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Sequence of Crystallization and Characterization of Bi_2O_3-CaO-CuO Ternary System

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VIA melt-quenching route, crystallization in the ternary Bi_2O_3-CaO-CuO glass was studied. The preparation of six samples within the ternary triangle gave two glasses and four devitrified glasses. The thermal effect pointed to softening and crystallization temperatures between 290℃ and 422 ℃ and between 360℃ and 550 ℃, respectively. The crystallized phases within the former heat-treatment were mixed oxides of bismuth, copper and calcium; however its ratios in oxide formula were different according to the composition. The microstructure of the devitrified samples show heterogenous crystallization in residual glass containing nano-scale crystals however, in the glassy samples scattered clusters containing more nano-scale crystals in glassy groundmass.

Keywords: Glass, dvitrified, Crystallization and Bi-containing oxide phases.

Superconductivity became one of the key technologies of the 21st century. Superconductor electronics, which are expected to play an important role in areas, where traditional semiconductor electronics have reached its performance limit. Today superconducting materials are routinely used in science, research and technological development and in medical diagnosis, using magnetic resonance imaging (MRI), nuclear reactors, satellites, nuclear weapons, etc. Some of these materials may be exposed to radiation [(1)].

Bi-based superconductors ($Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, n = 1,2 or 3) is one of the most important superconductor family which have been extensively studied due to their interesting superconducting properties, especially those that present transition temperature (Tc) around 30, 85 and 110 K, and have stable structure . It is suitable for the fabrication of long lengths of wire or tape material [(2–7)].

Bi-based superconductors, have critical current density, can be raised by fabricating composites consisting of superconducting and non-superconducting phases. The latter should be uniformly dispersed throughout the superconducting matrix in the form of fine inclusions and should cause no degradation of superconductivity. One effective way of producing such materials is by introducing inclusions of phases that contain an additional element and are

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nonreactive with the superconducting phase (do not change its chemical composition) [8, 9].

Different preparation methods are applied to produce these superconductors, which include co-precipitation, evaporation and others, but all of them present problems associated with the stoichiometry, which may be due to loss of some oxides during heating by volatilization [10–14]. Thus, accurate atmosphere control is necessary during fusion to avoid the volatilization of these components and consequently a stoichiometric composition can be obtained [15-17]. Bi-based superconductors ceramics were obtained by a rapid melt quenched followed by controlled thermal annealing to control the stoichiometry [6].

Bi-based superconductor via glass-ceramics process provides homogeneous and dense products to be made compared with the conventional solid-state reaction technique, and so strongly connected grains, good grain growth and also materials having a large current carrying capability can be achieved. In addition to this, the crystallization kinetics of the material is controllable and may allow fiber, films or thin sheets to be made directly from the molten material [18].

Most works incorporate different cations as Sr, Pb,…etc. to enhance the degree of crystallization or decreasing sintering temperatures in spite of adding impurities into superconductors always causes serious degradation of superconductivity [19,20].

In the present work, we aimed to prepare materials through melt quench route within the Bi_2O_3-CaO-CuO system. The crystallization behavior, the crystalline phases and the microstructure were studied.

Experimental

The chemical compositions in mole percent for different samples chosen for this study were illustrated in Table 1. Ingredient pure chemicals of Bi_2O_3, CuO and CaO (as $CaCO_3$) were used as starting materials. Homogenous mixtures were obtained by agate ball milling for 20 min. Batches for producing 50 g of sample were melted in a platinum crucible in a laboratory electric furnace in the 1000-1200°C range for 2 hr with interval stirring. The melts were poured on to a stainless steel plate at room temperature and pressed into a plate 1-2mm thick by another cold steel plate.

Glasses and the devitrified samples were thermally examined using differential scanning calorimetric analysis (DSC Diamond DSC Perkin Elmer). According to the DSC results the obtained samples were heated up to various temperatures at a rate of 3°C min for crystallization in a programmable muffle furnace. It is noticed that the synthesis process parameters (such as temperature, time and heating rate) plays a fundamental role for crystallization of different oxide phases.

TABLE 1. Chemical composition of different samples in mole %.

Sample No.	Chemical composition in mole%		
	Bi_2O_3	CaO	CuO
Semi1	60	20	20
Semi2	25	25	50
Semi3	25	50	25
Semi4	20	40	40
Semi5	40	20	40
Semi6	40	40	20

The heat-treated samples were subjected to powder x-ray diffraction analysis using Ni-filled Cu-Kα rays(n Ultima IV apparatus , Rigaku, Japan) for determination the types and contents of the crystalline phases precipitated in the samples. The fresh surfaces of heat-treated samples were examined with a scanning electron microscope (SEM (model JSM-5410LV, JEOL, Tokyo, Japan), after coating with 5 μm thickness gold layers sputtered over the surfaces.

Results and Discussion

The phase diagram of the ternary system Bi_2O_3-CaO-CuO used in this study is illustrated in Fig. 1a. To design the compositions which cover this system, the triangle was divided into three equal parts from each head. The interaction points of this division were chosen as representative sample for our system (Fig.1b). The melting process of the chosen samples gave two black samples of vitreous glassy state (Semi3&4) and four with some opaque or semi-devitrified nature (Semi1, 2, 5 and 6) (Table 1, Fig. 1 b).

