# Influence of $Cu_2O$ Addition on Crystallization Process and Microstructure of Transparent Mica Glass-ceramics

Seiichi Taruta [a], Keigo Sakai [b],

Tomohiko Yamakami [c] and Tomohiro Yamaguchi [d]

Faculty of Engineering, Shinshu University,

4-17-1, Wakasato, Nagano-shi, Nagano 380-8553, Japan

[a] staruta@shinshu-u.ac.jp, [b] t094028@shinshu-u.ac.jp,

[c] tyamaka@shinshu-u.ac.jp, [d] mtmouth@shinshu-u.ac.jp

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**Abstract.** The influence of $Cu_2O$ addition on crystallization process and microstructure of the transparent mica glass-ceramics was investigated. $Cu^+$ ions which were added as $Cu_2O$ were oxidized to $Cu^{2+}$ ions during preparation of parent glasses and the $Cu^{2+}$ ions were reduced to $Cu^+$ ions again during heating of the parent glasses. By heating the parent glasses to which 10-20 mol% $Cu_2O$ was added at 650-700°C, not only nano-sized micas but also $Cu_2O$ nano-particles separeted. Their separation temperatures were lowered as the additive amount of $Cu_2O$ increased. Micas separated at 750°C should contain $Cu^+$ and $Cu^{2+}$ ions in the structure. Metallic Cu was observed only in the specimen to which 1 mol% $Cu_2O$ was added.

## Introduction

Transparent glass-ceramics have been developed and practically used in many application fields [1]. We succeeded in preparing novel transparent and machinable mica glass-ceramics [2]. The separated micas were lithium-micas in which the interlayer cations are lithium ions. Because the lithium ions could transfer in the interlayer of the micas formed interlocking structure, the transparent glass-ceramics showed conductivity of $2.0\times10^{-3}$ S/cm at 600ºC. In this way, the novel transparent mica glass-ceramics have potential for applications not only as machinable ceramics but also as lithium ion conductors. In addition, we prepared Eu-doped transparent mica glass-ceramics [3]. The Eu-doped parent glasses emitted red light due to $Eu^{3+}$ ions that were added as $Eu_2O_3$, while the transparent mica glass-ceramics emitted purple light due to not only $Eu^{3+}$ ions but also $Eu^{2+}$ ions, which means that $Eu^{3+}$ ions were reduced to $Eu^{2+}$ ions on heating of the parent glasses. This reduction might be caused by the evolution of fluorine from the glasses during heating in air. So we inferred that $Cu^+$ ions which are added to starting materials of the transparent mica glass-ceramics will be reduced to metallic Cu during the preparation of the glass-ceramics. Furthermore, if the metallic Cu nano-particles separated as the percorative continuous phase, transparent conductive materials, which may be not colorless, will be obtained. As the glass containing metallic copper, copper-ruby glasses are well known [4]. One technique of the production of the glasses containing metals is based on the mixing of metal oxides and reducing agent during glass melting [5].

In this study, 1-20mol% $Cu_2O$ was added to the starting materials of the transparent mica glass-ceramics without reducing agents, and the influence of $Cu_2O$ addition on crystallization process and microstructure of the mica glass-ceramics was investigated.

## Experimental procedure

The composition of the base glass used in this study was 94.9 mass% $Li_{1.5}Mg_3AlSi_{4.5}O_{13.25}F_2$ and 5.1 mass% $MgF_2$. The base glass was doped with 0, 1, 5, 10, 15 and 20 mol% $Cu_2O$. The parent glasses were prepared as follows. The reagents of MgO, $Al_2O_3$, $SiO_2$, LiF, $MgF_2$ and $Cu_2O$ were mixed, melted in a sealed platinum container at 1450ºC for 2 h and then cooled outside of the furnace.

The obtained glasses were annealed at about 20ºC higher temperatures than their glass-transition temperatures and cooled at 2ºC/min to eliminate strain. The parent glasses prepared by such a method were cut and were heated at 600-800ºC for 1 h to be crystallized. The heating rate was 10ºC/min. The prepared specimens are referred to as Cu-1, Cu-5, Cu10, Cu-15 and Cu-20 according to the respective amounts of added $Cu_2O$.

