[6]

On the basis of the above-mentioned experimental facts obtained for the $Cu_2O–Al_2O_3–SiO_2$ glasses,[2] the present study was undertaken in order to prepare electricity conducting glass-ceramics. For that purpose, the precipitation process of the delafossite-type $CuAlO_2$ crystal in the $Cu_2O.Al_2O_3.nSiO_2$ glasses and the optimum processing condition for making glass-ceramics, containing as much as possible of the desired $CuAlO_2$ crystal, have been investigated and the electrical properties of the resultant glass-ceramics have been measured.

2 EXPERIMENTAL

2.1 Glass samples

The glasses of compositions of $Cu_2O.Al_2O_3.nSiO_2$ ($n = 2$, 2·5, 3 and 3·5) were made by melting, at 1500 ~ 1550°C in air for 2 h, the corresponding mixtures of reagent-grade CuO and Al_2O_3 and silica sand for optical glasses acid-washed to remove the impurity of iron. The melts were poured onto an iron plate to form glasses.

The chemical state of copper in the glasses is given in Table 1. The amounts of Cu^+ and total copper were determined by the redox titration after Close and Tillman[7] and iodometry, respectively. No detectable amount of metallic copper was found by X-ray diffraction. As seen in Table 1, 80 ~ 90% of copper in the glasses is present as Cu^+. Thin glass films were transparent and light brown in colour; bulk glasses were black with a metallic lustre.

TABLE 1
Chemical State of Copper in the $Cu_2O.Al_2O_3.nSiO_2$ Glasses

Glass *n*	*Analysed Cu content* (*wt*%)	*Cu^+ content* (*wt*%)	$\frac{[Cu^+]}{[Cu^+]+[Cu^{2+}]}$ (%)	*Added Cu content* (*wt*%)
2	30·8	24·0	77·9	34·8
2·5	28·8	24·3	84·4	32·1
3	26·3	23·3	88·5	29·9
3·5	25·8	21·5	83·1	27·9

2.2 Crystallisation of the glasses

The crystallisation behaviour of the $Cu_2O.Al_2O_3.nSiO_2$ glasses was investigated for powders and bulk samples (*c.* 2 × 3 × 5 mm in size). For that purpose, glass samples were heated to the desired temperatures at a heating rate of 10°C min^{-1} and held there for different times in air. The precipitated crystalline species were identified by X-ray diffraction, using Ni-filtered Cu $K\alpha$ radiation.

2.3 Measurements of electrical properties

The electrical conductivity measurements were carried out for the glasses and glass-ceramics using a three-terminal guarded alternating-current method with an LCR meter (model 4274A Yokogawa-Hewlett-Packard, Tokyo) and a conductance bridge (model TRS-1, Ando Denki, Tokyo). Disc samples with diameter 4 cm and thickness 4 mm were used for the measurements. Both sides of the disc samples were polished with No. 1000 alumina powders and doubly coated with chromium and then gold films by vacuum evaporation as the electrodes. The electrical conductivity, σ, measurement was based on conventional complex plane impedance analysis, using frequencies from 100 Hz to 100 kHz for $\sigma > 10^{-5}$ S cm^{-1} and from 5 Hz to 5 MHz for σ in the range $10^{-5} \sim 10^{-9}$ S cm^{-1}. For measuring $\sigma < 10^{-10}$ S cm^{-1} the voltage sweep method[8] was employed, in which a linearly changing triangular wave was applied across the electrodes instead of the application of a constant voltage; a linear relation between the monitored current response and the applied voltage gave the electrical conductivity.

Transport numbers of ions and electrons (or holes) in the samples were measured using Tubandt's electrolysis method.[9] Two sample plates of *c.* 20 × 10 × 3 to 5 mm in size were pressed together. The contacting surfaces of the sample were optically polished with CeO_2, and the other side was coated with chromium film by vacuum evaporation. The total charge passed through the specimen was measured with a silver coulometer.