Differential scanning calorimetric(DSC) which is very useful technique for determine different glass-ceramic processes such as annealing, softening, crystallization , transformation of metastable to stable phases and melting temperatures was used to study the crystallization behavior of this system. The endotherm is related to the transition range defined by Tg; which exhibits an increase in specific heat due to pre-crystallization processes. At this stage, the atoms being to arrange themselves in primary structural elements for the subsequent crystallization. The position and shape of DTA peaks are determined principally by the chemical composition and crystal structure of the sample.

Differential Scanning Calorimetric of the above materials show that, all samples exhibit broad endothermic effect followed by three exothermic ones, except Semi3 sample which show only two exothermic effects (Table 2 and Fig. 2). The broadness and increasing the temperature of endothermic effects are good indication for quick crystallization of these samples after cooling from melting temperature and so the remaining amount of amorphous phase ready for crystallization was small. The endothermic temperature was increased by increasing CaO content as in Semi3, Semi4 and Semi6 while increasing Bi_2O_3 leads to significant decrease in endothermic temperatures as in Semi1, Semi2 and Semi5. These results can be owing to, the effect of Ca ions on increasing the viscosity of the melt and the significant effect of Bi ions on decreasing it. Decreasing the viscosity of the melts leads to increasing in the mobility of different ions to arrange themselves at lower temperatures [21].

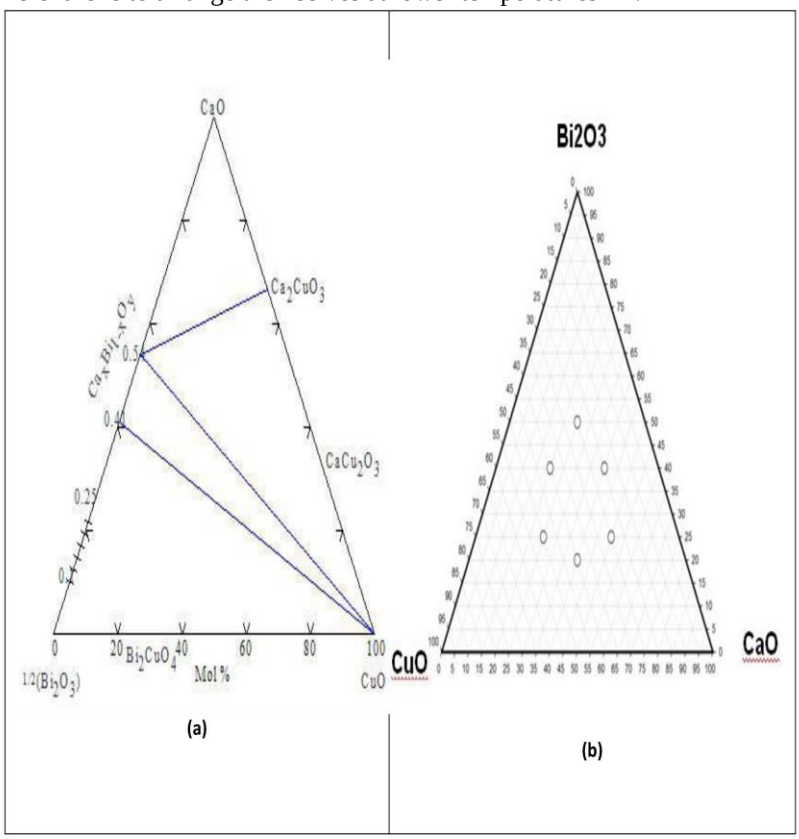


Fig.1 . a) Phase diagram for the ternary system; Bi_2O_3-CuO-CaO after Takano *et al.*, 1988 and b) The chosen points of chemical composition to study in the system Bi_2O_3-CuO-CaO.

TABLE2. Thermal effects of samples under investigation.

Sample No.	Endoth-ermic effect	1st exotherm ºC	ΔH of 1st exotherm J/g	2nd exotherm ºC	ΔH of 2nd exotherm J/g	3rd exothe-rm ºC	ΔH of 3rd exothe-rm J/g
Semi 1*	242.7	352	3.26	402	2.14	424.8	3.72
Semi 2*	220	373	11.55	422.5	1.725	437.86	8.535
Semi 3**	394			494.7	33.584	543.8	22.675
Semi 4**	396.68	453	6.774	465	5.57	483	1.034
Semi 5*	250	372.7	15.521	418	1.559	454	12.67
Semi 6*	315	400	0.756	434	0.352	451.69	0.759