The phase changes were analyzed using an X-ray diffraction (XRD) analyzer. The microstructures were observed using a transmission electron microscope (TEM) and scanning TEM (STEM). The luminescent properties were analyzed using a fluorescence spectrophotometer.

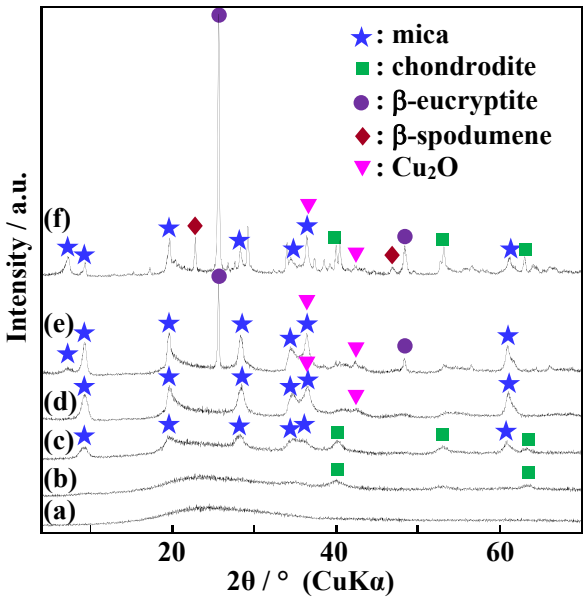


Fig. 1 XRD patterns of (a) Cu-10 parent glass and the Cu-10 specimen heated at (b) 600°C, (c) 650°C, (d) 700°C, (e) 750°C and (f) 800°C for 1 h.

## Results and discussion

XRD patterns of Cu-10 specimen are shown in Fig.1. Mica, $Cu_2O$ and β-eucryptite separated at 650ºC, 700ºC and 750ºC, respectively. The separation temperatures of mica tend to be lowered as the additive amount of $Cu_2O$ increased. Trace of mica was observed in the XRD patterns of Cu-1 and Cu-5 specimens heated at 650ºC and was observed in those of Cu-20 specimen heated at 600ºC. That is, the addition of $Cu_2O$ enhanced the crystallization of mica. The peak of $Cu_2O$ was weak in the XRD patterns of Cu-10 specimen and tended to be stronger and appear at lower temperaturs as the additive amount of $Cu_2O$ increased. The $Cu_2O$ did not appeaer in Cu-1 and 5 specimens, but only Cu-1 specimen heated at 800ºC showed a little peak of metallic Cu in the XRD pattern at 42-43º, which is not shown in this paper.

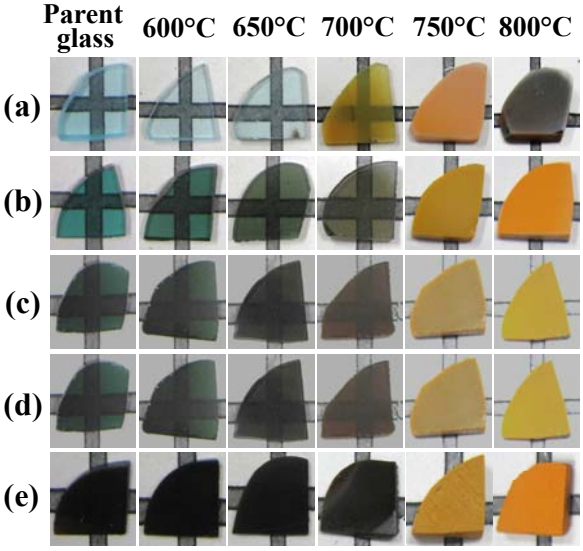


Fig. 2 Photographs of parent glasses and the glasses heated at 600-800°C for 1 h. (a) Cu-1, (b) Cu-5, (c) Cu-10, (d) Cu-15 and (e) Cu-20 specimens.

