

# Crystallization of Copper Metaphosphate Glass

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The effect of the valence state of copper in copper metaphosphate glass on the crystallization behavior and glass transition temperature has been investigated. The crystallization of copper metaphosphate is initiated from the surface and its main crystalline phase is copper metaphosphate ( $\text{Cu}(\text{PO}_3)_2$ ), independent of the  $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$  ratio in the glass. However, the crystal morphology, the relative crystallization rates, and their temperature dependences are affected by the  $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$  ratio in the glass. The crystal formed in the reduced glass is oriented and needle-shaped and less aligned at higher crystallization temperature. On the other hand, the totally oxidized glass crystallizes from all over the surface. The relative crystallization rate of the reduced glass to the totally oxidized glass is large at low temperature, but small at high temperature. The glass transition temperature of the glass increases as the  $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$  ratio is raised. This dependence may be used to explain the relative crystallization rates. It is also found that the atmosphere used during heat treatment does not influence the crystallization of the reduced glass, except for the formation of a very thin  $\text{CuO}$  surface layer when heated in air.

## I. Introduction

THE crystallization behavior of simple metaphosphate glasses and other phosphate glasses has been studied for several decades,<sup>1–19</sup> although the number of publications is more limited than for other glass systems. Calcium metaphosphate ( $\text{Ca}(\text{PO}_3)_2$ ) and other calcium phosphate glass-ceramics are of interest for their medical applications such as bone and teeth implants.<sup>20,21</sup> Also, glass-ceramics in sodium phosphate systems are suitable for fabricating seals to high thermal expansion metals, because of their high thermal expansion coefficients and greater fracture toughness than those of phosphate glasses.<sup>13</sup>

Abe and co-workers<sup>7,9,10</sup> have found unusual crystallization behavior in metaphosphate glasses. Those compositions which have chain structures in both glasses and crystals ( $\text{Be}(\text{PO}_3)_2$ ,  $\text{Ca}(\text{PO}_3)_2$ ,  $\text{Sr}(\text{PO}_3)_2$ ,  $\text{Ba}(\text{PO}_3)_2$ ) can crystallize below the glass transition temperature, but those systems having a ring crystalline structure ( $\text{NaPO}_2$ ,  $\text{Mg}(\text{PO}_3)_2$ ,  $\text{Ni}(\text{PO}_3)_2$ ) do not show crystallization below the glass transition temperature. In calcium metaphosphate glass, a unidirectional crystallization is obtained as a result of its chain-type structure.<sup>12,14,15</sup>

Glasses containing copper have been of interest for their potential use in fabricating superconductor ceramics.<sup>22</sup> Also, many studies have been performed on semiconducting oxide glasses based on copper phosphate.<sup>23,24</sup> Copper can exist in glasses as metallic copper ( $\text{Cu}^0$ ), cuprous ( $\text{Cu}^+$ ) or cupric

( $\text{Cu}^{2+}$ ) ions, although most oxide glasses are usually assumed not to contain metallic copper when melted in air. It is well known that the valence states ratio in glasses,  $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ , i.e.,  $[\text{Cu}^{2+}]$  ratio, affects electrical and optical properties because conduction is due to electron hopping from  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$  absorbs visible light. On the other hand, the effect of the valence states ratio of copper in glasses on their crystallization behavior has received very little attention. Recently, the effect of the  $[\text{Cu}^+]/[\text{Cu}_{\text{total}}]$  ratio on the crystallization behavior was investigated for Bi-Ca-Sr-Cu-O glasses used for superconductor glass-ceramic preparations.<sup>22</sup> It was found that crystallization is favored and a finer crystalline size is obtained as  $[\text{Cu}^+]/[\text{Cu}_{\text{total}}]$  increases.