*: Devitrified **: Glass

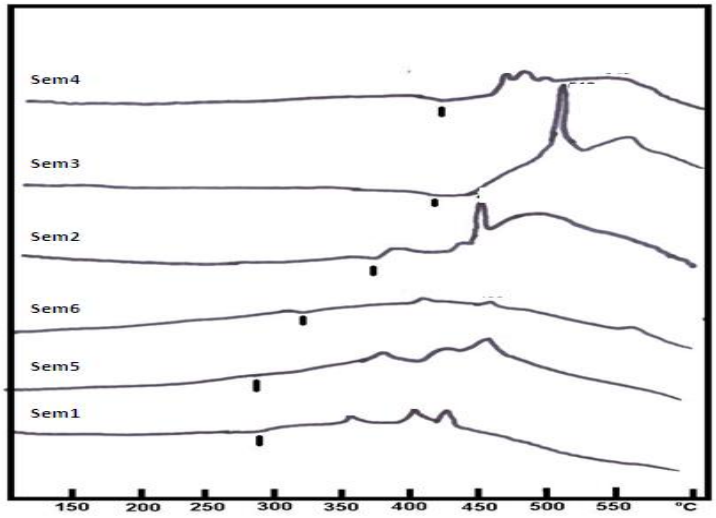


Fig.2: DSC traces of samples under investigation.

The number of exothermic peaks may reveal in most cases the number of crystallized phases which have un-overlapped range of crystallization. In this consequence, all samples exhibit three exothermic peaks revealing the crystallization of different phases whereas Semi3 revealed only two different phases too. These results will be confirmed later by XRD. Most exothermic peaks have wide span indicate broad crystallization propensity, also sharp and intense exothermic peaks were obtained in Semi2 and Semi3 indicate fast crystallization for the crystallized phases in this range. All the exothermic effects were increased by increasing CaO and decreased by increasing Bi_2O_3.

Figures 3, 4 and Table 3 revealed x-ray diffraction patterns and the developed phases in the samples under investigation. The quenched samples and samples after heat treatment at 350,550 and 750˚C for 2 hr were analyzed. Generally, the intense of the x-ray diffraction pattern were weaken by heat treatment at 350˚C and 750˚C and enforced at 550˚C. A detail of the crystallized phase was recorded as follow:

For sample containing high quantity of Bi_2O_3 (Semi1), the x-ray diffraction patterns of the devitrified sample show crystallization of $Ca_3Bi_8O_{15}$ with $Bi_6Ca_7O_{16}$ (Fig.3). During heat-treatment at 350˚C for 2 hr, $CaBi_2O_4$ was crystallized. Bi_2CuO_4 was crystallized beside $CaBi_2O_4$ with increasing the temperature up to 550˚C and 750˚C. The intensity was weakening largely by heat-treatment at 750˚C revealing partial re-melting. Although, the melting point of Bi_2O_3 is 824˚C, the partial re-melting of this sample at 750˚C may be due the partial reaction between Bi_2O_3 and CuO at lower temperature.

For Semi2 sample, containing high quantity of CuO , both $Ca_3Bi_8O_{15}$ with $CaBi_2O_4$ phases were formed in quenched glass and $CaBi_2O_4$ was crystallized by heat-treatment at 350˚C (Fig.3). By increasing the heat-treatment up to 550˚C, $Bi_6Ca_4O_{13}$ appeared beside $CaBi_2O_4$, while $CaCuO_2$ was crystallized beside $CaBi_2O_4$ at 750˚C. The sharpness of the x-ray diffraction patterns in this sample heat treated at 550&750˚C were confirmed by the above DSC data, where sharp and intense peak were appeared at 438˚C (Fig. 2).

Semi3 sample, containing high quantity of CaO, appeared almost amorphous. Small amount of $Ca_3Bi_8O_{15}$ was detected in the as prepared sample which is converted to $Ca_6Bi_6O_{15}$ phase at 350˚C (Fig.4). The later phase and $Ca_4Bi_6O_{13}$ were crystallized by heat-treatment at 550˚C. At 750˚C, $Ca_4Bi_6O_{13}$ was detected alone. The sharpness of XRD patterns for samples heat-treated at 550&750˚C were confirmed by the above DSC data, where sharp and intense peak appear at 495 ˚C (Fig. 2).

Semi4 sample (Fig.4) with high quantity of both CaO and CuO also appeared as amorphous structure. Ca_4 Bi_6O_{13} was detected by heat-treatment at 550˚C. Increasing the temperature up to 750˚C; $Ca_6Bi_6O_{15}$ was crystallized the former phase beside $Ca_4Bi_6O_{13}$.

