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Synthesis of Cu-containing Diopside through a One-Step Crystallization

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Abstract

The incorporation of copper into pyroxene structure was investigated through the melt quenching technique and one-step crystallization procedure. Two series of glasses have been studied, one set with Ca=Mg and another set with Ca>Mg in diopside formula $Cu_x(Ca\ Mg)_{2-x}Si_2O_6$. The glasses were nucleated by TiO_2, Cr_2O_3, or CaF_2 additions as nucleating agents to variably control the phases produced. X-ray diffraction (XRD), scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDX) were used to characterize the obtained samples. The heat treatment studied at 700, 800, 900 and 1000 °C for 2 h produced green and dark green glasses based on Cu-containing diopside. Various crystalline wollastonite, cuprite, tenorite, cristobalite, quartz, and fluorite phases were developed with different ratios combined with diopside formation depending on the heat treatment and nucleating agents used. As the heat treatment increased in temperature, the crystallized fraction increased with the development of nano-aggregates and the observed reticulated textures confirmed a radical change in the euhedral crystals. This emphasizes that the Cu-containing diopside can be created by a facile one step process. These compositions may find some applications in biological and optical fields.

Keywords: diopside, glasses, nucleation, crystallization, microstructure

1. Introduction

Well-known copper-containing minerals are layered silicate cuprorivaite, $CaCu[Si_4O_{10}]$ [1] and synthetic Cu-bearing chain silicates including $Na,Cu_3[Si_4O_{12}]$ [2], $Na_4Cu_2[Si_8O_{20}]$ [3], $[CuMg[Si_2O_6]]$ [4], and $CaBa_3Cu[Si_6O_{17}]$ [5]. Liebauite, $Ca_3Cu_5Si_9O_{26}$, is a bluish green new single silicate and was observed in the xenolith by Zoller et al. [6]. Recently, another Cu-bearing chain silicate, $Li_2(Mg,Cu)Cu_2[Si_2O_6]_2$ was synthesized and the structure was determined by single-crystal x-ray diffraction technique [7]. Even though some pyroxene group minerals like augite $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$, diopside $MgCaSi_2O_6$, and enstatite $MgSiO_3$ can be easily prepared through the crystallization of glasses and are already identified in glass-ceramic materials [8]. However, synthetic Cu-bearing chain silicates related to pyroxene are rare in comparison with other silicates containing Co, Ni, or Zn [9-11].

Numerous synthesis and structural studies have been carried out on the diopside crystalline form and because of its natural ability to host many elements due to its ability to host different types of elements in its internal network. Modification and improvement of its properties for different applications were extensively studied. Example are the use of diopside in medical applications, cell engineering, and biological adaptations by doping diopside with the elements strontium, manganese and fluoride [12-15]. For the same reason, the inoculation of diopside with monovalent elements [16] was also studied to improve the viability and degradability. Regarding its internal structure, the effect of addition of both manganese and copper on the biological properties of the diopside were also studied [17]. Incorporation of iron and magnesium for switching the magnetism in the structure of the diopside was also reported [18]. Other studies aimed at the modification and improvement of the physical properties of diopside such as sinterability

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and fluoride incorporation [19]. Addition of rare elements such as lanthanum, cerium, neodymium, praseodymium, and its influence on the structure of diopside was investigated [20]. The influence of adding titanium, yttrium and fluoride on the crystal structure and sinterability of diopside for its medical and bio-glass applications is reported [21]. Copper in silicate glasses has received much interest for its optical properties in the ultraviolet range and nonlinear optics [22, 23]. However, research on adding both Cu^+ and Cu^{2+} regarding their effect on the structure and possible applications.

We already prepared a double chain silicate Cu-containing K-fluor-richterite, $KNaCa(Mg,Cu)_5Si_8O_{22}F_2$, through the crystallization of glass [24]. EDX analysis of these glass-ceramic samples indicated a gradual substitution of Cu^{2+} for Mg^{2+}. In addition, substitution of Cu^+, (or even Ca^{2+}), for Na^+ in K-fluor-richterite structure was also reported [24]. Another case of glass-ceramics is that containing cuprite, Cu_2O. This type of crystal provides a favorable situation for ionic conduction due to the presence of copper in the fourfold sites, and, therefore, its presence in the crystalline state increases the superconductivity [25]. Among the many routes of synthesis of Cu-diopside doped materials as sol-gel, co-precipitation and melting, [12, 26], the last procedure was chosen in our study for its simplicity and ease to prepare Cu-diopside doped materials.