3 RESULTS AND DISCUSSION

3.1 Crystallisation behaviour of the $Cu_2O . Al_2O_3 . n\,SiO_2$ glasses

For both powdered and bulk glass samples, the β-spodumene-type $Cu_2O . Al_2O_3 . nSiO_2$ crystal was precipitated with a small amount of CuO for all values of n except $n = 2$, when heated up to 850°C in air, which is consistent with the previous results.[2] On further heating of the powdered samples up to 950°C, the precipitated β-spodumene-type crystal decomposed to spinel-type $CuAl_2O_4$ and quartz or cristobalite as shown in Table 2. As can be seen for the powdered glass with $n = 2$, Cu_2O and mullite crystals were precipitated by heating up to 950°C and holding there for 1 h; they then changed to $CuAlO_2$ on further heating. For $n = 2{\cdot}5$ and 3, β-spodumene-type $Cu_2O . Al_2O_3 . nSiO_2$ was first precipitated and changed to $CuAlO_2$ and SiO_2 by longer heating at 950°C. On the other hand, when bulk glass samples

TABLE 2

Crystalline Species Precipitated in $Cu_2O . Al_2O_3 . nSiO_2$ Glasses Heated under Different Conditions

Run	*n*	*Temperature (°C)*	*Time (h)*	*Precipitated crystalline phases*
1	2	950	1	$Cu_2O \gg$ Mullite
2		950	5	$CuAlO_2 \gg CuAl_2O_4$, Crist, CuO
3		950	10	$CuAlO_2 \gg$ CuO, $CuAl_2O_4$, Crist
*4		950	2	$CuAlO_2$, Crist $\gg$ CuO
5	2·5	950	1	β-Spodumene $\gg CuAlO_2$, $CuAl_2O_4$, CuO, Quartz
6		950	5	$CuAlO_2$, Quartz $\gg CuAl_2O_4$, CuO
7		950	10	Quartz, $CuAlO_2 \gg CuAl_2O_4$, Crist, CuO
8		950	30	Quartz, $CuAlO_2 \gg CuAl_2O_4$, CuO, Crist
*9		1 000	2	$CuAlO_2$, Crist $\gg$ CuO, $CuAl_2O_4$
10	3	950	1	β-Spodumene
11		950	5	β-Spodumene $\gg CuAlO_2$, Quartz, CuO
12		950	10	$CuAlO_2$, Quartz $\gg$ CuO, $CuAl_2O_4$
13		950	20	Quartz, $CuAlO_2 \gg$ CuO, Crist, $CuAl_2O_4$
*14		1 000	4	$CuAlO_2$, Crist $\gg$ CuO, $CuAl_2O_4$
*15	3·5	1 000	6	Crist, $CuAlO_2 \gg CuAl_2O_4$, CuO

* Runs in which bulk glasses were used. In other runs, powdered glass-samples were used.

were heated to 950°C or 1000°C (run 4, 9, 14 and 15 marked by asterisks in Table 2), the glass-ceramics containing the delafossite-type $CuAlO_2$ were obtained within several hours as shown in Table 2. In the bulk glass-ceramics, the content of coexisting CuO and the spinel-type $CuAl_2O_4$ was small relative to $CuAlO_2$ and SiO_2 as can be seen in the X-ray diffraction profiles shown in Fig. 1. The relative intensity of the delafossite-type $CuAlO_2$ crystal to cristobalite in the bulk ceramics decrease with increasing n or content of SiO_2.