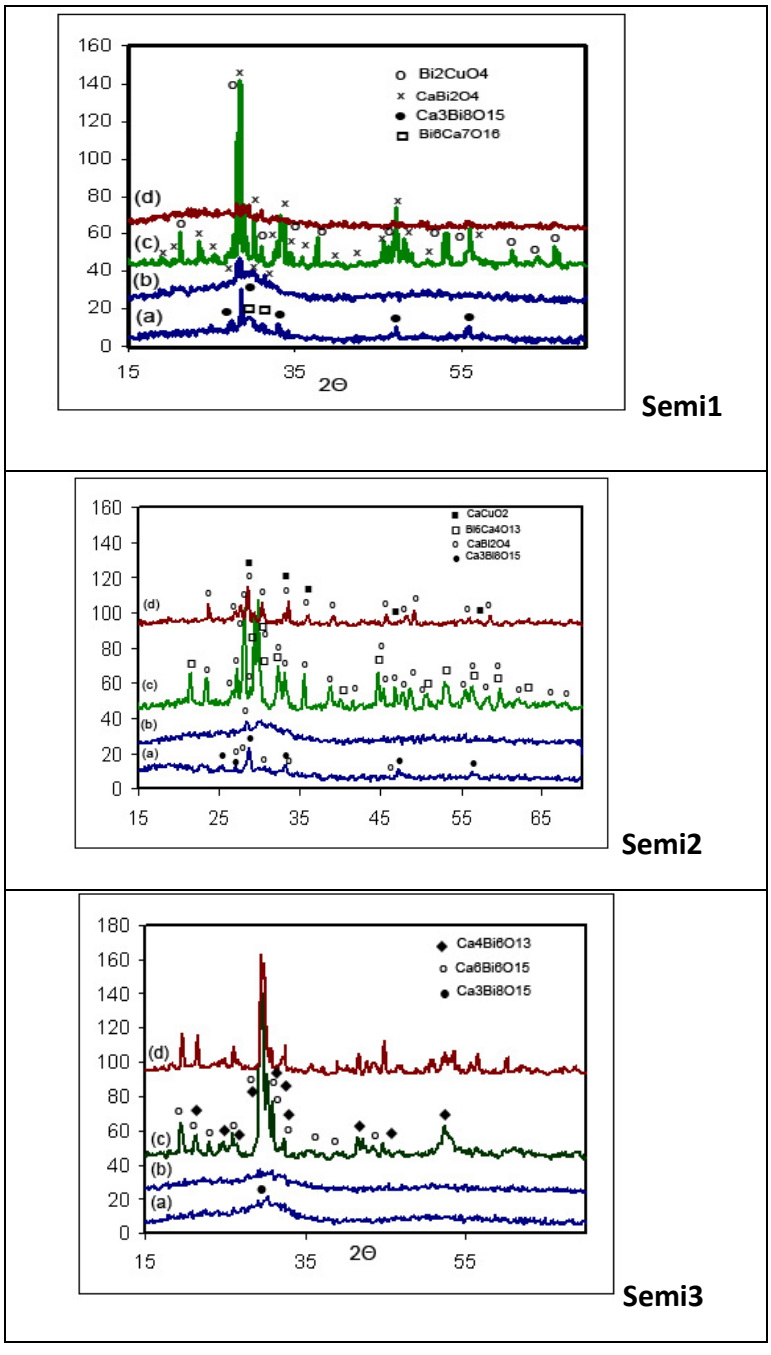


Fig. 3. X-ray diffraction patterns of devitrified Semi1, Semi2 and Semi3, samples (a) as received ,(b)heat-treated at 350˚C/2h, (c) heat-treated at 550˚C /2h and (d)750˚C/2hr