Photographs of the prepared specimens are shown in Fig. 2. $Cu^+$ and $Cu^{2+}$ ions show generally colorless and blue color, respectively, in the glasses and green color is caused by decreasing the coordination number of $Cu^{2+}$ ions and the green color transfer into brown color by coexistence of $Cu^+$ and $Cu^{2+}$ ions [7]. The parent glasses were transparent and were blue, green or dark green in color, which means that $Cu^+$ ions which were added as $Cu_2O$ were oxidized to $Cu^{2+}$ ions. The Cu-1, 5, 10 and 15 specimens heated under 700ºC kept transparency. The color of Cu-10 and 15 specimens heated at 700ºC became tinged reddish due to the separation of $Cu_2O$ which shows red color. This change means that $Cu^{2+}$ ions were reduced to $Cu^+$ ions. All specimens heated at 750ºC lost the transparency completely because of the separation of large β-eucryptite particles [2,3]. The change in color of Cu-1 specinmen from blue to raddish color might be caused by the separation of metallic Cu.

STEM and Z-contrast images of Cu-10 specimen heated at 700ºC and 750ºC are shown in Fig. 3. The particles with size of < 50nm were observed in Cu-10 specimen heated at 700ºC. They appeared as lighter images in the Z-contrast image (Fig. 3 (b)) which was taken in the identical location as the STEM image (Fig. 3 (a)). Because the contrast of Z-contrast image is lighter in proportional to the square of the atomic number, the particles sholud be $Cu_2O$. The $Cu_2O$ particles consisted of some