The purpose of the present study is to examine the effect of the valence states of copper on the crystallization behavior of glasses in the copper phosphate system. Previously we have investigated the oxidation and reduction equilibrium of copper phosphate glasses and demonstrated how the  $[\text{Cu}^{2+}]$  ratio could be controlled by changing melting conditions.<sup>25</sup> Here, copper phosphate glasses containing different  $[\text{Cu}^{2+}]$  ratios have been prepared applying this method, and their crystallization behavior has been examined and compared.

## II. Experimental Procedure

### (1) Glass Preparation and Analyses

$\text{CuO-P}_2\text{O}_5$  glasses having compositions with 50 mol%  $\text{CuO}$  were prepared using analytical reagent grades of chemicals,  $\text{CuO}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . Glasses with different valence states ratios of copper were made applying various melting times. About 60 g of chemicals were mixed with isopropyl alcohol and dried to obtain homogenized batches. Quartz crucibles (100-mL capacity) containing the batch were initially heated at  $500^\circ\text{C}$  for about 2 h in order to evaporate ammonia and water in the batch and minimize the tendency of subsequent phosphate loss. A quartz crucible was used since it was found that a quartz crucible was more inert when melting copper phosphate glass than an alumina crucible.<sup>25</sup> The crucible was transferred to another furnace, which was preheated to  $1000^\circ\text{C}$ . The batch was melted in air from 15 min to 6 h depending on the desired valence states ratio of copper in the glass. The melt was poured onto a clean copper plate and cast into a disk shape of 3-mm thickness. The prepared glasses were not annealed. All prepared samples were stored in a vacuum desiccator to prevent moisture attack.

All samples were confirmed to be amorphous by X-ray diffraction and to be homogeneous by optical microscopy and SEM. IR spectroscopies of the samples were used to ascertain that the hydroxyl content was relatively small. The concentrations of the total Cu and  $\text{Cu}^{2+}$  were determined using complexometric titration described previously.<sup>25</sup>

### (2) Glass Transition Temperature and Crystallization Studies

The glass transition temperatures ( $T_g$ ) of the glasses were measured using differential scanning calorimeter (DSC) heating from room temperature to  $600^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  in an argon atmosphere.

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**Table I. Glass Preparations, [Cu<sup>2+</sup>] Ratios, and Glass Transition Temperatures**

Glass	Melting temperature (°C)	Melting time	[Cu <sup>2+</sup> ]/[Cu <sub>total</sub> ] (%)	T <sub>g</sub> (°C)
A	1000	15 min	23.4 ± 7.3	165
C	1000	1 h	72.1 ± 3.5	333
E	1000	6 h	99.8 ± 0.8	427

Isothermal heat treatments of the bulk samples of 10 mm × 10 mm × 3 mm size were carried out in the furnace with air or argon atmospheres at 580°, 650°, and 730°C for a given period of time. The heat-treated samples were ground and the crystalline phases were identified by use of X-ray powder diffraction (SCINTAG, XDS 2000) using CuK $\alpha$  radiation. For microstructural analyses, the heat-treated samples were cut, mounted with epoxy, and polished using SiC abrasive papers up to 800 grit. Final polishing (sometimes omitted not to obscure crystalline morphology) was done utilizing a 0.05  $\mu$ m alumina suspension. The optical microstructural analysis was conducted by using a metallurgical microscope (Nikon, EPIPHOT-TME). The photomicrographs were taken in dark field and the size of the crystallization layer was measured by inserting a photo scale reticle into the microscope.

