Preparation and characterization of Calcium-Fluoroaluminosilicate glass fillers for dental composite

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ABSTERACT

Development of new glass filer of the composite is very important in dentistry due to their physical, mechanical and mainly anti-caries properties. In this research synthesis four new series of glass as filler. This filler usually consist of a fusion of aluminosilicate glass modified with other elements, and they contain large quantities of fluorine, (SiO_2, Al_2O_3, AlF_3, CaF_2, NaF and $AlPO_4$ (wt. %)). The method of preparing (Calcium-Fluoroaluminosilicate Glass) powder was carried out by medium temperature method. These series of glass characterized by X- ray diffraction XRD, Fourier transform infrared spectroscopy FTIR, Scanning electron microscopy SEM and differential thermal analysis DTA. XRD show the Crystallite size between (20-25) nm .The partial size of glass also find by using BET method. The morphology of glass measured by SEM. DTA/TG indicated that Calcium-Fluoroaluminosilicate Glass had better thermal stability than other glasses, the structures of the obtained glasses compared to the commercial material was also studied using FTIR measurements.

Keywords: Glass; Calcium Aluminosilicate; composite filling; dentistry; XRD, BET; FTIR.

Introduction

One of the most common materials contributing to any success in dental composite is the filler, due to its excellent esthetic and physical properties, biocompatibility, strength, optical properties etc. The dental composite materials are a mixture of inorganic glass filler and organic polymer [Lee *et al.* 2006]. The main material forming glass is calcium Fluoroaluminosilicate. Calcium-Fluoroaluminosilicate glass containing phosphorus and sodium consists of an inorganic polymeric network embedded in an aluminum and silicon matrix, comprising an amorphous structure [Culbertson 2001]. Fuoroaluminosilicate firstly described by Wilson and Kent in 1971[AD 1971] and have been well known in dental material science for nearly 40 years, particularly as a restorative material.

Alumina and silicate are the main material in the glasses which are thus called alumina silicate glasses. The ratio between the two plays the major role in defining the features of glasses. The addition of fluoride to glasses is of great interest for the development of dentistry or orthopedic biomaterials [De Maeyer *et al.* 1998]. Also existence of fluoride increases remineralization in adjacent tooth structure, the fluoride which is used for the surface treatment of the Calcium-Fluoroaluminosilicate glass powder is not particularly restricted, but in general, metal fluorides are preferred [Akahane *et al.* 1988]. In general, those fluoroaluminosilicate glass powders which are prepared by melting a mixed component containing 25 to 50% of silica, 15 to 40% of alumina, 10 to 40% of a fluoride, and 0 to 20% of a phosphate at high temperatures of 1000 ºC. or higher, followed by cooling and grinding are preferably used.[Akahane *et al.* 1988]

Composites are one of the most common materials used in dentistry. For fluoride-containing dental restorative materials, is well documented as an anticariogenic agent. Fluoride-releasing restorative materials may be able to reduce the recurrent caries at the restoration margins [Donly and Gomez 1994; Griffin *et al.* 1992; Jensen *et al.* 1991; Tysowsky *et al.* 1988; Zimmerman *et al.* 1984].

In vivo and *in vitro* studies have demonstrated that fluoride stimulates osteoblastic proliferation, which is the reason why sodium fluoride (NaF) is widely used in the treatment of osteoporosis [Kassem *et al.* 1994; Marie *et al.* 1992]. NaF employed as fluoride-releasing fillers can exhibit extremely high levels of fluoride release. Materials that have high fluoride release, high recharge capability, excellent mechanical properties and bonding properties are highly desirable [Xu and Burgess 2003].

Many method have been used to prepare Calcium-Fluoroaluminosilicate Glass such as the sol-gel method, nonhydrolytic sol–gel method [Cestari *et al.* 2009b], the polymeric precursor method [Bertolini *et al.* 2004]. The fusion method has been widely used for the preparation of these vitreous systems. In this process Calcium-Fluoroaluminosilicate Glass (SiO_2 , Al_2O_3,AlF_3, CaF_2, NaF, and $AlPO_4$) are prepared by melting the mixture of oxides and fluorides within a temperature range from 1200 ºC to 1550ºC.[Nicholson 1998; Zhao *et al.* 2009]

The aim of this study is the preparation and characterization four types of Calcium-Fluoroaluminosilicate Glass as composites filler. This composite filler is characterized by XRD, FTIR, SEM and DTA/TG in order to choice the best series mixed with organic polymer.