The present work reports a study of single-step crystallization processes of Cu-containing diopside $Cu_x(CaMg)_{2-x}Si_2O_6$ glasses by aid of nucleating catalysts like TiO_2, Cr_2O_3, or CaF_2. The main object of this paper is to show the effect of glass composition and heat-treatment impact on the crystallization behavior and microstructures of the resultant samples.

A previous experience with up to 5wt% of CuO in anorthite-diopside glass-ceramics proved that during a heat treatment of 1h at 1100 °C, the colored metal was segregated at the grain boundary [27]. In this study we chose a higher amount of copper to verify the possibility to enclose it in a silicate crystalline structure.

1   Experimental Procedure
1.1   Glass preparation
Samples were synthesized by melt and quench route using calcium carbonate ($CaCO_3$, Sigma Aldrich), magnesium oxide (MgO, Sigma Aldrich), silicon dioxide (SiO_2, Sigma Aldrich) as the raw materials for diopside base and copper (II) oxide (CuO, Merck) as the replacement for Mg and Ca in diopside crystalline structure. All the reactants were of 99% purity and were used as received from the producers. The nucleating oxides, used to catalyze the crystallization processes, chromium oxide (Cr_2O_3), titanium oxide (TiO_2) or calcium fluoride (CaF_2) (all purchased from Sigma Aldrich) were added separately in amount of 0.5, 5 and 5 %, respectively, in all sample preparations (Table 1).

Two series of glasses with partial substitution of both Ca and Mg by Cu with the formulae $Cu_{0.50}Ca_{0.75}Mg_{0.75}Si_2O_6$ (CaO=MgO) and $Cu_{0.50}Ca Mg_{0.50}Si_2O_6$ (CaO>MgO) were prepared. Table 1 presents the nominal glass batch compositions. The glass batches were weighed, mixed, homogenized and melted inside Platinum crucibles in electrical furnace at 1400-1450 °C. After complete melting, the melts were poured into steel molds. All the cast pieces of glasses were then annealed at 450 °C. The glasses were subjected to heat-treatment at 700, 800, 900 and 1000 °C for 2 hours with heating rate 10°C/min.

Sample No.	Mole%				Wt%				Nucleating oxide %		
	CuO	CaO	MgO	SiO_2	CuO	CaO	MgO	SiO_2	Cr_3O_4	TiO_2	CaF_2
G1[a]	0.5	0.75	0.75	2	17.13	18.11	13.02	51.75	--	--	--
G1C	0.5	0.75	0.75	2	17.13	18.11	13.02	51.75	0.5	--	--
G1T	0.5	0.75	0.75	2	17.13	18.11	13.02	51.75	--	5	--
G1F	0.5	0.75	0.75	2	17.13	18.11	13.02	51.75	--	--	5
G2[b]	0.5	1	0.5	2	16.84	23.74	8.53	50.88	--	--	--
G2C	0.5	1	0.5	2	16.84	23.74	8.53	50.88	0.5	--	--
G2T	0.5	1	0.5	2	16.84	23.74	8.53	50.88	--	5	--
G2F	0.5	1	0.5	2	16.84	23.74	8.53	50.88	--	--	5

Table 1. Glass Batch compositions
G1a Cu replaced both Ca and Mg in diopside (CaO=MgO) [$Cu_{0.50}Ca_{0.75}Mg_{0.75}Si_2O_6$]
G2b Cu replaced Mg in diopside (CaO>MgO) [$Cu_{0.50} Ca Mg_{0.50}Si_2O_6$]

1.2   X-ray diffraction analysis
Glass-ceramic samples were characterized by powder X-ray diffraction (XRD) at room temperature. The samples were ground to powder with an average size below 63 μm and XRD patterns were recorded on an XRD (model-Bruker AXS D8, Germany) using Cu Kα- radiation.

1.3   Scanning electron microscopy and energy-dispersive x-ray analysis
The microstructure of the glass-ceramic samples was studied via scanning electron microscopy and energy

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dispersive microanalysis (SEM/EDX - Philips-XL30). For SEM examination, the fresh fracture glass-ceramic samples were chemically etched by soaking in 1% HF+1%HNO$_3$ for one minute and then rinsing with distilled water. Before SEM observation, all specimens were coated with a thin film of graphitic carbon.

