

## Microstructure properties of lead silicate glasses

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### Abstract

In the present work, lead silicate glasses have been prepared with different amount of lead oxide content. Structure properties such as X-ray diffraction, AFM, and FTIR analyses have been done. The exceeding of PbO content more than 25wt% revealed a decreasing in density. The X- ray revealed that the strongest peak related to Hexagonal silica dioxide and the other crystal phases formed were related to silica oxide (SiO<sub>2</sub>) and lead oxide (PbO). Growth and decayed phases in X-ray have been observed with changing lead oxide content. Homogeneous surface was obtained using AFM analyzer with an average diameter around 100 nm. Infrared spectrum is characterized by the presence of large absorption band between 1200 and 900cm<sup>-1</sup> and have its maximum at 1080 cm<sup>-1</sup> which is typical to stretching vibrations of Si–O–Si bonds, another bands noticed were attributed to Pb–O–Pb, Pb–O–Si, [AlO<sup>4</sup>]-tetrahedron, and to Si–O–Al bond.

### Key words

lead glasses,  
microstructure, green  
and bulk density.

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## الخصائص التركيبية لزجاج سلكات الرصاص

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### الخلاصة

في العمل الحالي، تم تحضير زجاج سيليكات الرصاص وإضافة كميات مختلفة من أوكسيد الرصاص. تم إجراء التحليلات التركيبية مثل حيود الأشعة السينية وميكروسكوب الامتصاص الذري AFM وتحليلات فورير للأشعة الحمراء FTIR. ان زيادة نسبة اوكسيد الرصاص لاكثر من 25 بالمائة أظهرت نقصان في الكثافة. أظهرت نتائج حيود الأشعة السينية ظهور القمة العظمى التي تعود الى سداسي اوكسيد السلكا وبقية الاطوار الناشئة تعود الى اوكسيد السلكا واوكسيد الرصاص. تم ملاحظة نمو وازمحلال الأطوار باختلاف محتوى اوكسيد الرصاص بواسطة حيود الأشعة السينية. تم تحليل تجانس السطح بواسطة مايكرو سكوب الامتصاص الذري وبمعدل قطر بحدود 100 نانومتر. تمييز طيف الامتصاص تم بوجود قمة امتصاص كبيرة ما بين 1200 و 900 سم-1 وتمتلك قمة امتصاص عظمى عند 1080 سم-1 والتي تعود نمط اهتزاز الشد لأصرة Si–O–Si، تم ملاحظة أواصر أخرى ترجع الى Pb–O–Pb، Pb–O–Si، ورباعي [AlO<sup>4</sup>] وأصرة Si–O–Al.

### Introduction

As for ceramics, inorganic glasses, glass-ceramic and glaze materials have long gone beyond their traditional uses to address a wide array of modern technological challenges in fields such as electrical engineering / electronics / sensors, solar energy, protective and decorative coatings, optics / optical telecommunications, structural mechanics, medical, nuclear

technology, superconductors and microfluidics [1].

Glasses find wide applications, among others, in process technologies, vacuum science and technology etc. because of their desired thermo-mechanical properties and chemical durability. PbO-based glasses are technologically important due to their high refractive indices and relatively low melting temperatures. Among the

various lead oxide containing glasses, PbO–SiO<sub>2</sub> system has been found to form glass over a wide composition range and has got many applications in making ultrasonic delay cables, electron multiplier, TV picture tubes and glass-to-metal (GM) seals[2].

Oxide glasses based on PbO are of great interest in material field because they can form amorphous materials without traditional network formers like SiO<sub>2</sub>, and they can be used to produce glass ceramics, optical and optoelectronic devices, thermal and mechanical sensors, and reflecting windows.[3-4]. Lead oxide is not a glass-forming oxide by itself, but it can be incorporated in substantial quantities into other glass-forming oxide systems such as silicates, borates and phosphates [5,6].