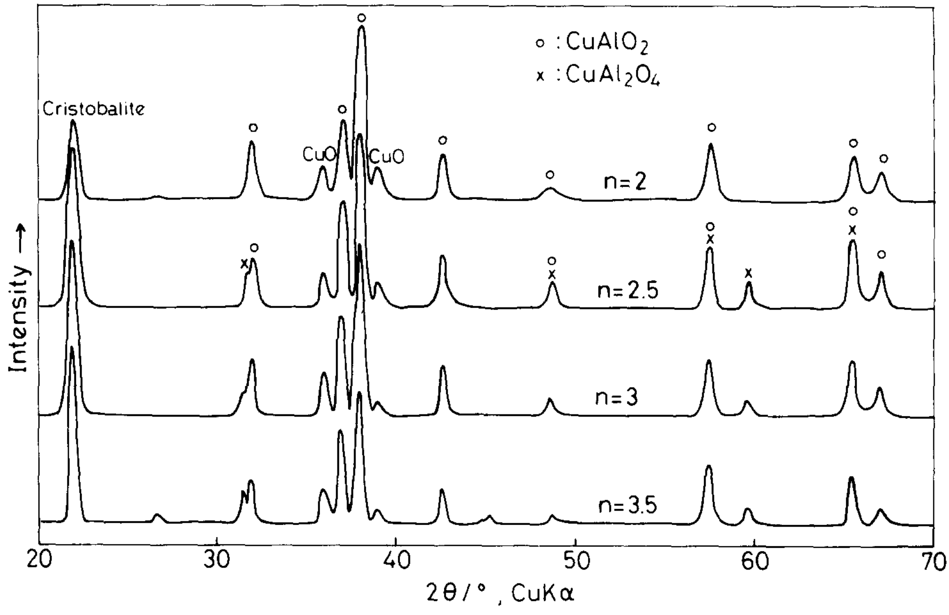

Fig. 1. X-ray diffraction patterns of the glass-ceramics, obtained from the bulk Cu_2O. $Al_2O_3.nSiO_2$ glasses.

3.2 Description of the $CuAlO_2$–SiO_2 glass-ceramics for the electrical measurements

The glass discs of *c*. 4 cm in diameter and 0·4 cm in thickness were heated to be crystallised for the electrical conductivity measurements. In this case, a slow heating rate of 2·5°C min^{-1} was used to avoid crack formation. The heating conditions indicated in Table 2 for bulk samples (run 4, 9, 14 and 15 for $n = 2$, 2·5, 3 and 3·5) were employed. No appreciable difference between X-ray diffraction patterns taken from the disc surface, from the perpendicularly cut surface and from the powder pattern was observed in any glass-ceramics, which implies that no preferential growth of the $CuAlO_2$ and cristobalite occurs during crystallisation. The volume fractions of the

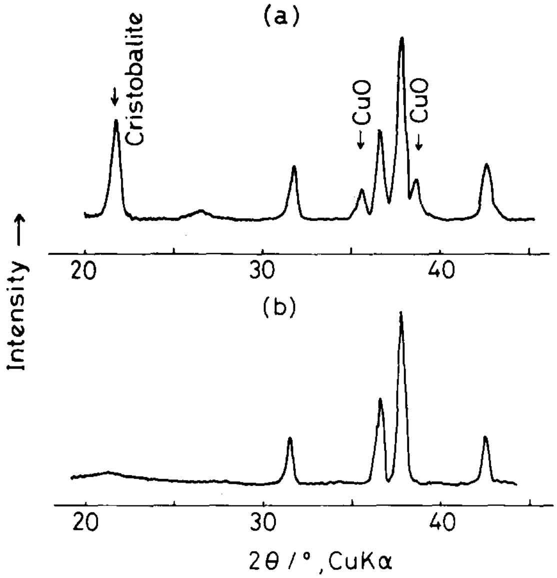

Fig. 2. X-ray diffraction profiles of the $CuAlO_2 . SiO_2$ glass-ceramics taken at the surface. (a) As-prepared; (b) after etching by dilute HF solution.

$CuAlO_2$ in glass-ceramics so obtained, calculated by assuming that the glass-ceramics are composed merely of $CuAlO_2$ and cristobalite, are 48, 42, 38 and 34% for n of 2, 2·5, 3 and 3·5, respectively.

Under the optical microscope the glass-ceramics were observed to be composed of grains of 10 ~ 30 μm. If the glass-ceramic discs were etched by dilute HF solution, the cristobalite crystals were removed selectively to leave a fragile layer of $CuAlO_2$ or $CuAlO_2$ powders on the surface (the diffraction patterns taken at the surface before and after etching by HF are shown in Fig. 2 for $n = 2$). This indicates that the $CuAlO_2$ crystals are distributed randomly in the cristobalite matrix, not forming a continuous phase in the glass-ceramics.

