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Structural changes of glass–ceramics of the Cu_2O–Al_2O_3–SiO_2 system on heating in air

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The behaviour of copper ions in low thermal expansion glass–ceramics prepared from $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glasses, or in β-spodumene type $Cu_2O \cdot Ae_2O_3 \cdot nSiO_2$ crystals included in the glass–ceramics on heating in air was investigated. On heating at 300 to 500° C, the copper ions behaved as in the corresponding glasses. Cuprous ions in the glass–ceramics or β-spondumene type crystals were oxidized into the cupric state, and at the same time an equal amount of cuprous ions to those oxidized were expelled out of the specimen for the requirement of electrical charge neutrality and then reacted with oxygen to form CuO on the surface. The oxidation of cuprous ions and the decrease of the copper content of the β-spondumene type crystals brought about a considerable decrease in the lattice spacings.

1. Introduction

Copper aluminosilicate glasses having the composition of $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ (mol) have been known to show thermal expansion as low as about $10 \times 10^{-7}\,^{\circ}C^{-1}$ [1]. It has been found that glass–ceramics prepared by crystallizing copper aluminosilicate glasses were composed of crystals which had almost the same compositions as the starting glasses and were isostructural with the tetragonal β-spondumene $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (or $LiAlSi_2O_6$), and they exhibited very low thermal expansion, possibly even a small negative thermal expansion [2].

The copper ions in those glasses and corresponding glass–ceramics are predominantly present in the cuprous state. In general, copper ions in oxide glasses can be present in the univalent cuprous or divalent cupric state. The oxidation state of copper ions in the glasses is considerably affected by the processing temperature, atmosphere and/or basicity of the glasses.

The present authors [3] have reported that on heating of the $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass in air at temperatures up to 500° C, some cuprous ions were oxidized into cupric ions and, at the same time, cuprous ions, of which the amount was equivalent to those oxidized to cupric state, were expelled out of the glass in order to maintain the electrical charge neutrality. It has been demonstrated that the variation of the fraction of cupric ions in the $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass on heating in air follows a formula $x/1 - x$, where x is the loss of copper.

In the present work, the behaviour of copper ions in the glass–ceramics derived from the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glasses on heating in air at temperatures up to 500° C was investigated and was compared with that in the corresponding glasses. Furthermore, the structure change of the crystalline constituents of the glass–ceramics, which should be caused by heating in air was also studied and discussed.

2. Experimental procedure

2.1. Preparation of $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glasses and glass–ceramics

Reagent grade CuO and Al_2O_3, and SiO_2 sand of high purity were used as starting materials. The oxide mixtures corresponding to glass compositions of $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ (n = 4 and 8) were melted in alumina crucibles in air at 1500 to 1550° C for several hours. The CuO was assumed here to be completely converted to Cu_2O during melting, since the cuprous state is more stable than the cupric state above ~1100° C according to thermochemistry [4]. Accordingly, the composition of the glasses and corresponding glass–ceramics used in the present study is nominally expressed as $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$, although a small part of the copper ions are present in the cupric state in the glasses and glass–ceramics as will be seen in the following sections.

The glasses thus prepared were heat treated in air for crystallization at temperatures slightly higher than the peak temperatures of crystallization (~900° C) determined beforehand by differential thermal analysis (DTA). Rectangular plate specimens were cut out of the glass–ceramics. The surfaces of the plates were polished with SiC and Al_2O_3 powders and optically

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finished with CeO_2 powders. Particles of mean diameter ranging from 150 to 500 μm were also prepared by pulverising the glass–ceramics.

2.2. Reheating of the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics in air

The plates and particles of the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics were reheated in air at temperatures up to 500° C for different times. The plate specimens were placed on a porous firebrick and particulate specimens were put in an alumina crucible during reheating. Those specimens reheated in air were subjected to the chemical analyses and X-ray diffraction.

2.3. Chemical analyses of cuprous and cupric ions included in the glass–ceramics

The content of cuprous ions in the glass–ceramics was determined on the basis of the redox titration after Close and Tillman [5]. The crushed sample was dissolved in a H_2SO_4–HF solution followed by an addition of excess amounts of ferric ions. The ferrous ions produced by the reaction $Fe^{3+} + Cu^{+} \rightarrow Fe^{2+} + Cu^{2+}$ were titrated by Ce^{4+} ions. The total copper content of the sample was determined by iodometry. The content of cupric ions was estimated as the difference between the total copper content and the cuprous ion content.