2   Results

Incorporation of CuO into the diopside batches produced transparent green to dark green glasses. The crystalline phases developed during the one-step heat-treatment in the temperature range of 700-1000 $^\circ$C and ~~nucleating agents with its~~ their morphology changes are presented in Table 2. Diopside (CaMgSi$_2$O$_6$), cuprite (Cu$_2$O), tenorite (CuO), wollastonite (CaSiO$_3$), cristobalite (SiO$_2$) and fluorite (CaF$_2$) crystals were developed.   The crystallization of these glasses depends on both the CaO/MgO ratio and the heat-treatment schedule.

2.1   Crystallization of Cu$_{0.50}$Ca$_{0.75}$Mg$_{0.75}$Si$_2$O$_6$ glass (series CaO=MgO)

Crystallization of such glasses is based on the nominal substitution of Cu$_{0.50}$ for both Ca$_{0.25}$ and Mg$_{0.25}$ in the diopside formula MgCaSi$_2$O$_6$. The X-ray diffraction analysis of the heat-treated glasses at 700 $^\circ$C showed the formation of cuprite Cu$_2$O, JCPDS card 77-199 [28], as a single phase in G1T and G1F samples, but jointly with cristobalite and quartz in the parent G1 sample. While for G1F glasses at 800 $^\circ$C, cuprite was developed as a single phase,
pyroxene, (diopside), CaMg)$_2$Si$_2$O$_6$ JCPDS card 89-830 and tenorite, CuO JCPDS card 48-1548 were formed in TiO$_2$ containing G1T glass at the same temperature. At 900 ^{o}C, diopside, cuprite and cristobalite were formed in G1, G1C and G1F glasses, and tenorite appeared only in G1T glass. At the highest temperature of 1000 $^\circ$C, diopside, tenorite, cristobalite and traces of cuprite were developed in all glasses but with little fluorite in G1F glass (Fig. 1A and 1B).

SEM micrographs of fresh fractured surfaces showed the crystallization features of the glasses heat-treated at 1000 $^\circ$C for 2h (Fig.1C). It can be seen that irregular accumulated crystals were developed in G1 parent sample. However, in high magnification euhedral monoclinic and tetragonal-like crystals were clear and pointed to diopside and cuprite phases (Fig. 1C, G1). In G1C sample, containing Cr$_2$O$_3$, square-like fine crystals of 0.5-1.0 μm were seen in the groundmass with some mature crystals > 2 μm (Fig. 1C, G1C). The microstructure of TiO$_2$-containing G1T glass depicted rod- and square-like crystals in the groundmass andwith some stout euhedral crystals as well (Fig. 1C, G1T). A reticular-like microstructure with uniform fine euhedral crystals of 0.5-1 μm appeared in F-containing G1F glass (Fig. 1C, G1F).

2.2   Crystallization of Cu$_{0.50}$Ca Mg$_{0.50}$Si$_2$O$_6$ glasses (series CaO >MgO) Crystallization of such

glasses is based on the substitution of Cu$_{0.50}$ for Mg$_{0.5}$ in the diopside formula MgCaSi$_2$O$_6$. The heat-treatment of these glasses at 700 $^\circ$C forms cuprite as single phase in all glasses while, at 800 $^\circ$C, cuprite was formed only in the G2 base and G2F glasses and diopside and tenorite were formed in G2C and G2T samples (Fig. 2A). The later phases; i.e. diopside, tenorite and cuprite, were crystallized with cristobalite, at 900 $^\circ$C, or with wollastonite at 1000 $^\circ$C in G2 base, G2C, G2T and in G2F glasses (Fig. 2B). A small amount of fluorite was also developed at 1000 $^\circ$C in G2F glass. The excess of CaO over MgO in this glass composition has led to the formation of wollastonite:

CaO + SiO$_2$ in (residual glass) → Wollastonite CaSiO$_3$
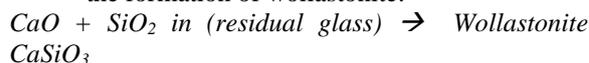
SEM micrographs depicted volume crystallization in these glasses (Fig. 2C). In the base G2 glass, indistinct square or rounded-like crystals were developed in the groundmass with little stout rounded to subrounded grains. On the other hand, irregular aggregates were developed in G2C and G2T samples. In fluorine containing G2F sample, clear euhedral to subhedral crystals were formed (Fig. 6-b-G2F).