3.3 Stability and stoichiometry of the delafossite-type $CuAlO_2$ included in glass-ceramics

In ambient atmosphere conditions ($pO_2 = 0{\cdot}21$ atm) the delafossite-type $CuAlO_2$ is stable above 1000°C.[10] It should transform to the spinel-type $CuAl_2O_4$ at lower temperature. We have investigated the thermal stability of the $CuAlO_2$–SiO_2 glass-ceramics. In Fig. 3, as an example, the change of the diffraction intensity of the strongest peak of $CuAlO_2$ ($2\theta = 38{\cdot}2°$/Cu Kα) with respect to the cristobalite peak, with duration of heating at 500°, 700° and 900°C in air, is shown for the bulk glass-ceramics with $n = 2{\cdot}5$ of which

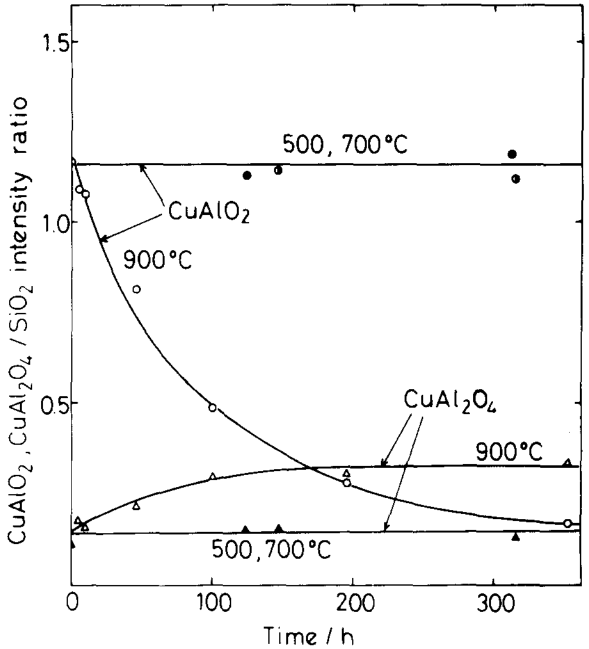

Fig. 3. Variation of the diffraction intensity ratio of delafossite-type crystal to cristobalite with heating time for the glass-ceramics prepared from the $Cu_2O.Al_2O_3.2{\cdot}5SiO_2$ glass.

the whole diffraction pattern is shown in Fig. 1. In the same figure, the variation of the peak intensity of $CuAl_2O_4$ ($2\theta = 58{\cdot}9°$) with heating time is also shown. As can be seen, at 500° and 700°C, no appreciable change of the diffraction intensity of $CuAlO_2$ is found, while at 900°C the $CuAlO_2$ changes gradually to the spinel-type $CuAl_2O_4$. Therefore, the $CuAlO_2$–SiO_2 glass-ceramic prepared in the present work is rather stable up to about 700°C in air, although thermodynamics predicts its instability. This discrepancy may be attributed to kinetics and different oxygen potential in the glass-ceramics which differs from the standard state.

As described above, a small amount of CuO coexists with $CuAlO_2$ and SiO_2 in all the investigated glass-ceramics. For example, the content of CuO in the glass-ceramics with $n = 2$, which was evaluated from the X-ray diffraction intensity, was 8 to 10 wt %. The formation of CuO may arise from the assumption, as in the case of glass-ceramics based on the β-spodumene-type $Cu_2O.Al_2O_3.nSiO_2$ crystal,[11] that a portion of the Cu^+ in the $CuAlO_2$ crystal is oxidised to Cu^{2+} during crystallisation and at the same time the equivalent amount of Cu^+ is expelled out of the crystal grain for the electrical neutrality as in eqn (1),

$$Cu^+AlO_2 \longrightarrow Cu_x^{2+}Cu_{1-2x}^+AlO_2 + xCu^+ \qquad (1)$$

This is followed by migration of Cu^+ to the grain boundary or surface of the glass-ceramics where they react with oxygen to form CuO as in eqns (2) and (3),

$$xCu^+ \xrightarrow[\text{migrate}]{} xCu^+ \text{ (grain boundary or surface)} \tag{2}$$

$$xCu^+ + \tfrac{x}{2}O_2 \longrightarrow xCuO \tag{3}$$

Then the whole reaction can be represented as follows:

$$Cu^+Al_2O + \tfrac{x}{2}O_2 \longrightarrow Cu_x^{2+}Cu_{1-2x}^+AlO_2 + XCuO \tag{4}$$