2.4. X-ray diffraction

The crystalline species in the glass–ceramics and those formed on reheating in air were identified by X-ray diffraction using Ni-filtered $CuK\alpha$ radiation. The lattice spacings a_0 and c_0 of the crystal with tetragonal β-spondumene type structure in the glass–ceramics were determined from d-spacings of about 20 diffraction lines which were observed in the range of diffraction angle from 10 to 70° in 2θ. For the precise determination of d-spacings, powdered silicon of very high purity was used as an internal standard, and a slow goniometer scanning rate (1/4 to 1/8° per min) was adopted. By using the equation

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a_0^2} + \frac{l^2}{c_0^2}$$

a_0 and c_0 spacings which satisfied all d_{hkl} values within an error of less than 0.1% were determined.

3. Results

3.1. Characteristics of the starting glass–ceramics

Some properties of the glass–ceramics used in the present work are given in Table I. As already shown in a previous paper [2], the main crystalline constituent of glass–ceramics was β-spondumene type crystal with almost the same composition as the corresponding glass, irrespective of the n values. Very minor amounts of CuO (less than 1 wt %) were observed to coexist in the glass–ceramics. The lattice spacings a_0 and c_0 are seen to decrease with increasing n value.

The fractions of cuprous ions in the glass–ceramics are 83 and 95% for $n = 4$ and 8, respectively. The contents of copper are slightly less than those calculated from batch compositions, indicating that some copper is lost during processing. As mentioned in a previous paper [3], copper has been lost also in the stage of glass making. Therefore, about half of the loss of copper for the glass–ceramics should be attributed to that encountered during glass making process.

3.2. Formation of CuO in the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics on reheating in air

Small light reddish brown patches were dispersed over the polished and glossy surface of glass–ceramics. On reheating of the glass–ceramics having $n = 4$, the surface was covered with a greyish layer through which coloured patches were no longer observed. The layer consisted of crystalline CuO, as seen from the X-ray diffraction profile shown in Fig. 1a. As in the case of the corresponding glass reported previously [3], the greyish CuO layer was easily removed and the coloured patches over the surface were recovered by washing the glass–ceramic specimens heated in air in an aqueous acid solution. This indicates that CuO is formed on the surface of the glass–ceramic specimens when it is heated in air at temperatures up to 500° C. Small X-ray diffraction peaks due to CuO were observed along with the strong peaks due to β-spondumene type crystal in the glass–ceramic even after washing in acidic solution as shown in Fig. 1b. Small peaks due to CuO were still observed for the pulverized specimen, in contrast with the corresponding glass specimen for which no diffraction peaks were observed if the glass heated in air was washed in acidic solution and then pulverized. This indicates that a small amount of crystalline CuO is also formed in the interior of the specimen.

In Fig. 2, the variation of the amount of CuO formed on the surface of the glass–ceramics of nominal composition of $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ with heating time at 300, 400 and 500° C in air is shown. At 300° C, only a very thin layer of CuO is formed on the surface even after heat treatment for 16 h. The rate of CuO formation increases with increasing reheating

TABLE I Description of $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics

Composition n	Crystallizing temperature (° C)	Crystalline species*	Lattice constants of crystal (nm)		Content of $Cu^{\dagger}$ (wt %)	Fraction of Cu (nm) (%)
			a_0	c_0		
4	900	Sp ≫ CuO	0.7571	0.9336	22.6 (26.2)	83
8	900	Sp ≫ CuO	0.7516	0.9169	15.9 (17.5)	95

*Sp: β-spodumene type crystal.