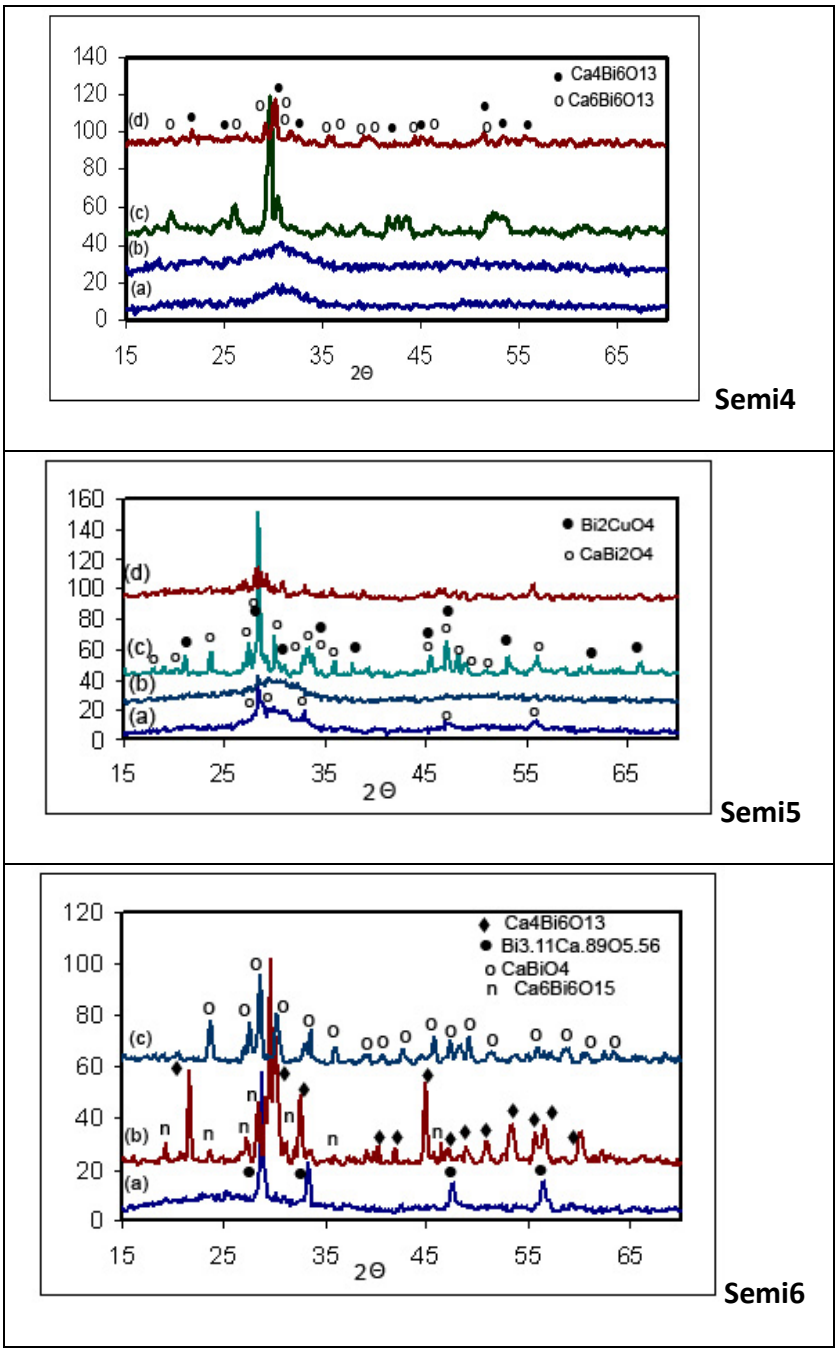


Fig.4. X-ray diffraction patterns of Semi4 , Semi5 and Semi6 samples (a) as received, (b)heat-treated at 350˚C/2h, (c) heat-treated at 550˚C /2h and (d)750˚C/2hr.

TABLE 3.The developed phases after different heat treatment.

Sample No.	Heat treatment parameters	Crystallized phases
Semi1	Devitrified	$Ca_3Bi_8O_{15}$+$Bi_6Ca_7O_{16}$
	350ºC/2hs	$CaBi_2O_4$
	550ºC/2hs	Bi_2CuO_4+$CaBi_2O_4$
	750ºC/2hs	Bi_2CuO_4+ $CaBi_2O_4$
Semi2	Devitrified	$Ca_3Bi_8O_{15}$+ $CaBi_2O_4$
	350ºC/2hs	$CaBi_2O_4$
	550ºC/2hs	$CaBi_2O_4$+$Bi_6Ca_4O_{13}$
	750ºC/2hs	$CaBi_2O_4$+$CaCuO_2$
Semi3	Glass	$Ca_3Bi_8O_{15}$
	350ºC/2hs	$Ca_6Bi_6O_{15}$
	550ºC/2hs	$Ca_4Bi_6O_{13}$+$Ca_6Bi_6O_{15}$
	750ºC/2hs	$Ca_4Bi_6O_{13}$
Semi4	Glass	Amorphous hump
	350ºC/2hs	Amorphous hump
	550ºC/2hs	$Ca_4Bi_6O_{13}$
	750ºC/2hs	$Ca_6Bi_6O_{15}$+$Ca_4Bi_6O_{13}$
Semi5	Devitrified	$CaBi_2O_4$
	350ºC/2hs	$CaBi_2O_4$
	550ºC/2hs	Bi_2CuO_4+$CaBi_2O_4$
	750ºC/2hs	$CaBi_2O_4$+ Bi_2CuO_4

TABELE 3. Cont.

Sample No.	Heat treatment parameters	Crystallized phases
Semi6	Devitrified	$Bi_{3.11}Ca_{0.89}O_{5.56}$
	350ºC/2hs	$Bi_{3.11}Ca_{0.89}O_{5.56}$
	550ºC/2hs	$Ca_4Bi_6O_{13}$+$Ca_6Bi_6O_{15}$
	750ºC/2hs	$CaBi_2O_4$

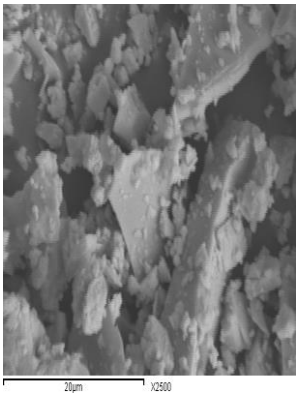
For Semi5 sample (Fig.4) with high quantity of Bi_2O_3 and CuO : $CaBi_2O_4$ was detected in both quenched sample and sample heat-treated at 350˚C for 2hr , while Bi_2CuO_4 was appeared with $CaBi_2O_4$ by increasing the temperature of heat-treatment either at 550˚C and 750˚C.

For Semi 6 (Fig.4) with high amounts of Bi_2O_3 and CaO: $Bi_{3.11}Ca_{0.89}O_{5.56}$ was developed with high quantity in quenched sample. The heat-treated sample at 550˚ C revealed crystallization of $Ca_4Bi_6O_{13}$ and $Ca_6Bi_6O_{15}$, while that treated at 750˚C revealed crystallization of $CaBi_2O_4$ alone.