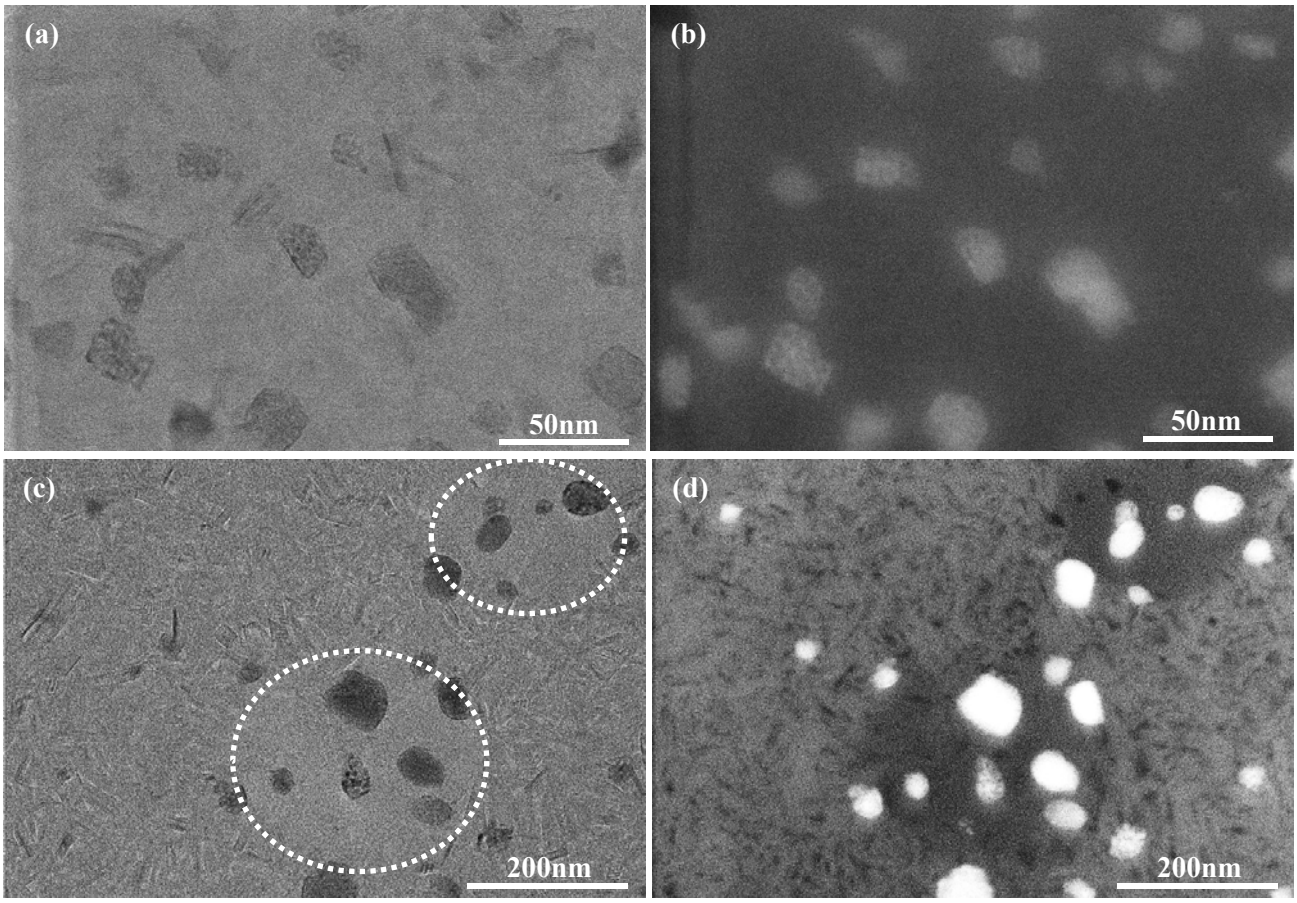


Fig. 3 (a) STEM and (b) Z-contrast images of Cu-10 specimen heated at 700°C for 1 h, and (c) and (d) those of Cu-10 specimen heated at 750°C for 1h, respectively.

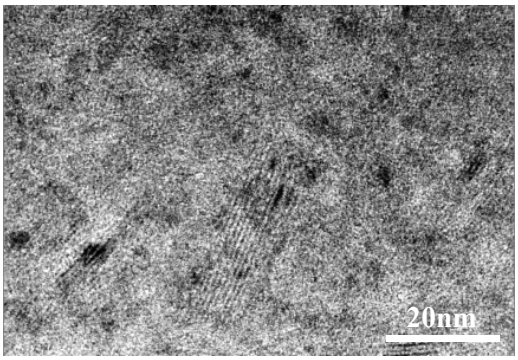


Fig. 4 TEM images of Cu-5specimen heated at 700°C for 1 h.

smaller particles and seems to grow slightly by heating at 750ºC. The other sides, mica were observed in Cu-10 specimens heated at 700ºC and thier size were < 50nm. The micas grew to the size of < 80nm at 750ºC. Some large β-eucryptite particles with the size of about 200nm, which were enclosed by dotted circles in Fig. 3 (c), were observed, which made the transparency of specimens lose. These β-eucryptite did not containe Cu element in the crystal structure because thier contrast was darker in the Z-contrast image. Meanwhile, there were both lighter parts and darker parts in the areas which were not $Cu_2O$ and β-eucryptite particles in the Z-contract image of Cu-10 specimens heated at 750ºC though there were no differnces in the area of Cu-10 specimens heated at 700ºC. The differnce in the contrast was caused by the difference in Cu concentration, that is, the lighter parts contained more Cu. The many lighter parts were corresponded to micas. Therefore, Cu ions ($Cu^{2+}$ and $Cu^{+}$ ions ) must be incorporated in the structure of mica. The composition of mica separated in the specimen containing no Cu element was $Li(Mg_{2+y}Li_{1-y})(Al_ySi_{4-y})O_{10}F_2$ ($0<y<1$) [2]. $Li^{+}$ ions were interlayer ions, $Mg^{2+}$ and $Li^{+}$ ions occupied the octahedral sites in the structure of mica and $Al^{3+}$ and $Si^{4+}$ ions occupied the the tetrahedral sites. Because ionic radius of $Cu^{+}$ ion is almost the same with that of $Li^{+}$ ion and that of $Cu^{2+}$ ion is almost the same with that of $Mg^{2+}$ ion, $Cu^{+}$ ions should exist as interlayer ions in the mica and $Cu^{2+}$ ions should occupy the octahedral sites. Therefore, the composition of mica separated in Cu-10 specimen heated 750ºC could be shown as $(Li_{1-x}Cu_x)(Cu_zMg_{2+y-z}Li_{1-y})(Al_ySi_{4-y})O_{10}F_2$ ($0\leq x,y\leq 1$, $0\leq z\leq 3$).

Cu-5 specimen heated at 700ºC is shown in Fig. 4. Small spherical particles with size of < 5nm were observed while they were not observed clearly in STEM image. It is not clear that they were

metallic Cu or $Cu_2O$ because metallic Cu or $Cu_2O$ were not detected by XRD analysis of Cu-5 specimen heated at 600-800ºC.