†Values in parentheses are those calculated from batch composition

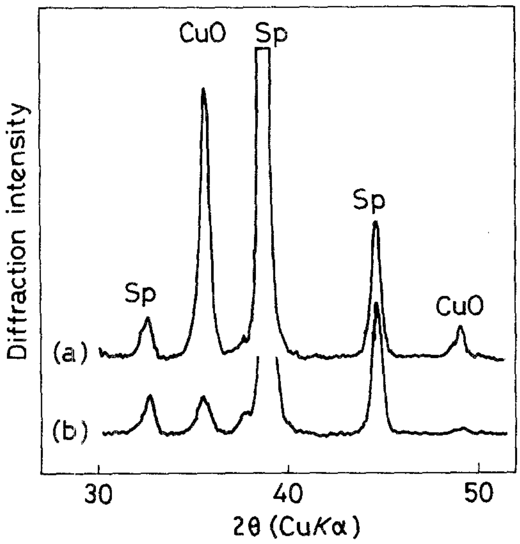

Figure 1 X-ray diffraction profiles of the $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass–ceramics taken at the surface: (a) reheated in air at 500° C, and (b) after washing (a) in acidic solution.

temperature. At 500° C, the amount of CuO parabolically increases with heating time, levelling off after about 5 h. This is in contrast with the behaviour of the corresponding glass of the same composition. In the latter, the amount of CuO formed on the surface continued to increase with heating time under the same conditions.

3.3. Oxidation state and content of copper in $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics reheated in air

In Fig. 3, the content of copper and the fraction of cupric ions in the particulate glass–ceramics having the original compositions of $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ and $Cu_2O \cdot Al_2O_3 \cdot 8SiO_2$ are plotted against time of reheating in air. The fraction of cupric ions is seen to increase abruptly above 300° C and reach about 80% at 600 to 700° C. The copper content is represented as the loss of copper, ΔCu/Cu, which is defined here by a ratio of the amount of copper lost by reheating in air to that calculated from the batch composition. It is seen from Fig. 3 that the loss of copper increases with heating temperature.

The behaviour of copper ions in the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics, as described above, is very similar to that for the corresponding glasses [3], namely, oxidation of cuprous ions in the specimens may accompany the loss of copper. This is clearly seen in Fig. 4, in which the fraction of cupric ions in the glass–ceramics heated in air is plotted against the loss of copper. In this figure, the relation between those two parameters for the corresponding glasses is shown for comparison. The solid curve in the figure shows the plot of the variation of the fraction of cupric ions as $x/1 - x$ where x is the loss of copper. As can be seen, the fraction of cupric ions in the glass–ceramic varies following this relation as in the corresponding glasses. This means that if a cuprous ion is oxidized in the glass–ceramics, another Cu^+ ion is lost or expelled from the specimen.

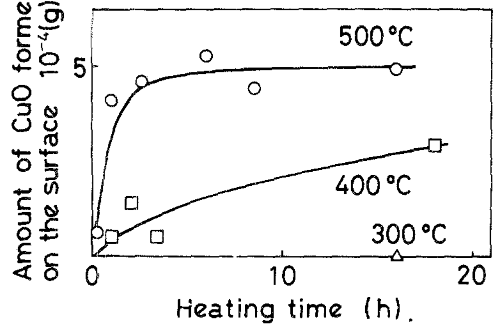

Figure 2 Variation of the amount of CuO formed on the surface of the $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass–ceramics at 300, 400 and 500° C with reheating time.

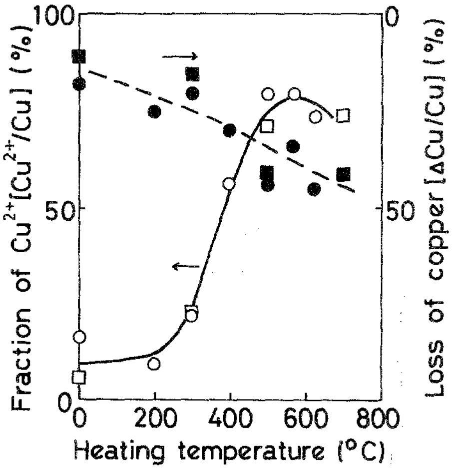

Figure 3 Variation of the fraction of cupric ions and the loss of copper (for definition, see text) of the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics with heating temperature. ○, ●, $n = 4$; and □, ■, $n = 8$.