3. Discussion

In general, copper ions in oxide glasses can be found in the monovalent 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 and this, consequently, affects its properties. In our glass-ceramic samples, the presence of a dark film or jacket layer at the surface of the bulk samples was easily noticed. Similar observations already reported by Kamiya et al. [29]. ~~He~~ suggested that oxygen does not diffuse into the glass but Cu$^+$ ions migrate to the surface from the interior to balance the surplus positive charge produced by the oxidation of Cu$^+$ to Cu^{2+} ions inside the glass. Others mentioned that copper induces the highest extent of both the inward and outward diffusion and, hence, the thick surface layer of both amorphous silica and crystalline alkaline earth oxides [30, 31] is found. In fact, the presence of Cu$^+$ in a fourfold site is favorable for ionic conduction because a high rate of ion exchange gave high electrical conductivity of glass samples [24]. In the present samples the decrease of cuprite with increasing heat treatment (up to 1000 °C) indicates a significant decrease in the number of Cu$^+$ ions via oxidation into the divalent state according to the reaction:

2Cu$_2$O + O$_2$ → 4CuO
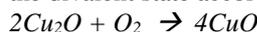
On the other hand, the similarity of the ionic radii of Ca^{2+} and the monovalent Cu$^+$ (0.95 and 0.96 Å, respectively) justifies the possible substitution of Cu$^+$ for Ca^{2+} in the diopside phase. In addition, the ionic radius of divalent Cu^{2+} (0.80 Å) is close to the ionic radius of Mg^{2+} (0.78 Å) and the Cu-O bond length is

2.12 Å compared with an Mg-O bond length of 2.10 Å [30, 31] and that confirms an easy and spontaneous replacement. These results imply that Cu^+ and Cu^{2+} can partially substitute for Ca^+ and Mg^{2+} in the diopside structure. Horiuchi, et al [7] found that Cu-bearing pyroxene becomes stable only when Cu is not a major component. That is why, if Cu is one of the main constituent elements, a finite ladder-like ribbon of $[Cu_nO_{2n+2}]$ is formed in the structure and this affects the arrangement of the $[Si_2O_6]$ chain and leads to various unique chain structures [6].
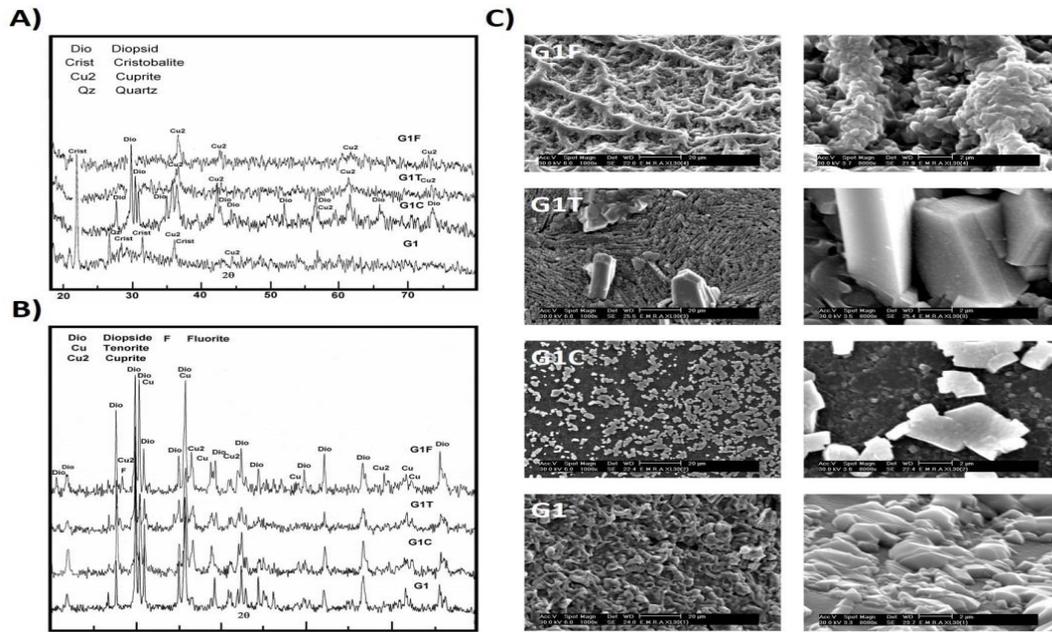