2. Materials and methods

The raw reagents used to prepare the powders were SiO_2 (99%, Sigma), Al_2O_3 (99%, Merck) CaF_2 (99%, UNI- Chem), AlF_3

(99%, LOBA Chemie), NaF (99%, MERCK) and $AlPO_4$ (MERCK).

3. Preparation of glasses

The glass components silica SiO_2, Alumina Al_2O_3, Calcium Fluoride CaF_2, Aluminum Phosphate Al_2PO_4, Aluminum Fluoride AlF_3 and Sodium Fluoride NaF were weighted in the appropriate ratios, four samples with different compositions have been prepared as show in Table 1. The mixed for 2 h in a ball mill. The powders were sieved to particles size < 75 μm. The resulting mixture were heated in an electric furnace (ivoclar vivadent programat P500 Germany), from room temperature to 1200°C (5°C min^{-1} for 50 to 500°C , 10°C min^{-1} for 500 to 1200°C) for 2 hours to obtain glass. After this period, the glass slowly cooled (25°C min^{-1}) down to room temperature. The glass produced was then ground in ball-milled (RETSCH PM 100 Germany) for 2hrs and then sieved with a mesh (opening of < 25μm) to produce powder which have been used for subsequent analysis.

To confirm the amorphous state and the glass formation, the prepared specimens were analyzed by (XRD) and differential thermal analysis (DTA). Fourier transform infrared spectroscopy (FTIR) was used to investigate structural aspects of the glasses. Scanning electron microscopy (SEM) was used to study the morphology of the glass powder obtained after the heat treatment

Table 1- Batch composition (W%) of Calcium-Fluoroaluminosilicate Glass after melting coupled with Al_2O_3:SiO_2.

sample	SiO_2	Al_2O_3	CaF_2	Al_2PO_4	AlF_3	NaF	Al_2O_3/ SiO_2
N1	22	18		22	15	23	0.8181
N2	22	19	10-11%W	39	13	7	0.8636
N3	29	16.6	34.2	9.9	5.3	5	0.5742
N4	35	25	20	8	6	6	0.7142

4. Measuring devices

A. X-ray Powder Diffraction

X-ray diffraction (XRD) was performed using Philips Powder Diffract meter with a copper (Cu K□ X-ray source (Philips PW 1700 series diffract meter, Leiden, Netherlands). The powder samples (< 25 μm particle size) were scanned between 2θ (10 - 70◦) with a step size of 2θ = 0.02◦ in continuous mode and a count time of 0.35Sec per step. The crystallite size (D) of the glass samples was determined by using Scherrer equation [D.CULLITY 1956]

$$D = \frac{\beta\,\lambda}{\mathrm{W}\,cos\theta} \quad \text{----------(1)}$$

where λ is the wavelength of the incident X-ray (0.154060 nm), β Scherrer constant between 0.85 -0.99 depending on the particle morphology (β = 0.89 for spherical crystals with cubic symmetry), θ is the diffraction angle, and W is the full width at half maximum (FWHM in radian).

B. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transformed infrared analysis (FTIR; Nicolet Magna-IR 550 spectrometer, Madison, Wisconsin) was performed to identify the factual group of material and the chemical bonds between atoms. The samples were obtained by pressing the glass powder

with KBr into small pellets, of 0.5 cm diameter,

C. Brunauer, Emmett and Teller (BET)

Brunauer-Emmett-Teller (BET) surface analysis is a technique for measuring specific surface area of the powders and porosity. A sample is degassed under heat and vacuum, after which it is cooled to liquid N_2 (Nitrogen 77K) temperatures and an inert gas is added in controlled amounts. The gas adsorbs on the surface to form one monolayer as pressure builds up in the sample chamber. The monolayer of gases forms a dipole and allows for a second layer to build up on it. Brunauer-Emmett Teller (BET) method using a CHEMBET 3000 QUANTACHROME , using nitrogen as the adsorption/desorption gas. The mean diameter obtained by applying the BET method, d_{BET} is represented by[Brunauer *et al.* 1938]