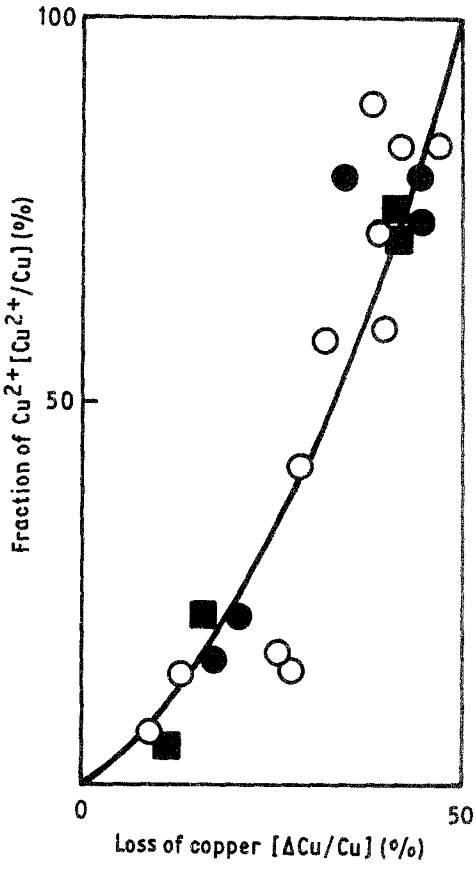

Figure 4 Relation between the fraction of cupric ions and the loss of copper of the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics. ●, n = 4; ■, n = 8; and ○, glasses with $n = 4$ [3].

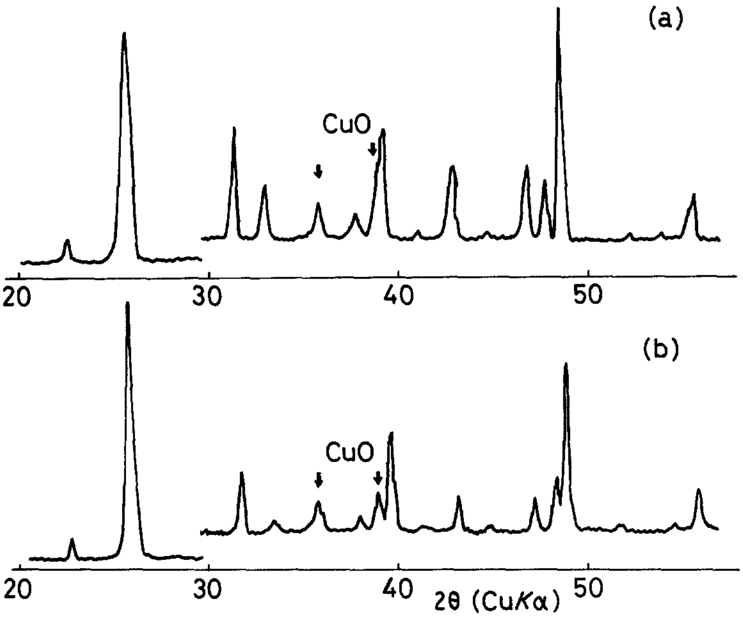

Figure 5 X-ray diffraction patterns of the glass–ceramics with the nominal starting composition of $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$:(a) as-prepared glass–ceramics, and (b) glass–ceramics reheated in air at 500° C for 1 h.

3.4. Structure change of β-spondumene type crystals contained in the glass–ceramics on heating in air

Fig. 5 shows X-ray diffraction patterns covering diffraction angles from 20 to 60° in 2θ of the glass–ceramics of nominal composition $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ and that reheated at 500° C in air for 1 h. The fraction of cupric ions and the loss of copper of the glass–ceramics reheated in air are 79.1% and 44.3%, respectively. Although about half the copper ions are lost and a large part of remaining copper ions are in the divalent state, the diffraction pattern of the reheated glass–ceramics is very similar to the non-reheated one. In fact, their diffraction lines could be indexed based on the β-spodumene structure as is given in Table II, although both a_0 and c_0 spacings were smaller than those of the non-reheated glass–ceramics. It can be, therefore, concluded that the reheating of the glass–ceramics in air does not bring about the fundamental structure change of the crystalline constituent.

In Figs. 6a and b, lattice spacings a_0 and c_0 of the β-spodumene type crystal contained in the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ with $n = 4$ and 8 are shown as a function of reheating temperature. It is seen that both a_0 and c_0 decrease above ~ 300° C with increasing reheating temperature. The temperature at which lattice spacings start to decrease seems to correspond with that for the oxidation or decrease of copper content, which indicates that the lattice spacings are related to the oxidation state or copper content. Fig. 7 shows the lattice spacings a_0 and c_0 of the β-spodumene type crystals contained in the reheated glass–ceramics plotted against the loss of copper. It is seen that both a_0 and c_0 decrease with increasing loss of copper for both glass–ceramics with $n = 4$ and 8.