Figure 1 A) X- ray diffraction patterns of glasses of G1 series heat-treated at 700 $^{\circ}$C /2h; and B) heat-treated at 1000 $^{\circ}$C /2h; and C) SEM micrographs of G1 series at 1000°C at low magnification (left) and high magnification (right).
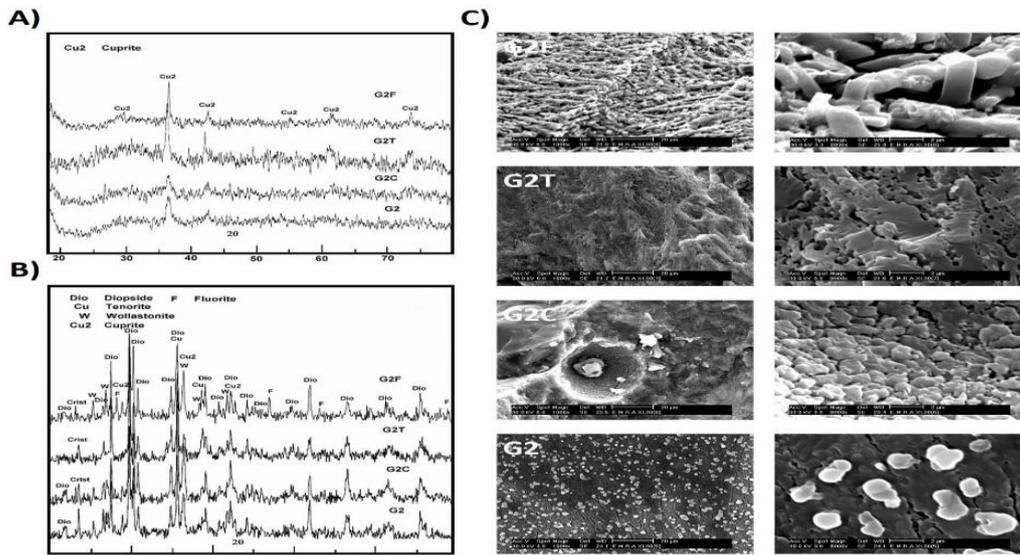

Figure 2 A) X- ray diffraction patterns of glasses of the G2 series heat-treated at 700 °C/2h; and B) heat-treated at 1000 $^{\circ}$C /2h; and C) SEM micrographs of G2 series at 1000 $^{\circ}$C in low magnification (left) and high magnification (right)
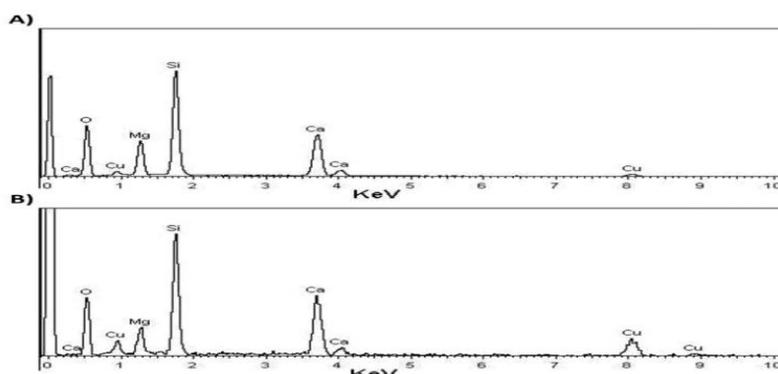
Figure 3 EDX analysis of the: A) crystallized G1 at 1000 °C /2h; and B) Crystallized G2 at 1000 °C /2h