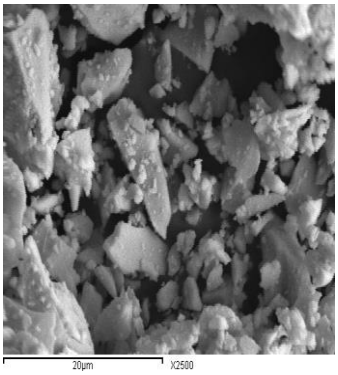
Generally, the crystallized phases were matched with increasing amount of oxide in the sample composition where, as Bi_2O_3 increased, phases rich with Bi_2O_3 were appeared, and so on for CaO and CuO. Also, it was noticed that, the amount of re-melt of the crystallized samples at 750˚C was decreased in the order Semi3 < Semi2 < Semi1 where the melting temperature of CaO (2572 °C) > CuO(1326°C) > Bi_2O_3 (817 °C).

Presence of CaO in high quantity was found to shift the onset of crystallization to higher temperature as in Semi3 and Semi4, while the presence of Bi_2O_3 and/ or CuO leads to more shift the onset of crystallization to lower temperature. These may be referred to the increase in the viscosity caused by adding CaO and decrease it by adding Bi_2O_3 and/ or CuO as discussed before. Figure 1-a illustrates phase diagram of our system. It is clear that phases detected and confirmed by XRD analysis are matched with that cited in phase diagram.

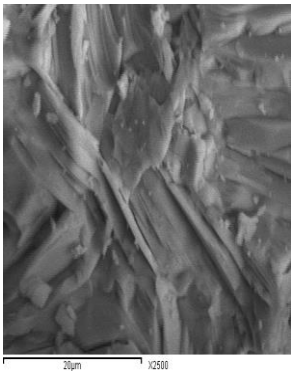
SEM is good technique to study the microstructure of glass-ceramics as grain size, homogeneity and the crystal shape. In general, all samples exhibited heterogeneous crystallization of large unhedral crystals with rounded minute crystals developed from it (Fig.5). The compactness of the structure was increased, due to partial re-melt of the glassy phase or both Bi_2O_3 and CuO by increasing heat-treatment parameters. It can be noticed that, the crystallite size was decreased by increasing temperature of heat-treatment (Fig. 5).