$$d_{BET} = \frac{6}{A_s \rho} \quad (2)$$

where A_s is the specific surface area (m^2/g) and ρ is the theoretical density of the phase, The glass density is measured using the pycnometric method based, with an uncertainty of ± 0.02 g/cm^3.

D. Scanning electron microscopy SEM

Scanning Electron Microscope (SEM) was used to take high magnification photographs of the sample glass and areas of crystallization on the glasses. This high magnification view was helpfully in understanding the crystallization that was occurring. The morphology and size of glasses was characterized by SEM (VEGA TESCAN - Czech).

E. Differential Thermal Analysis (TG/DTA)

Thermal Analysis (TG/DTA/DSC) was carried out in a thermal analyzer using Model STA 409 PC, Netzsch instrument of Germany in air atmosphere in the temperature interval 20-1100^oC using a heating rate of 10 $^oC\ min^{-1}$.

5. Results and Discussion

Fig. 1. Shows the XRD patterns of Calcium-Fluoroaluminosilicate Glass, XRD patterns of glass can be seen that the peaks of the crystalline phases are superimposed on the broad bands of the amorphous glass phase. As you can see that N1 and N2 samples are in the vitreous, for N3 have peaks for 2θ at 31º and 59º with addition of CaF_2 and N2 have peak 2θ at 24º for addition of SiO_2, It also shows some additional peaks of low intensity which we were not able to assign. The additional peaks in two system has no strong influence on the glass characteristic of these systems [Cestari *et al.* 2009a]. systems studied by Bertolini *et al.*[Bertolini *et al.* 2004] presented the anorthite phase ($CaAl_2Si_2O_8$) when heat-treated at 1020 °C. In the present work, an amorphous structure predominates in the system 1050°C, confirming the glass structure. Therefore, the results in this study were in accordance with previous reports of crystallization in calcium fluoroa-luminosilicate glasses. According to the XRD patterns, the crystallinity of glasses were calculated by Equ.(1), the calculated size of crystallites was in the range 20–25 nm. As show in Table 2. Smaller size for N2 and the larger size for N1. The final results indicate that this glass has a totally amorphous structure.

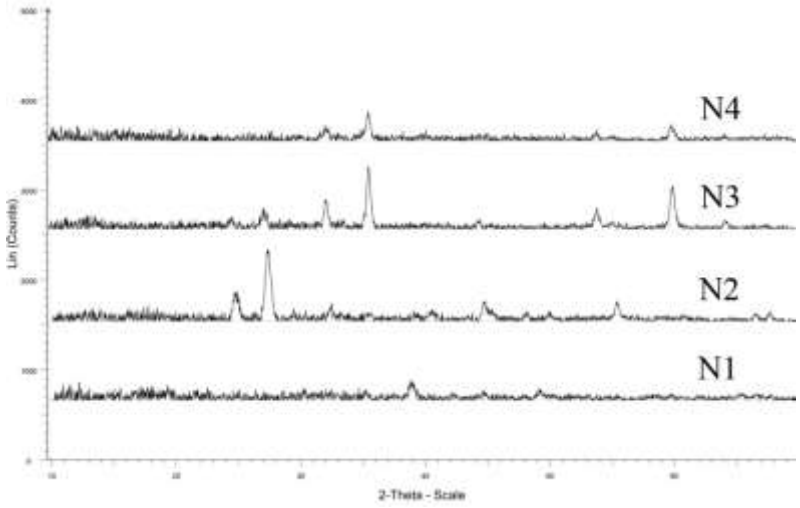


Figure 1. XRD patterns of Calcium-Fluoroaluminosilicate

Table 2 crystallite size (d_{XRD} in nm) calculated by Gaussian adjust of the XRD For compo glass:

Glass	*Crystallite size (nm)*
N1	25.97334
N2	20.30862
N3	24.48306
N4	24.13212

The FTIR spectra are shown in Fig. 2. for all specimens, The main characteristic of a former glass uses filler is the presence of Si–O–Si and Al–O–Si bonds, which can be identified by FTIR analysis. These bonds constitute the vitreous network, and they are susceptible to acid attack needed to form the dental composites [Nicholson 1998; Wilson and McLean 1988]. The broad peak at 1100 cm^{-1} and the peak at 720 cm^{-1} assigned to the asymmetric and symmetric Si–O–Si stretching modes, respectively, and The vibrations of the Si–O–Si, Al–O–Al, and Si–O–Al are located peak at 450 cm^{-1}.[Cestari *et al.* 2009b; Upadhya 2011] Additionally, the presence peak at 530 and 620 cm^{-1} in all spectra, in which is attributed to the bending of P–O mode revealing the crystallization of a Ca–P phase and it's clearly shown in N3 sample 601 cm^{-1}. The functional group tabulated in Table 3

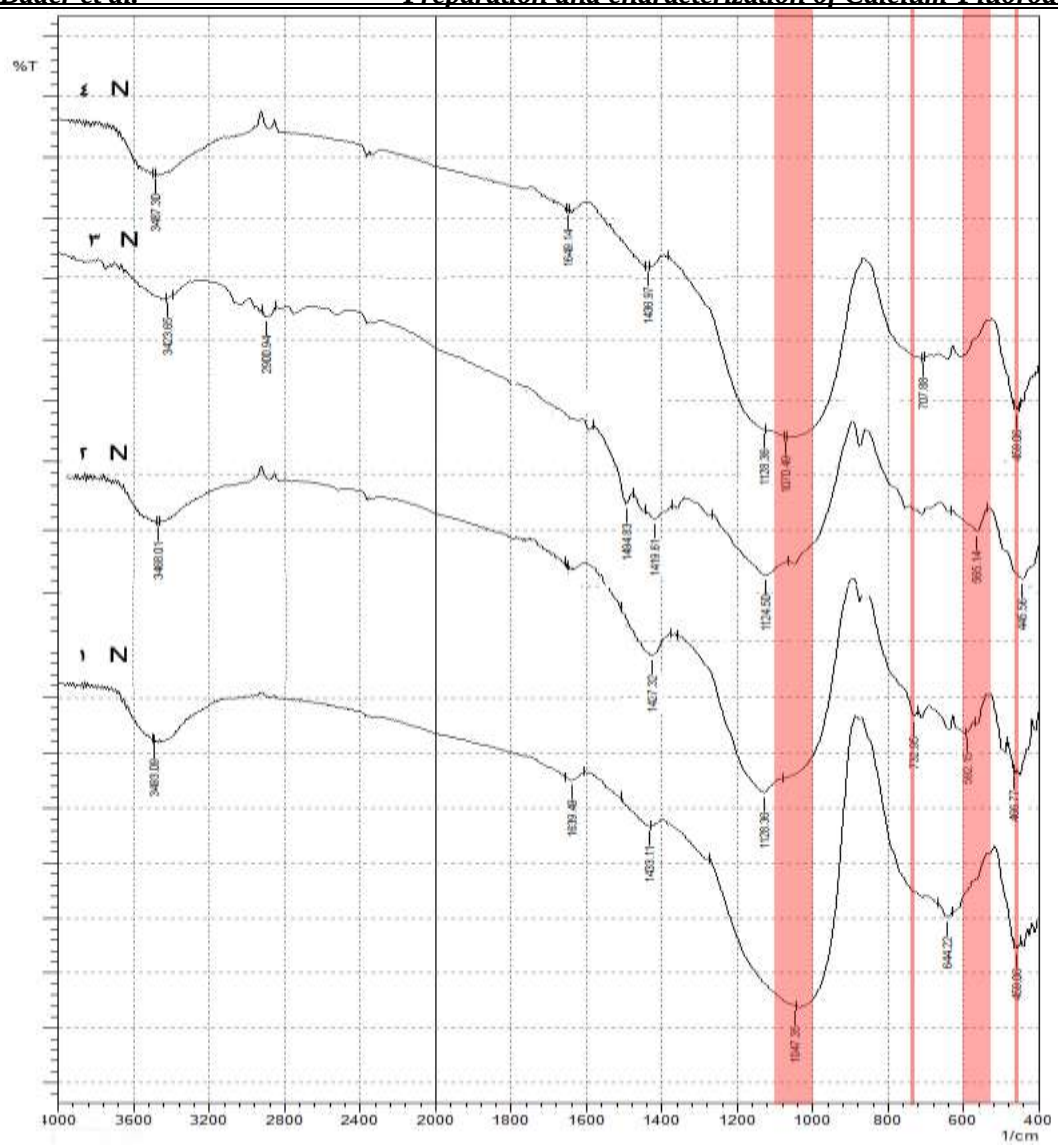


Figure 2. The FTIR spectra of Calcium-Fluoroaluminosilicate

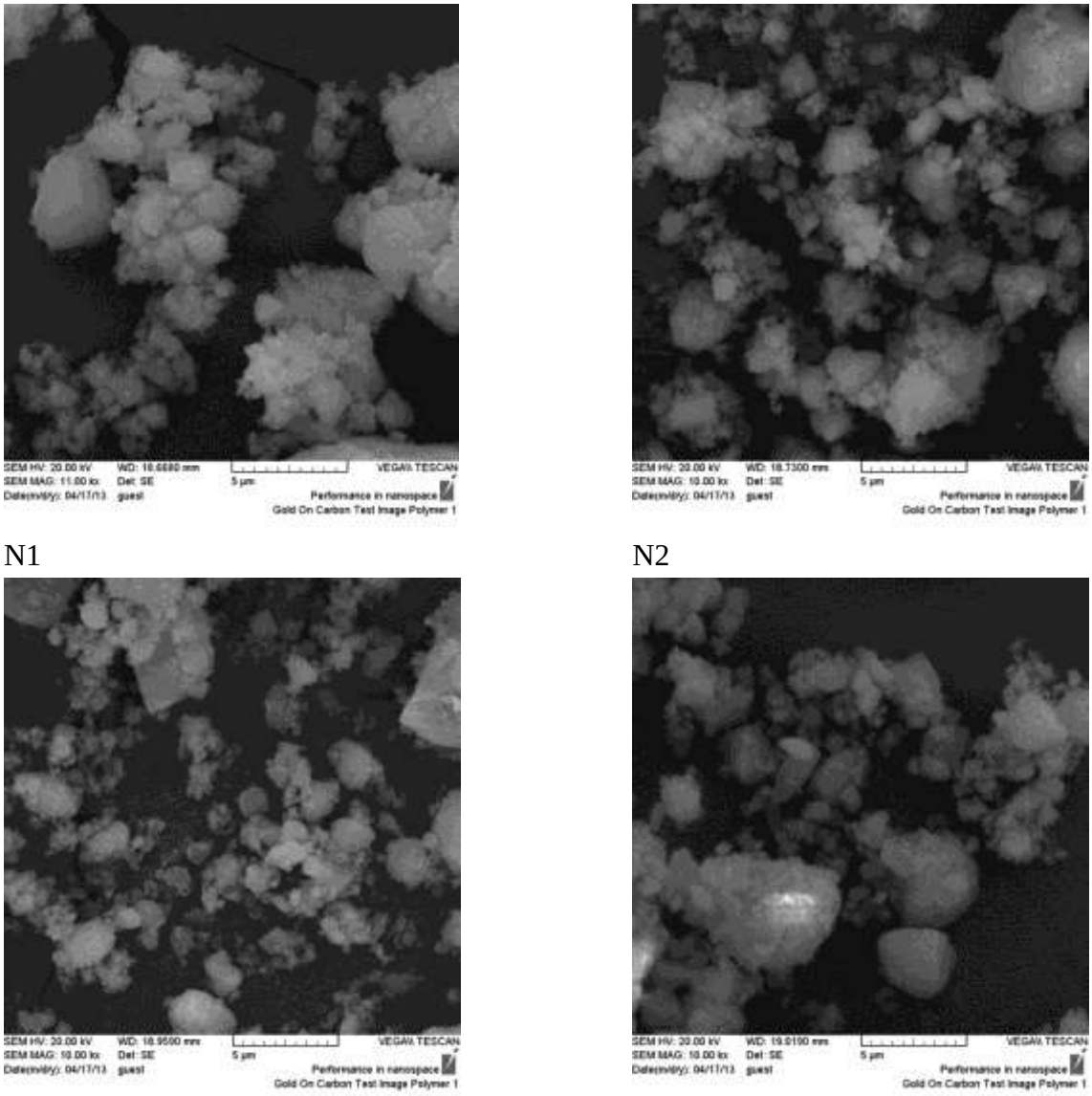
Table 3: the FT IR peaks of Calcium-Fluoroaluminosilicate