Assuming the formation of a mixture of $Cu_x^{2+}Cu_{1-2x}^+AlO_2$ and xCuO or $Cu_{1-x}AlO_2 . xCuO$, the content of CuO formed in the glass-ceramics are calculated to be 8·6, 10·6 and 20·9 wt% for the fraction of Cu^{2+} or copper deficiency x of 0·2, 0·25 and 0·5, respectively. Comparing the observed CuO content with the calculated value, it can, therefore be concluded that the delafossite-type copper aluminate crystal in the present work contains both Cu^+ and Cu^{2+} and has the composition of $Cu_{0\cdot7-0\cdot8}AlO_2$ (or $Cu_{0\cdot4}^+Cu_{0\cdot3}^{2+}AlO_2$ to $Cu_{0\cdot6}^+Cu_{0\cdot2}^{2+}AlO_2$) rather than $CuAlO_2$. Although nonstoichiometry is expected as stated above, the present $Cu_{1-x}AlO_2$ crystal has lattice constants a_0 of 2·857 Å and c_0 of 16·94 Å, which are very close to those of a single crystal ($a_0 = 2\cdot860$Å and $c_0 = 16\cdot95$).[5] A similar situation may be encountered in other glass-ceramics with different n values, although evaluation of copper deficiency of the included $CuAlO_2$ could not be made because of the coexistence of a small amount of $CuAl_2O_4$ as well as CuO.

3.4 Electrical properties

In Fig. 4, plots of log σ vs. $1/T$, where σ is the electrical conductivity in S cm^{-1}, are shown for the glass-ceramics and starting glasses. The electrical conductivity of the $Cu_2O . Al_2O_3 . nSiO_2$ glasses is relatively low and shows just a slight dependence on the concentration of copper ions, which may be due to the fact that the nature of Cu^+–O bonding in those glasses is covalent rather than ionic (Yoko, T., Okugawa, I., Tanaka, K. & Kamiya, K., unpublished data). On the contrary, the conductivities of the glass-ceramics are much higher than those of the starting glasses. The conductivity is increased with an increase in the content of $CuAlO_2$ in the glass-ceramics. The activation energy for electrical conduction of the glass-ceramics was 27 kJ mol^{-1}, showing no composition dependence.

Table 3 shows results on the measurements of transport number for the glass-ceramics with $n = 2$. It is found that the weight change of the two contacting glass-ceramics discs is negligibly small, indicating that cations, i.e. Cu^+, scarcely contribute to the electrical conduction; electrons or holes

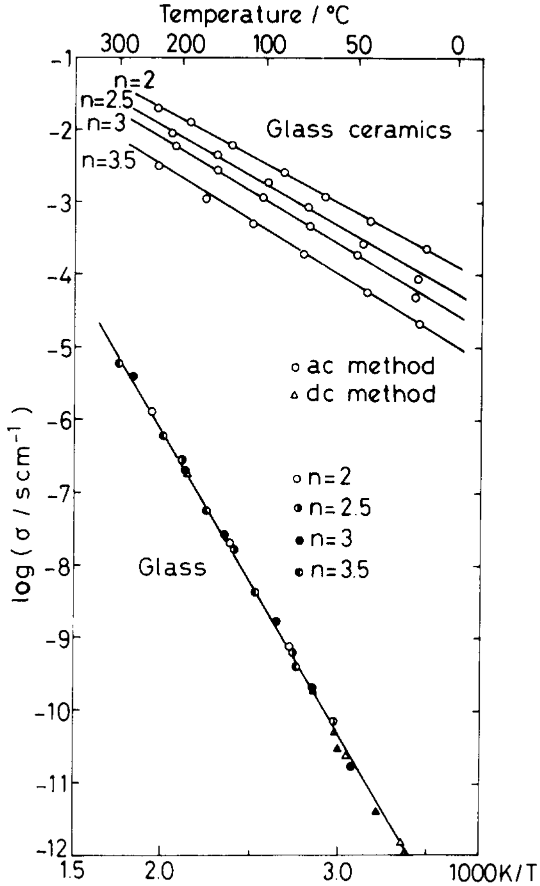

Fig. 4. Temperature dependence of the electrical conductivity of the $Cu_2O.Al_2O_3.nSiO_2$ glasses and glass-ceramics.