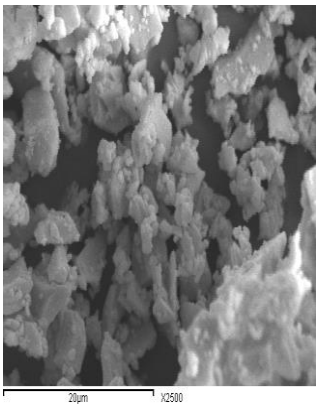
Semi 1- as prepared



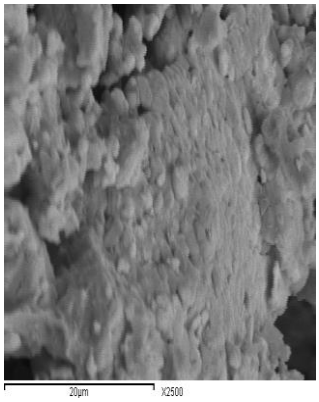
Semi 1 -550°C/ 2h



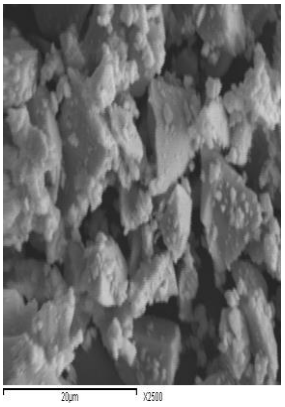
Semi 1- 750°C/ 2h



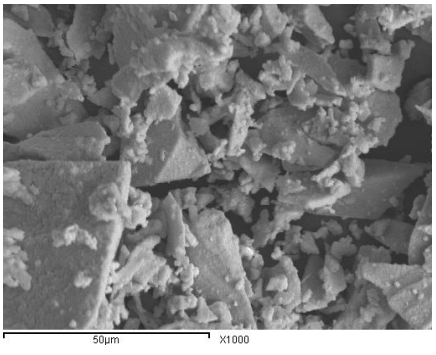
Semi 2- as prepared

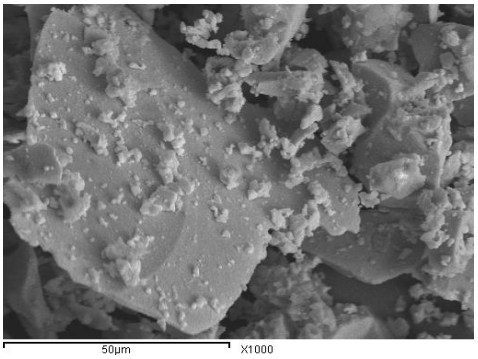


Semi 2 - 550°C/ 2h

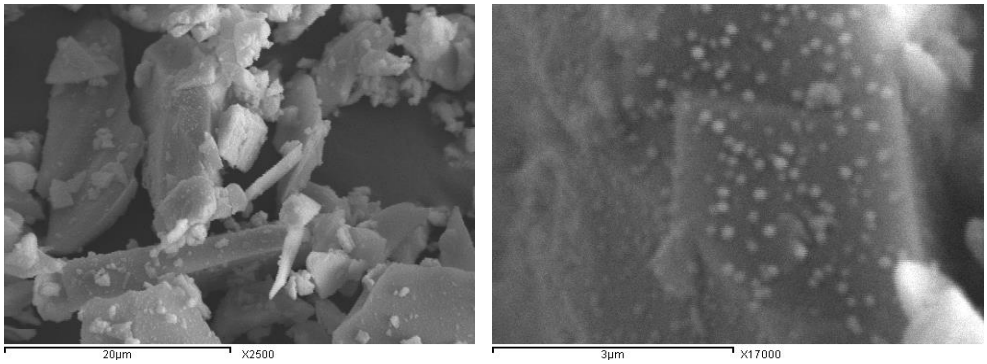


Semi 2- 750°C/ 2

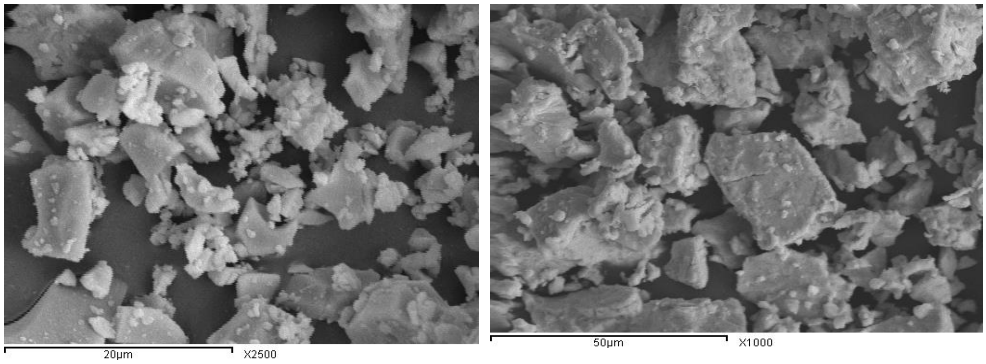




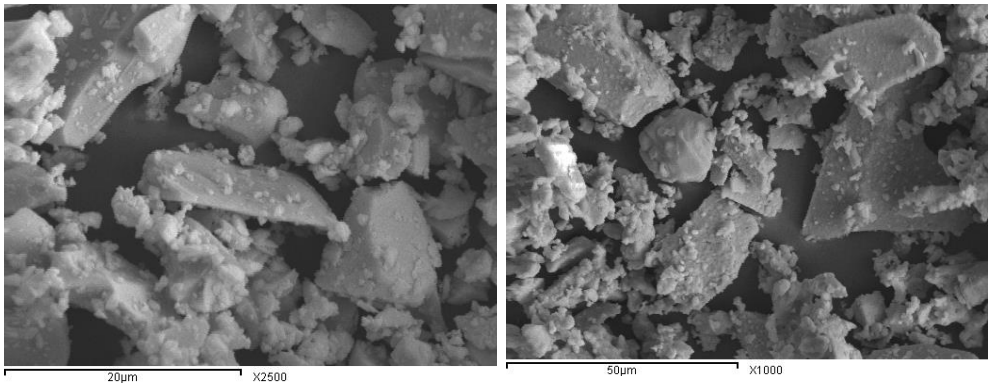
Semi 3- 750°C/ 2



Semi 4- 550°C/ 2h



Semi 5- 550°C/ 2h **Semi 5- 750°C/ 2**



Semi 6 -as prepared **Semi 6- 750°C/ 2**

Fig.5.SEM of the studied samples at different heat treatment.

Conclusions

The crystallization within the Bi_2O_3-CaO-CuO ternary system via heat-treatment was searched. The DSC results of both glass and devitrified samples revealed clear endothermic effects which are good indication for influence the residual glass for crystallization or re-crystallization of the separated phases. The endothermic temperature was increased by increasing CaO content while both Bi_2O_3 and CuO lead to significant decrease in endothermic value. Also the exothermic peaks in devitrified samples indicate the ability of the residual glass for crystallization.

The intensity of x-ray diffraction patterns of crystallized phases were decreased in the samples heat treatment at 350˚C and 750˚C and increased by heat treatment at 550˚C. It is noticed that, the crystallized phases were matched with increasing amount of oxide in sample composition where, as Bi_2O_3 increased, phase rich with Bi_2O_3 were appeared, and so on for CaO and CuO.

The compactness of the structure was increased, due to partial re-melt of glassy phase at high temperature or by increasing the heat-treatment parameters. The compactness was changed according to glass composition; as Bi_2O_3 increased it increased largely while as CaO increased significant decrease in compactness was observed. The microstructure of heat-treated glass samples gave clusters of nano-size crystals spread in glassy matrix, while heterogeneous crystallization unhedral crystals with rounded minute crystals developed in the pre-devitrified samples.

References

1. **Evik ,U. C. and Baltas, H.,** "*Nuclear Instruments and Methods in Physics Research*" B 256, pp. 619–625 (2007).