### III. Results and Discussion

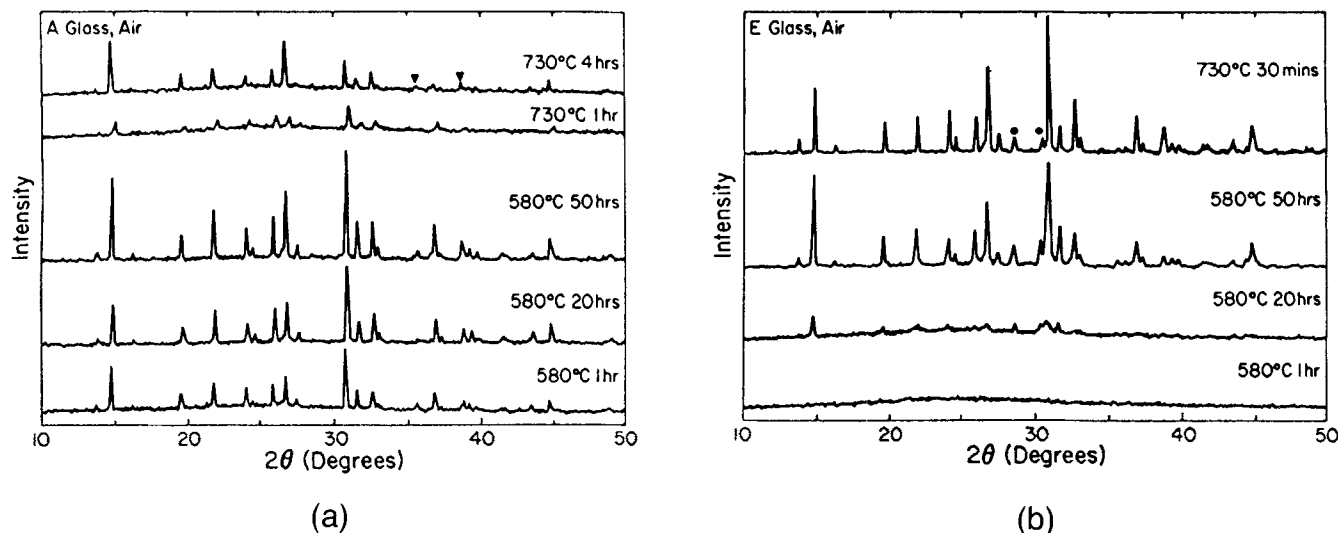
The melting conditions and [Cu<sup>2+</sup>] ratios of the copper metaphosphate glasses which were prepared are given in Table I. The actual compositions of the glasses may differ from the nominal composition, copper metaphosphate, because of vaporization of phosphorus, but its departure is not too great as illustrated in previous work.<sup>25</sup> As mentioned, the purpose of this work was to evaluate the influence of the valence state of copper upon the crystallization behavior of copper metaphosphate glass. This assessment was made with respect to three characteristics of the crystallization process: (1) the crystalline phases which formed upon isothermal heating, (2) the crystalline morphologies, and (3) the relative crystallization rates. In addition, glass transition temperature measurements were performed in order to assist in the interpretation of the results.

#### (1) Crystalline Phases

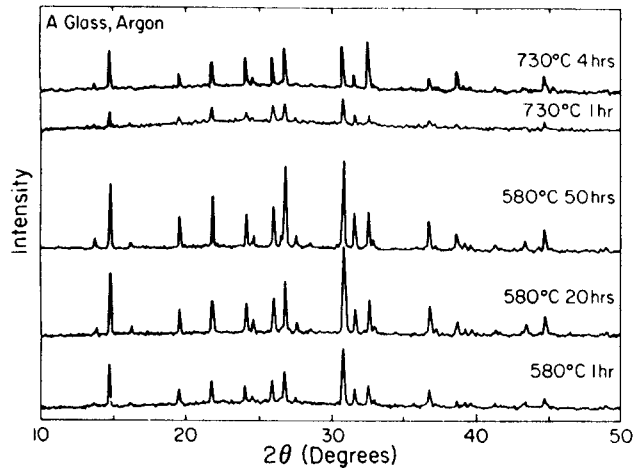
Figure 1 shows the XRD patterns obtained from powders of the A and E glasses whose bulk samples were heated in air at 580° and 730°C for the indicated periods of time. The main crystalline phase is copper metaphosphate (Cu(PO)<sub>3</sub>) for both

glasses, regardless of the [Cu<sup>2+</sup>] ratio in the glass and the heat treatment temperature. Also, small amounts of copper-rich copper phosphate (Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) crystalline phase are detected for the E glass, and trace amounts of CuO are formed for the A glass. The dark gray color of the surface of the A glass is most likely due to small amounts of CuO formation upon heating. The actual glass compositions contain excess copper with respect to the nominal copper metaphosphate composition because of the vaporization of phosphorus. This nonstoichiometric composition produces copper-rich copper phosphate (Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) crystalline phase for the E glass.