Emission and excitation spectra of Cu-1 parent glass are shown in Fig. 5. This emission was caused by $Cu^+$ ions [8], which confirm that the parent glasses contained not only $Cu^{2+}$ ions but also $Cu^+$ ions. Cu-1 parent glass emitted blue light under UV light irradiation.

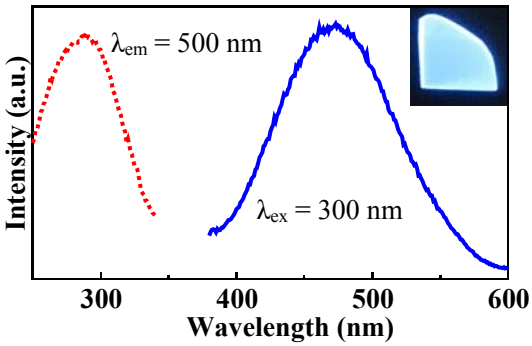


Fig. 5 Emission (solid line) and excitation (dashed line) spectra of Cu-1 parent glass; excitation spectrum, $\lambda_{ex}$ = 300 nm; emission spectrum, $\lambda_{em}$ = 500 nm. Photograph: Cu-1 parent glass under UV light irradiation.

## Summary

1-20mol% $Cu_2O$ was added to the starting materials of the transparent mica glass-ceramics without reducing agents, and the influence of $Cu_2O$ addition on crystallization process and microstructure of the mica glass-ceramics was investigated. $Cu^+$ ions were oxidized to $Cu^{2+}$ ions during the preparation of the parent glasses and then the $Cu^{2+}$ ions were reduced to $Cu^+$ ions again during heating the parent glasses. However, it was difficult for $Cu^+$ and $Cu^{2+}$ ions to be reduced to metallic Cu by the evolution of fluorine during heating the parent glasses. Only in the specimen to which 1 mol% $Cu_2O$ was added, a few metallic Cu was observed. By heating the parent glasses to which 10-20 mol% $Cu_2O$ was added at 650-700°C, not only nano-sized micas but also $Cu_2O$ nano-particles separeted in the specimens. Their separation temperatures were lowered as the additive amount of $Cu_2O$ increased. Micas separated at 750°C, particularly, in Cu-10 specimen heated 750ºC, should contain $Cu^+$ and $Cu^{2+}$ ions in the structure. The composition of the micas could be shown as $(Li_{1-x}Cu_x)(Cu_zMg_{2+y-z}Li_{1-y})(Al_ySi_{4-y})O_{10}F_2$ ($0 \le x,y \le 1$, $0 \le z \le 3$).

## References


[1] G. H. Beall, L. R. Pinckney, Nanophase glass-ceramics, J. Am. Ceram. Soc., 82 (1999) 5-16.

[2] S. Taruta, M. Suzuki, T. Yamaguchi, K. Kitajima, Preparation and ionic conductivity of transparent glass-ceramics containing a large quantity of lithium-mica, J. Non-Cryst. Solids, 354 (2008) 848-855.

[3] S. Taruta, M. Matsuki, H. Nishikiori, T. Yamakami, T. Yamaguchi, K. Kitajima, Preparation and luminescent properties of Eu-doped transparent mica glass-ceramics, Ceram. Int., 36 (2010) 1303-1309.

[4] J. E. Shelby, Introductiuon to Glass Science and Technology 2nd Edition,The Royal Science of Chemistry, Cambrige, 2005, 211-214.

[5] A. Quaranta, R. Ceccato, C. Menato, L. Pederiva, N. Capra, R. D. Maschio, Formation of copper nanocrystals in alkali-lime silica galss by means of different reducing agents, J. Non-Cryst. Solids, 345&346 (2004) 671-675.

[6] S. Wang, Y. Liu, H. Miao, G. Tan, F. Zhao, Y. Gao, H. Luo, Synthesizing and stabilizing copper nanoparticles by coating with a silica layer in aqueous solution, J. Ceram. Soc. Japan, 120 (2012) 248-250.

[7] A. Naruse, Glass Technology, Kyoritsu Shuppan, Tokyo, 1958, 308-336 [in Japanese].

[8] A. Yasumori, F. Tada, S. Yanagida, T. Kishi, Yellow photoluminescence properties of copper ion doped phase-separated glasses in alkali borosilicate system, J. Electrochem. Soc., 159 (2012) J143-J147.