2. **Pavuna, M. C. D.,** "*Introduction to Superconductivity and High-Tc Materials*", World Scientific Publishing Co. Pte. Ltd. (1992).

3. **Burns, G.,** "*High-Temperature Superconductivity: An Introduction*", Academic Press, Inc. (1992).

4. **Scheel , H. J.,** *Mater. Res. Bull.* **19**, 26-32 (1994).

5. **Larbalestier, D. C.,** High-temperature superconductors , *MRS Bulliten*, 8, 16-19 (1992).

6. **Carvalho, C. L., Yukimitu, K., Reynoso, V. C. S., Moraes, J. C. S., Arau´ Jo, E. B., Alves, N. and Rainho, S.,** *Journal of Materials Science: Materials in Electronics*, **16**, 135– 138 (2005).

7. **Gazda, M., Kusz , B., Stizza , S., Natali, R., Klimczuk ,T. and Murawski, L.,** *Journal of Non-Crystalline Solids*, **353,** 1023–1029(2007).

8. **Kazin, P.E., Lennikov, V.V., Shuba, R. A., Eremina, E. A., Tretyakov, Pu. D., Jansen, M., Freitag, B., del la Fuente, G. F. and Larrea, A. , "***Formation of Stable Phase Inclusion in Bi-2212 and Bi (Pb)-2223 Materials , in High-Temperature Super Conductors and Novel Inorganic"* G.Van Tendeloo, E. V. Antipov and S. N. Putilin, (Ed). pp.69–74, Kluwer Academic Publishers, Dordrecht (1999).

9. **Kazin, P. E., Zaitsev, D. D., Tret'yakov, Yu. D. and Jansen, M.,** "*Inorganic Materials*", Vol. 37, No. 10, pp. 1046–1050. Translated from Neorganicheskie Materialy, Vol. 37, No. 10, pp. 1230–1234 (2001).

10. **Matheis, D. P. and Snyder, R. L.,** *Powder Diffract*. **5**(1), 8 (1990).

11. **Tarascon, J. M., Le Page, Y., Barboux, P., Bagley, B. G., Greene, L. H., Mckinnon, W. R., Hull, G. W., Giroud M. and Hwang, D. M.,** *Phys. Rev*. **B 37**16, 9382(1988).

12. **Tripathi, R. B. and . Johnson Jr., D.,** *WMater. Lett.* **10**(3), 118(1990).

13. **Wang, J., Wakata, M., Kaneko,T., Takano, S. and Yamauchi, H.,** *Physica,* **C 208** 323(1993).

14. **Sheen, S. R., Chen, D. H., Chang, C.T., Kao, C. H., Huang, J. C., Chou, Y. C., Hsieh, Y. C., Hsieh ,Y. H. and Wu, M. K.,** *Journal of Materials Science*, **30**, 1827-1831(1995).

15. **Sun, Y. K. and Lee, W. Y.,** *Physica*, **C 212**, 37(1993).

16. **Bansal, N. P.,** NASA Contractor Report 185162 October, NASA (1989).

17. **Bahgat, A. A.,** *J. Non-Cryst. Solids*, **226**, 155(1998).

18. **Balci ,Y., Ceylan , M. and Yakinci , M.E.,** *Materials Science and Engineering*, **B86** 83–91(2001).

19. **Li, Q., Pan, H. B., Zhu, C. G., Xu, P. S. and Zhang, X. Y.,** *Journal of Superconductivity: Incorporating Novel Magnetism,* **13** (4), 603-606 (2000).

20. **Gazda, M. and Winiarski, A.,** *Physica*, **C 432**, 35–42 (2005).

21. **El-Shennawi, A.W.A., Morsi, M. M., Khater, G. A. and Abdel-Hameed, S. A. M.,** *J. Therm. Anal*. **51,** 553-60 (1997).

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عملية التبلور والتوصيف للنظام الثلاثى (أكسيد البزمث و أكسيد النحاس)

سلوى عبدالحميد ، محمد رجب و عصمت حمزاوى
قسم بحوث الزجاج – المركز القومى للبحوث – القاهره – مصر.

تم تحضير عدد ٦ عينات فى النظام اكسيد البزمث- اكسيد الكالسيوم- اكسيد النحاس حيث نتج عدد ٤ عينات متبلوره عشوائيا و عدد ٢ عينه من زجاج. من نتائج التحليل الحرارى التفاضلى لكل العينات (متبلوره و غير متبلوره) تبين ان درجه الليونه و التبلور ما بين ٢٩٠ إلى ٤٢٢ و ما بين ٣٦٠ إلى ٥٥٠ درجه مئويه على التوالى. الاطوار المتبلوره مع البزمث تعتمد على نسبه الاكاسيد الاخرى الموجوده. النسيج البلورى المتكون فى العينات المتبلوره عشوائيا عباره عن بلورات فى حجم النانو منتشره فى ارضيه من الزجاج كما ان تبلور عينات الزجاج انتج بلورات فى حجم النانو فى تجمعات منتشره من الزجاج المتبقى.