In order to form copper metaphosphate crystalline phase for A glass, oxygen must be provided for Cu<sup>+</sup> to be oxidized to Cu<sup>2+</sup> since the glass composition is deficient in oxygen to form copper metaphosphate. One may envision at least two mechanisms by which additional Cu<sup>2+</sup> can be produced in the surface region of the glass where the crystallization is observed to occur. First, one might postulate that Cu<sup>+</sup> ions are oxidized by atmospheric oxygen prior to crystallization. In order to test this hypothesis, the A glasses were heated in an argon atmosphere, and then the samples were subjected to XRD analyses. The results are shown in Fig. 2. One observes that the XRD peak patterns of the A glass heat-treated in air and argon atmosphere do not differ, except for the peaks due to the very thin CuO surface layer for the samples heat-treated in air. Thus, the oxygen diffusion from the atmosphere is an unlikely mechanism. A second possible mechanism would entail copper ion migration toward or from the interior of the glass, depending upon whether the diffusing ion is Cu<sup>+</sup> or Cu<sup>2+</sup>.<sup>26,27</sup> In either event, if such a diffusion process occurred, then one would expect a change in the concentration of copper in the interior of the glass after crystallization of the glass surface region. However, examination of the chemical composition of the A glasses heat-treated in air and argon atmosphere with an energy dispersive X-ray spectrometer (EDX, Tracor Northern 5500) did not show a composition gradient from the inside of the glass to the surface. Also, the [Cu<sup>2+</sup>] ratio of the residual glass phase in the heat-treated samples (after removing the crystallization region on the surface) was analyzed. No significant change in the [Cu<sup>2+</sup>] ratio was found after heat treatment. Thus, the oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup> needed for the formation of copper metaphosphate crystalline phase is accompanied neither by the diffusion of oxygen from the air nor by the long-range migration of ionic species, but by reaction and/or local migration in the region where crystallization occurs. Since the crystallization of the A glass is governed by the oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup>, only copper metaphosphate crystalline phase is formed although the glass



**Fig. 1.** XRD patterns for the (a) A glass and (b) E glass heat-treated in air at 580° and 730°C for the indicated times: (▼) CuO phase, (●) Cu<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase; unmarked peaks correspond to copper metaphosphate (Cu(PO)<sub>3</sub>) phase.



**Fig. 2.** XRD patterns for the A glass heat-treated in argon atmosphere at 580° and 730°C for an indicated time. All peaks correspond to copper metaphosphate ( $\text{Cu}(\text{PO})_3$ ) phase.

composition has more copper than the copper metaphosphate composition.