Glass	ν_B $Si-O-Si$ 460cm^{-1}	ν_P $P-O$ 530-620cm^{-1}	ν_s $Si-O-Si$ 730cm^{-1}	ν_{As} $Si-O-Si$ 1000-1100cm^{-1}
N1	460	623	716	1032
N2	463	596	733	1125
N3	450	566	733	1049
N4	460	601	721	1052

An SEM images are shown in Fig. 3. The particles were sharp-edged, polygonal, and the particles size with most ranged from 1 to 10 μm in diameter. Particle analysis using the NIH Image program [Abràmoff *et al.* 2004; Rasband 2011] showed that mean particle size distribution of Calcium-Fluoroaluminosilicate glasses between 1.1 to 1.6 μm, calculated from approximately 90 particles in presented in Table 4. From the SEM images, it was observed that N3 powder

contained finer particles compared to N1, N2 and N4.

The density of this glass was measured by using pycnometric method as shows in Table 4, variation in densities is not large and the reason is due to similar elements composition of the glasses. BET surface area method was used for specific surface area determination. The specific surface areas of glass and particles size measurement from equation 2 are shown in Table 4.



N1 N2

N3 N4

Figure 3. SEM micrographs for N1.N2,N3, and N4 samples

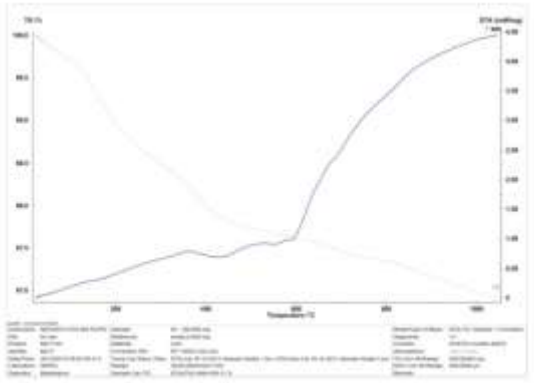
Fig. 4 depicts the DTA curves of the material prepared in this work. Transition temperature (Tg) of the glasses decreased with increasing CaF_2 content also Crystallisation temperature (Tc) eratures also decreased with increasing CaF_2 content.

The TG curves obtained for the sample before it was submitted to thermal treatment reveal a considerable mass loss between 30 and 400 °C, which is attributed to ethanol and water molecules. Therefore, the results in this study were in accordance with previous

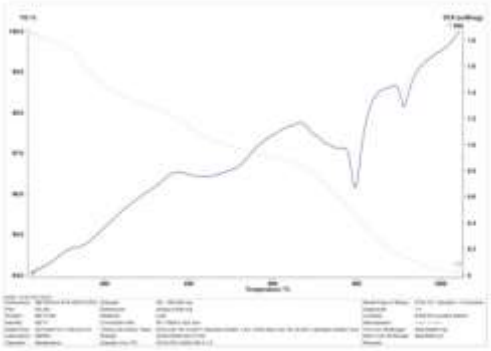
reports of crystallization in calcium fluoroalumino- silicate glasses.