Sample Name	°C /h	Crystalline Phases	Morphology
G1	------	A	Transparent green glass
	700/2	Crist -Qz-Cup	Translucent gray with metallic luster
	800/2	Di - Crist -Cup	Orange red core with gray surface
	900/2	Di-Cup-Crist	Orange red core with gray surface
	1000/2	Di-Ten- Crist- Cup(t)	Dark orange core with gray surface
G1C	------	A	Transparent dark green glass
	700/2	Di-Cup	Orange core with dark grey translucent surface
	800/2	Di-Cup	Interlocked orange and gray core with gray surface
	900/2	Di-Cup-Crist	Interlocked orange and gray core with gray surface
	1000/2	Di-Ten- Crist- Cup(t)	Interlocked orange and gray core with gray surface
G1T	------	A	Transparent green glass
	700/2	Cup	Translucent light gray
	800/2	Di-Cup-Ten	Orange gray core with gray surface
	900/2	Di-Cup- Ten-Crist	Dark orange core with gray surface
	1000/2	Di-Ten- Crist- Cup(t)	Interlocked orange and gray core with gray surface
G1F	------	A	Transparent deep green glass
	700/2	Cup	Translucent gray
	800/2	Cup	Orange gray core with gray surface
	900/2	Di-Cup-Crist	Orange gray core with gray surface
	1000/2	Di-Ten- Crist- Cup(t)-Fl(t)	Interlocked orange and gray core with gray surface
G2	------	A	Transparent green glass
	700/2	Cup	Translucent dark gray with metallic luster
	800/2	Cup	Orange core with opaque gray surface
	900/2	Di-Ten-Cup-Crist	Orange core with opaque gray film
	1000/2	Di-Ten-Cup-Wol	Dark orange grayish core with dark ray surface
G2C	------	A	Transparent dark green glass
	700/2	Cup	Translucent dark gray
	800/2	Cup-Di-Ten	Orange core with opaque gray film
	900/2	Di-Ten-Cup-Crist	Orange core with opaque gray film
	1000/2	Di-Ten-Cup-Wol	Dark orange reddish core with dark ray surface
G2T	------	A	Transparent deep green glass
	700/2	Cup	Translucent dark gray with some dark creamy layer
	800/2	Di-Ten-Cup	Orange core with opaque gray film
	900/2	Di-Ten-Cup-Crist	Orange core with opaque gray film
	1000/2	Di-Ten-Cup-Wol	Gray reddish core with gray surface
G2F	-------	A	Transparent deep green glass
	700/2	Cup	Translucent gray with creamy layers in between
	800/2	Cup	Orange gray core with gray surface
	900/2	Di-Ten-Cup-Crist	Orange gray core with gray surface
	1000/2	Di-Ten-Cup-Wol-Fl	Interlocked orange and gray core with gray surface

Table 2. Crystalline phases developed at different temperatures

a: Amorphous, Di: Diopside (JCPDS card 89-830), Cup: Cuprite (JCPDS card 77-199), Ten: Tenorite (JCPDS card 48-1548), Wol: Wollastonite (JCPDS card 72-2284), Crist: Cristobalite (JCPDS card 82-512), Fl: Fluorite (JCPDS card 77-2245)

Sample	Element Constituents								
Name	weight%					atomic%			
	O	Mg	Si	Ca	Cu	O	Mg	Si	Ca	Cu
G1	57.65	9.85	21.64	9.31	1.56	71.56	8.05	15.3	4.61	0.49
G2	54.89	6.52	20.79	9.83	7.97	71.33	5.57	15.39	5.1	2.61

Table 3. EDX analysis of G1 and G2 heat-treated at 900 °C.

Incorporation of TiO_2, Cr_2O_3 and CaF_2 to the base glasses has led to changes in microstructures and the order of crystallization of the developed phases (Fig 1 and 2, Table 2). Cr_2O_3 and TiO_2 enhanced crystallization of diopside at lower temperatures with respect to the base glasses, whereas CaF_2 favored the early formation of cuprite as a sole phase but it also encouraged diopside formation as the major phase at the higher temperatures.

3   Conclusion

Copper in both oxidation states Cu^+ and Cu^{2+} were successfully introduced as doping cation into diopside $(MgCaSi_2O_6)$ glass by melting process, followed by crystallization at 800, 900 and 1000 °C. The one-step heat-treatment was sufficient to devitrify all the studied glass compositions that showed a color change from green to gray then from gray to orange depending up on the copper oxidation states. The XRD examination of the glass-ceramics showed several silicates or chain silicates phases, such as wollastonite, cuprite, tenorite, cristobalite and quartz. Microstructure observations indicated mass of crystallization in both series of prepared glasses accomplished with aggregates and reticulated texture intermittent with clear euhedral crystals. The EDX microanalysis showed that the major changes in the diopside crystal phase, which revels the incorporation of copper into the diopside network. This emphasizes that the Cu-containing diopside can be created by a one step process. Further studies are necessary to fully understand the possibility to use these glass-ceramics for biological and optical applications.

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