### (2) Crystalline Morphology

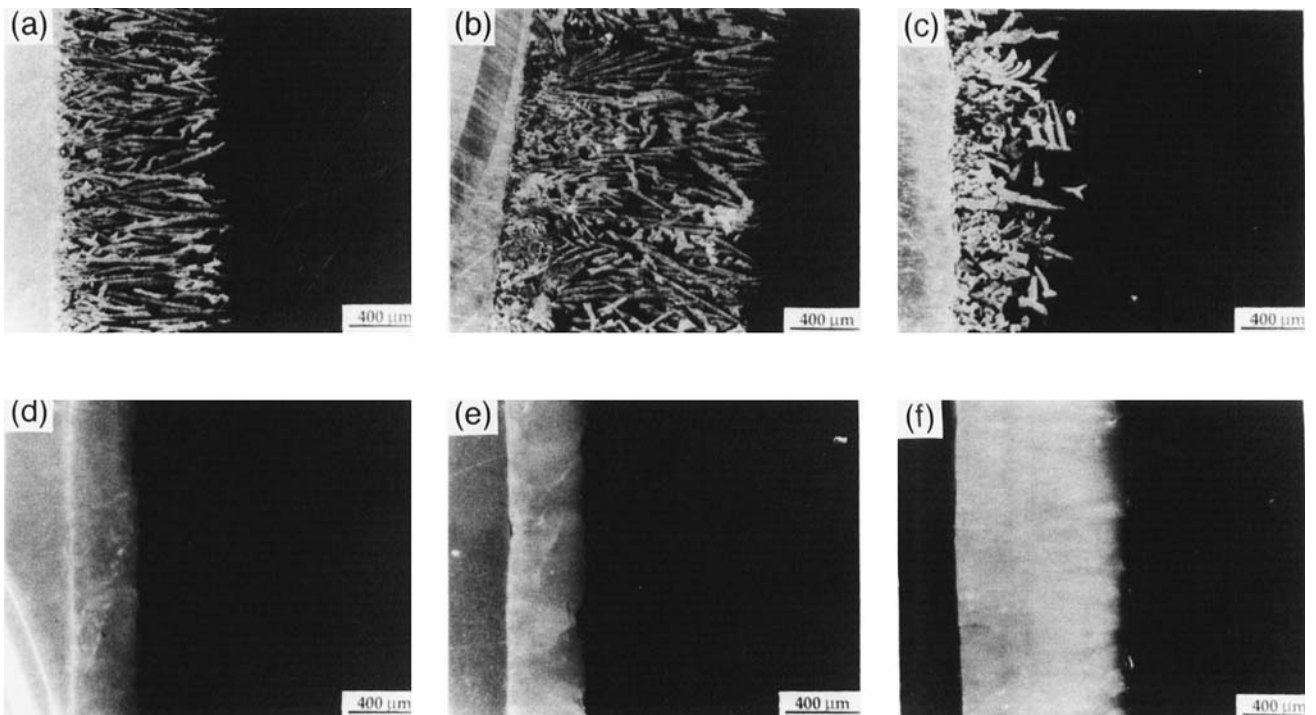
Optical micrographs of polished samples of the A and E glasses heat-treated in air at various temperatures are shown in Fig. 3. The crystallization of both the A and E glasses is initiated at the surface of the glasses. However, the crystalline morphologies of the A and E glasses are quite different, even though their main crystalline phase is the same. The A glass forms a needle-shaped crystalline phase which is oriented from the surface to inside the glass, while the crystallization in the E glass covers the surface. The needle-shaped crystals of the A glass are less aligned and oriented at higher crystallization temperature. Unlike some previous investigations of crystallization of phosphate glasses,<sup>12,14,15,17,19</sup> we do not observe crystallographic orientation effects. The XRD pattern taken from a bulk sample of the crystallized A glass does not differ from that of

the powder shown in Fig. 1. Thus, specific crystallographic orientation is not found in these needle-shaped crystals. The needle-shaped crystalline morphology is present in the glass heat-treated in argon atmosphere, too, as shown in Fig. 4. This illustrates that the oxide layer which forms when heating in air has no effect on the crystalline morphology.

In other phosphate glasses, needle-shaped crystallization morphology has been observed in which crystals form in aggregates, often growing radially from a central nucleus to form a spiky spherulite.<sup>3,13</sup> Similar crystal morphologies have been observed in other glassy systems.<sup>28,29</sup> Kirkpatrick *et al.*<sup>28</sup> have noted that such needle-shaped crystallization morphologies are associated with diffusion-controlled crystal growth. Since the chemical composition and copper valence state in the E glass and crystal are identical, one might not anticipate needle-shaped crystals to form in this glass. On the other hand, crystal formation in the A glass requires an enhancement of the local cupric ion concentration, which might imply a local diffusion process, as mentioned above. Hence, fibrillar or acicular crystal growth appears possible in the A glass. Also, one observes that the needle-shaped crystalline morphology in the A glass is more pronounced at lower temperatures (see Figs. 3(a) to (c)) or larger undercoolings. This result is consistent with the findings of other investigations.<sup>28,29</sup> The increase in spherulitic-type crystal growth with greater undercooling has been explained in terms of a concomitant increase in the ratio of the crystal growth to the diffusion coefficient.<sup>29,30</sup>