Table 4: Results of crystalline size and particles size for Calcium-Fluoroaluminosilicate glass.

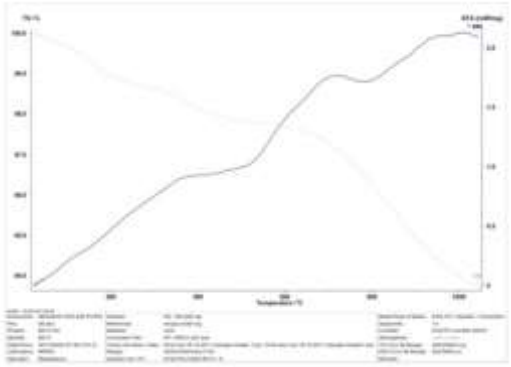
Glass	**Density** g/Cm^3	d_{XRD} nm	**Specific surface area** m^2/g	d_{BET} µm	d_{SEM} µm
N1	2.598	32.655	1.9066	1.211	1.404
N2	2.414	25.533	3.0384	0.818	1.605
N3	2.526	30.781	2.0836	1.135	1.284
N4	2.49	30.340	2.1675	1.111	1.1674



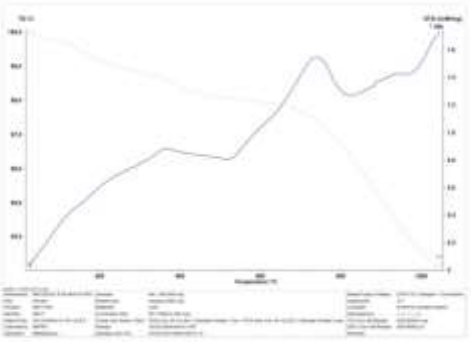
N1



N2



N3



N4

Figure 4. DTA/Tg micrographs presenting

Table 5. DTA for Calcium-Fluoroaluminosilicate:

Glass	Tc (ºC)	*Tg* (ºC)
N1		516
N2	913	412
N3	781	443
N4	963	423

A measure of the stability of glasses is the difference between the crystallization temperature (T_c) and the glass transition temperature (T_g).

6. Conclusions

SEM observation revealed the irregular nature of the powder particles. XRD analysis showed crystallites size in nano rang. From DTA curves, Tg of the respective glass compositions was measured. FTIR showed the frame work of AlO4 and SiO4 tetrahedra for all the glasses. The powder obtained by this methology was tested and showed to be a composites resin.

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تحضير ودراسة الخصائص الحشوة الاسنان (للكالسيوم ،فلورو،سلكا) الستسخدمة فى الموادالسنية المركب

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الملخص

ان تطوير نوع جديد من الفلر الزجاجي مهم جدا للغاية في محال طب الاسنان نظرا للخصائص الفيزياوية والبايولوجية ،ومكافحة التسوس .في هذه البحث تم تصنيع أربعة انواع جديدة من الفلر الزجاجي. يتكون الفلر عادتا من مزيج من الزجاج كالسيوم-ألومينوسيليكات المعدل مع العناصر الأخرى، حيث تتكون من نسب وزنية مختلفة من العناصر المحتوية على الفور،هذه المواد (SiO2، AL2O3، AlF3، CaF2،AlPO4)w%. تم تحضير الكالسيوم-فلوروامونيا سلكيت بواسطة طريقة درجة حرارة متوسطة.وشخصت النماذج المحضرة بواسطة حيود الاشعة السينية XRD، مطياف الاشعة تحت الحمراء FTIR، المجهر الإلكتروني SEM وكذلك التحليل الحراري تحليل DTA.اظهر تحليل XRDحجم حبيبي بين (20-25) نانومتر. الحجم الجزئي للزجاج أيضا وجد باستخدام طريقة BET. طبيعة السطح الفر الزجاجي تم تشخيصها بواسطة SEM و DTA TG / واظهرت النتائج ان الكالسيوم –فلورو اامينوسلكيت تمتلك استقرار حراري أفضل من ال انواع الاخرى من الزجاج والتي تم مقارنتها مع مواد االتجارية،وكذلك تم قياس FTIR.