4. Discussion

4.1. Behaviour of copper ions in $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass–ceramics on reheating in air

It was reported [3] that the formation of CuO on reheating of the glass–ceramics of the nominal composition $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ appears to occur just on the surface of the specimen as in the case of the corresponding glasses. This conclusion was derived on the basis of the following facts: (a) the glossy appearance of the polished surface and the pattern of small reddish brown patches dispersed on the specimen were recovered by removing the CuO layer by washing in aqueous acidic solution, and (b) the very strong diffraction peaks due to CuO were remarkably decreased in intensity after being subjected to the above processes.

However, small diffraction peaks due to CuO have been observed to remain for the crushed glass–ceramic specimen in this work, indicating that minor CuO formation takes place even in the interior of the specimen. It is assumed that the boundaries or interfaces of

TABLE II The *d*-spacings of β-spodumene type crystal in the $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass–ceramics reheated in air at 500° C

hkl	Remark*	d_{obs}	d_{calc}
102		3.902	3.901
201		3.469	3.465
211	Si		3.145
103		2.819	2.822
212		2.701	2.702
310		2.369	2.369
311		2.292	2.293
222			2.291
004		2.285	2.285
213		2.252	2.254
104	w	2.188	2.186
312		2.099	2.103
321	w	2.021	2.026
303		1.929	1.931
214		1.887	1.888
311		1.870	1.870
400			1.873
421		1.649	1.647
324		1.535	1.537
305		1.470	1.475
404		1.449	1.450
512		1.398	1.398
334			
521		1.376	1.375

$a_0 = 0.7490$ nm; $c_0 = 0.9141$ nm.

*Si; overlapping with Si(1 1 1), w; weak.

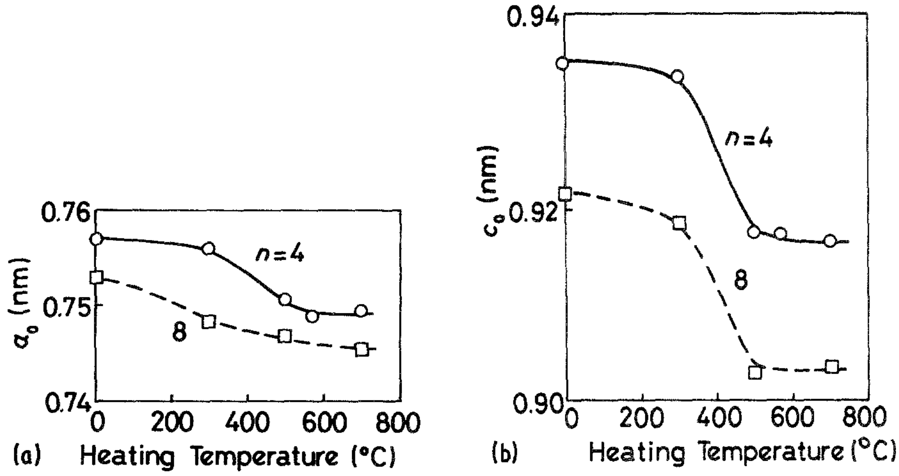

Figure 6 Variation of the lattice spacing of β-spodumene type crystal contained in the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass-ceramics with reheating temperature: (a) a_0 spacing, and (b) c_0 spacing.

crystalline grains in the glass–ceramics may give rise to the formation of CuO in the interior of the specimen. Therefore, the assumption [3] which has been made for the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glasses can be applied to the corresponding glass–ceramics. The formation of CuO on the surface of the glass–ceramics tells us that oxygen does not diffuse into the specimen, but cuprous ions migrate from the interior to the surface where they form CuO.

It was discussed [3] for the corresponding glasses that the rate of CuO formation on the surface is controlled by the diffusion process of cuprous and/or oxygen ions through the CuO layer. As can be seen in Fig. 2, in the earlier stage of reheating of the glass–ceramics at 500° C, the CuO formation shows the parabolic dependence on heating time or square root time dependence, indicating that the process is controlled by diffusion. At a later stage of reheating, the amount of CuO formed seems to level off. It should be noticed that the amount of CuO at saturation is similar to that in the glasses. This may seem inconsistent with the fact that CuO also deposits in the grain boundaries of glass–ceramics. The apparent saturation may be regarded as resulting from the long paths that have to be taken for cuprous ions to move to the specimen surface, which makes a very slow process.