### (3) Relative Crystallization Rate

The crystallization of the A glass is much faster than that of the E glass at 580°C as can be seen in the XRD results of Fig. 1. However, at 730°C, the E glass is crystallized more rapidly than the A glass. This reversal of relative crystallization rate depending on the crystallization temperature is confirmed by the optical micrographs shown in Fig. 3. At 580° and 650°C, the thicknesses of the crystallization layers in the glass are larger than those in the E glass even for shorter heat treatment time. However, the situation is reversed at 730°C. The thickness of the crystallization layer from the surface is uniform in all cases. It is found to increase linearly with time and is plotted in Fig. 5. The crystal growth rates are determined from the



**Fig. 3.** Optical micrographs of the polished samples of the A glass heat-treated in air at (a) 580°C for 1 h, (b) 650°C for 1 h, (c) 730°C for 4 h, and the E glass heat-treated in air at (d) 580°C for 30 h, (e) 650°C for 3 h, (f) 730°C for 30 min.

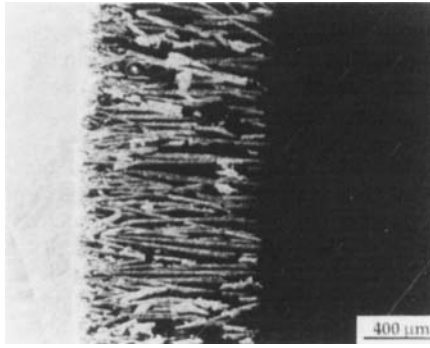


Fig. 4. Optical micrograph of the polished sample of the A glass heat-treated in argon atmosphere at 580°C for 1 h.

slopes of the linear plots. A time-independent crystal growth rate has been observed in some glasses even where the crystal growth is diffusion-controlled.<sup>28</sup> The relative crystal growth rate of the A glass to the E glass is fast at 580°C (around 1080 to 34  $\mu\text{m}/\text{h}$ ) and 650°C, but slow at 730°C (about 130 to 2400  $\mu\text{m}/\text{h}$ ), as demonstrated in Fig. 5. Also, the crystal growth rates in the A and E glasses exhibit different behavior as a function of temperature, as shown in Fig. 3. For the E glass, the time for a certain thickness of crystallization from the surface decreases with increasing heat treatment temperature. However, the thickness of crystallization layer formed at 730°C in A glass is shorter than those formed at lower heat treatment temperatures, even when longer heat treatment times are used. In brief, whereas the crystal growth rate of the E glass greatly increases (from 34  $\mu\text{m}/\text{h}$  at 580°C to 2400  $\mu\text{m}/\text{h}$  at 730°C) with increasing crystallization temperature, that of the A glass does not (1080  $\mu\text{m}/\text{h}$  at 580°C and 130  $\mu\text{m}/\text{h}$  at 730°C), as shown in Fig. 5. One observes from Fig. 5 that three of the linear plots of thickness of crystallization layer vs heating time appear to go through or close to the origin, but the plot corresponding to the E glass heated at 580°C intersects the abscissa at a positive value. This implies that for the A and for the E glass at higher temperature, the time required for nucleation of the crystalline phase is negligible. However, the positive  $x$  axis intercept shown by the plot for the E glass heated at 580°C indicates the existence of a substantial induction time for nucleation at this temperature. Therefore, the nucleation rate and the crystal growth rate of the E glass heat-treated at 580°C are much lower than those of the others.