TABLE 3

Transport Numbers of the $CuAlO_2$–SiO_2 Glass Ceramics

Sample	*$Cu_2O.Al_2O_3.2SiO_2$ glass ceramics*	
Temperature (°C)	Ambient	253
Time (h)	107	17
Weight of deposited Ag (g)	1·2819	1·6334
Quantity of electricity (c)	1 147	1 461
Weight change of anode (g)	−0·0002	−0·0003
Weight change of cathode (g)	+0·0003	+0·0003
Calculated weight change (g)	0·7551	0·9622
Transport number of cation	0·00026	0·00031

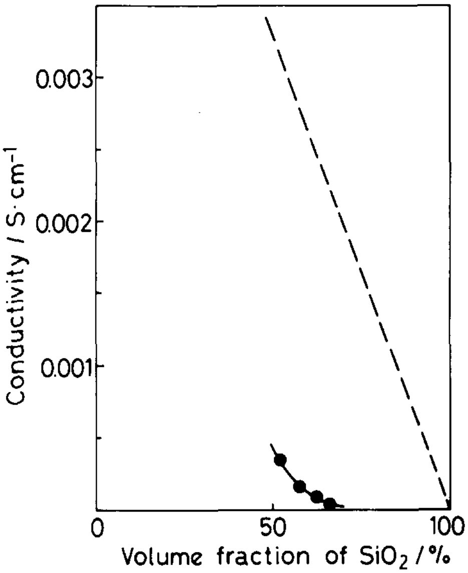

Fig. 5. Variation in the electrical conductivity of the $CuAlO_2$–SiO_2 glass-ceramics with the volume fraction of SiO_2.

are the main carrier of electricity. As has been stated above, the delafossite-type $CuAlO_2$ is a *p*-type semiconductor.[3] The glass-ceramics based on the nonstoichiometric $Cu_{1-x}AlO_2$ are also *p*-type semiconductors.

The investigated glass-ceramic is viewed as a composite, consisting of conducting and non-conducting materials. For such a composite, it has been known that the electrical conductivity follows the mixture law up to about 50% volume fraction of nonconducting materials, but then departs from it for further increases of non-conducting materials.[12] The conductivities of the $CuAlO_2$ single crystal at 25°C are 10^{-1} S cm^{-1} in the *a* direction and 10^{-3} S cm^{-1} in the *c* direction,[5] giving an average conductivity of $0{\cdot}67 \times 10^{-1}$ S cm^{-1}. Figure 5 shows the variation of the electrical conductivity of the glass-ceramics with volume fraction of non-conducting SiO_2. The broken line represents the mixture law. It can be noticed that the conductivity of the glass-ceramics having a volume fraction of $CuAlO_2$ of 48% is far below the expected value. This may be attributed to the loss of copper from the included $CuAlO_2$ crystal.

5 CONCLUSIONS

The crystallisation behaviour of the $Cu_2O.Al_2O_3.nSiO_2$ glasses was extensively investigated to find the optimum conditions for making glass-ceramics containing an electricity conducting $CuAlO_2$ crystal as a major phase. As a result, the glass-ceramics consisting of $CuAlO_2$ and cristobalite phases have been fabricated, of which electrical conductivity is in the range from 10^{-3} to 10^{-5} S cm^{-1}, increasing with the increase of the amount of precipitated $CuAlO_2$ or the decrease in n.

This material may be useful as one of the electricity conducting ceramics, and also as a crystallising solder glass for ceramic parts where electrical conductivity is required, because the starting glass becomes viscous below 1000°C.

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