The fraction of cupric ions produced by oxidation of cuprous ions in the glass–ceramics on reheating in air was intimately correlated with the loss of copper as seen in Fig. 4. The fraction of cupric ions varied with the loss of copper x as $x/1 - x$ just like the corresponding glasses [3]. This means [3] that the oxidation of a cuprous ion is accompanied by the expulsion of another cuprous ion out of the specimen. Accordingly, the same reaction scheme as for the glasses of the nominal compositions of $Cu_2O \cdot Al_2O_3 \cdot 4SiO_2$ can be applied in the case of the corresponding glass–ceramics on reheating in air.

$$2Cu^+ \text{ (interior)} + \tfrac{1}{2} O_2 \text{ (surface)}$$
$$\rightarrow Cu^{2+} \text{ (interior)} + CuO \text{ (surface)}$$

4.2. Structure change of β-spodumene type crystals contained in $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass-ceramic

Since the present glass–ceramics are composed mainly of the β-spodumene type crystal of nomial composition $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$, the beahviour of copper ions in these glass–ceramics can be regarded as that of copper ions in the β-spodumene type crystal. It can be restated that part of the copper ions of the β-spodumene type crystal are oxidized and the other part are lost on reheating in air. The composition of the crystal after reheating can be expressed as $(Cu^+_{1-2x} \cdot Cu^{2+}_x)_2O \cdot Al_2O_3 \cdot nSiO_2$ where x is the loss of copper or the amount of cupric ions. The oxidation of cations accompanying the expulsion of mobile univalent cations on heating in air has been reported in R_xMO_2 type crystals in which transition metal ions M form layers with oxygens and alkali ions R are located between those layers [6].

It has been reported that β-spodumene

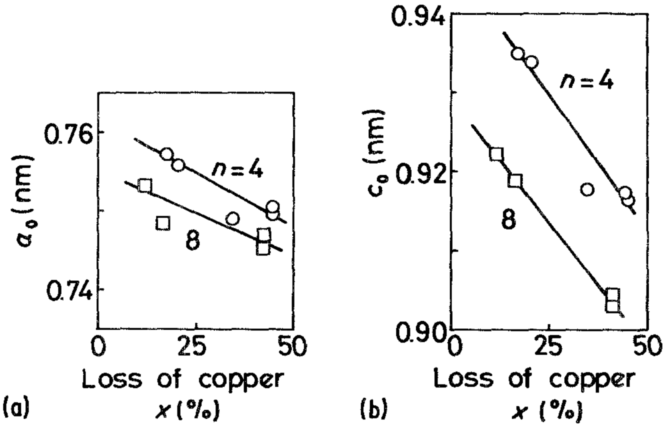

Figure 7 Variation of lattice spacing of β-spodumene type crystal contained in the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ glass-ceramics with the loss of copper: (a) a_0 spacing, and (b) c_0 spacing.

$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (or $LiAlSi_2O_6$) belonging to the tetragonal crystal system forms a solid solution of composition $Li_2O \cdot Al_2O_3 \cdot nSiO_2$ with keatite (a SiO_2 polymorph) with its lattice spacings a_0 and c_0 decreasing with increasing n [7]. The $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ crystal which is isostructral with β-spodumene has been found to decrease in a_0 and c_0 with increasing n as well. A large part of the decrease of lattice spacings on increasing n may be attributed to the decrease in the number of aluminium ions replacing silicon ions in the (Si, Al)O_4 tetrahedra framework of the crystal. Reheating the $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ ($n = 4$ and 8) glass–ceramics in air caused a decrease in copper content and lattice spacing of the main crystalline constituent β-spodumene type $Cu_2O \cdot Al_2O_3 \cdot nSiO_2$ crystal. In this case, however, the decrease in lattice spacing can not be attributed to the same reasoning as above, because the Al/Si ratio of the crystal is kept unchanged during reheating. Vacant sites in the crystal, produced by the replacement of two cuprous ions by a cupric ion, and the smaller ionic radius of the replacing cupric ion than that of a cuprous ions should bring about the decrease in lattice spacing of the crystal in reheating in air. Such a situation has been known in the non-stoichiometric compounds, for example, compounds consisting of transition metal ions and oxygen or halogen ions.

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