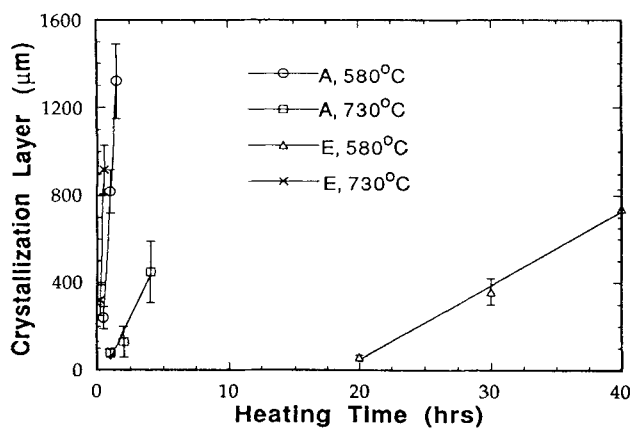


Fig. 5. Relative crystallization rate of the A and E glass at 580°C and 730°C.

#### (4) Glass Transition Temperature and Discussion of Crystallization Kinetics

In order to explain the results which were obtained for the relative crystallization properties of the A and E glasses, the glass transition temperatures of these glasses are considered first.

DSC curves for the glasses which have different  $[\text{Cu}^{2+}]$  ratios are given in Fig. 6. The glass transition temperatures ( $T_g$ ), defined as the extrapolated onset, are listed in Table I.  $T_g$  increases from 165° to 427°C as the  $[\text{Cu}^{2+}]$  ratio of the glass is raised. The glass transition temperature of copper metaphosphate glass varies widely depending on the  $[\text{Cu}^{2+}]$  ratio of the glasses. These findings are in contrast with the results that the glass transition temperature of iron phosphate glass is not dependent on the valence states ratio of iron.<sup>11</sup>

It has been found that the glass transition temperatures of binary alkali phosphate and other alkali-containing phosphate glasses are in the range 150–300°C, and vary with the glass composition.<sup>31–33,35,36</sup> The dependence of the glass transition temperatures on the alkali fraction in binary alkali phosphate glasses has been explained by the progressive change of non-bridging oxygens and phosphate chain length.<sup>36</sup> However, the general trend of the glass transition temperature with changing alkali fraction is not well described in this manner since the glass transition temperature is not a monotonic function of alkali fraction. Also, it is known that the glass transition temperatures of some alkali-free phosphate glasses are above 500°C,<sup>34</sup> and those of alkaline-earth phosphate glasses such as calcium and magnesium metaphosphate glasses are as high as 550°C.<sup>5,7</sup> These glass transition temperatures are much higher than those of the alkali phosphate glasses. Thus, the glass transition temperature of phosphate glasses depends more on the nature of the modifying ions and their bondings with phosphates rather than on the structural change of polymeric phosphates, such as forming nonbridging oxygens and varying chain lengths.

Actually, it has been shown that the glass transition temperature of the metaphosphates is linearly proportional to the intermolecular force between phosphorus and oxygen ions.<sup>35</sup> The intermolecular forces of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  can be calculated using ionic charge data and Pauling radii. The intermolecular force of  $\text{Cu}^{2+}$  is higher than that of  $\text{Cu}^+$  in phosphates, and thus glasses containing more  $\text{Cu}^{2+}$  possess higher glass transition temperatures. This is in accord with the observations that alkaline-earth phosphates usually have higher intermolecular forces and glass transition temperatures than alkali phosphates.

The higher glass transition temperature of the oxidized glass implies that a temperature region exists where the viscosity of this glass is greater than that of the reduced glass. In other

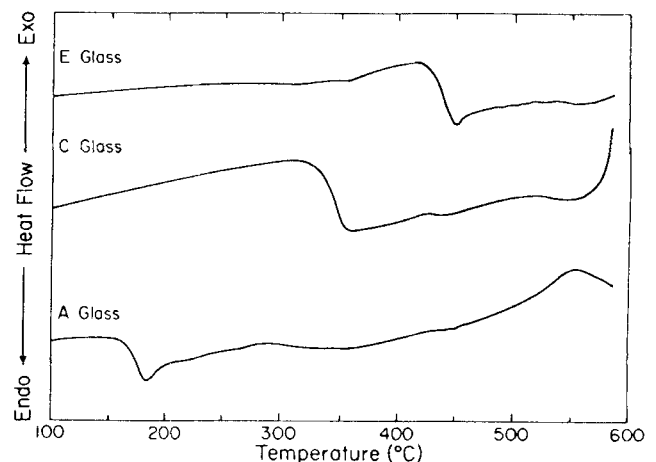


Fig. 6. DSC curves for glasses having different  $[\text{Cu}^{2+}]$  ratios.

words, the viscosity of copper metaphosphate glass increases as the  $[\text{Cu}^{2+}]$  ratio is raised at a given temperature. The change of the viscosity of the copper phosphate glass with the  $[\text{Cu}^{2+}]$  ratio is not unexpected because of the dissimilar coordinations of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  in phosphate glass discussed previously.<sup>25</sup>

Several aspects of the crystallization behavior can be explained in terms of these findings. First, one observes that the A glass exhibits an exothermic peak at 540°C in the DSC trace shown in Fig. 6, while the C glass has an exotherm near 600°C. The E glass, however, does not exhibit an exotherm in this temperature region. Since the  $[\text{Cu}^{2+}]$  ratio of these glasses is such that  $E > C > A$ , one anticipates that the E glass has high viscosity in this temperature region, while the A glass tends to be fluid. Thus, the crystallization is detected at the lowest temperature for the most fluid glass, i.e., the A glass. Second, the relative crystallization rates can be explained by the above results. Surface crystal nucleation usually occurs very quickly as seen in most glasses (except for the E glass heat-treated at 580°C) so that the crystallization kinetics are most likely governed by crystal growth rates.<sup>37</sup> In crystal growth theory, the crystal growth rate has contributions from both the kinetic term, represented by the viscosity of the glass, and the thermodynamic term related to the undercooling. In other words, the crystal growth rate should exhibit a maximum with respect to temperature, since at low temperature the growth rate is small because of the large value of viscosity, while at high temperature it is small because of the small undercooling. Since at low temperatures (large undercoolings) the viscosity controls the crystal growth kinetics and the E glass is much more viscous than the A glass in this regime, it is not surprising that here the crystal growth rate in the E glass is much less than in the A glass. Also, the slow nucleation rate in the E glass at low temperatures contributes to its overall sluggish crystallization rate. At high temperature the situation is a bit more complicated. Although the A and E glasses possess the same liquidus temperature, at any given undercooling they have different driving forces for crystallization since they correspond to thermodynamically distinct states. Also, since the glass transition temperature of the A glass is lower than that of the E glass, the A glass is expected to have its maximum crystal growth at a temperature much lower than that of the E glass. Therefore, at higher temperature the crystallization rate of the A glass could be reduced because of the relatively small driving force for crystallization. On the other hand, the driving force for the E glass could still be large and its viscosity would be greatly reduced. Hence, under such circumstances, the crystallization rate at high temperature would be greater for the E glass than for the A glass.

#### IV. Conclusions

The glass transition temperature of the copper metaphosphate glass increases as the  $[\text{Cu}^{2+}]$  ratio in the glass is raised since  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  exhibit different intermolecular forces in phosphates and have different coordination in the glass structure. Thus, the relative crystallization rates and their temperature dependences are affected by the  $[\text{Cu}^{2+}]$  ratio in the glass because of the variation of viscosity with the  $[\text{Cu}^{2+}]$  ratio. However, the main crystallized phase is copper metaphosphate ( $\text{Cu}(\text{PO}_3)_2$ ) and crystallization is initiated from the surface, regardless of the  $[\text{Cu}^{2+}]$  ratio in the glass. The crystal morphology of the reduced glass is oriented and needle-shaped, while the totally oxidized glass is crystallized from all over the surface. The atmosphere used during the heat treatment does not affect the crystallization of the reduced glass, except for the formation of a  $\text{CuO}$  surface coating when heated in air.

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