In pure PbO lead atoms are bonded to four oxygen atoms, giving rise to a puckered layer structure with large Vander Waals (Pb-Pb) interactions.

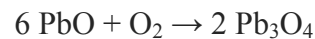
However, few studies have been reported on the PbO-based glasses. It was pointed out that Pb<sup>+2</sup> cations are highly polarizable and the asymmetry of their polyhedra inhibits crystallization processes in the melts in which they participate [7].

In many oxide glasses, PbO is known to play a dual structural role both as a network former [8] and as a network modifier [9] depending upon its concentration in the glass. When PbO enters the network, it is expected to form PbO<sub>4</sub> units in which lead is coordinated to four oxygen's in a covalently bonded configuration [10].

In the present work, the incorporation of different PbO content in silica feldspar glass (with a fixed alkali oxides NaO 4wt%, K<sub>2</sub>O 9wt% ,and 2wt% of alumina ) have been prepared using conventional glass technology. The glass structure were discussed using X-ray. AFM and FTIR techniques.

## Experimental work

The starting materials used in the preparation of the lead silicate glasses were red lead (Pb<sub>3</sub>O<sub>4</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), and feldspar (containing some amount of sodium and potassium) as a source of quartz (SiO<sub>2</sub>). It was well known that Pb<sub>3</sub>O<sub>4</sub> decomposes to lead oxide (PbO) completely at 500 °C. Pb<sub>3</sub>O<sub>4</sub> (2PbO.PbO<sub>2</sub>, minium, red lead) – red powder, good oxidizer, at 500 °C decomposes to PbO and oxygen.



Samples contain 15wt%, 20 wt%, 25 wt%, 30 wt% of PbO, feldspar, and fixed amount of Al<sub>2</sub>O<sub>3</sub> (2 wt%) were weighted.

Lead glass samples were synthesized using a powder technology technique. The starting material was prepared by mixing and grinding of pre-determined of appropriate amounts of mentioned material. 100g from each glass batches were melted in platinum crucible using an electrically heated furnace at 1150 °C in air for a period of time 2h followed by normal cooling of molten liquids onto room temperature. Re-grinding process in a planetary mono mill ( Retzh, Model PM100) using zirconia jar and ball to obtain final glass powders has been done for homogenization product. Two gram from each batches were weighted and pressed to a disk samples have a diameter 1.5 cm by subjected uniaxial pressure holder of 5 ton/cm<sup>2</sup> to produce clear homogenous discs. Prepared samples have sintered at 650°C for 2h.

## Results and discussion

### 1. Green and bulk density

Fig. 1 shows the variation of green and bulk density as a function of PbO wt% content. Glass density measurements were determined at room temperature using the standard

Archimedes method with water as the immersion fluid. A mass of glass disc was weighed in air ( $W_{ob}$ ) and then immersed in water and reweighed ( $W_w$ ), water density is  $1 \text{ g/cm}^3$ . Thus the density of the object is calculated by the following relation [11]:

$$\rho_{ob} = \rho_w (M_{ob} - (M_{ob} - M_w)) \quad (1)$$

As it can be seen that the green and bulk density have the same behavior for all prepared samples. The increase of PbO wt% content leads to increasing in both densities till it reach the highest value for green density  $\sim 2.1 \text{ gm/cm}^3$  and  $\sim 2.4 \text{ gm/cm}^3$  for bulk density of the specific PbO 25wt%. Additions of PbO wt% higher than this percentage producing an obvious decreasing in densities for these compositions. However, increasing in bulk density is very conceivable in contrast with green density. This can be attributed to the effective role of heat treatment on the bulk density leading to removing of the bubbles content in the samples and generation of liquid phases formed from dissolving of the constituents. This situation leads to a homogeneous of sample compositions to produce more dense material. Besides, it is well known the fact that inclusion of PbO in most glass structure must leads to increasing of density because Pb has a high density  $9.53 \text{ gm/cm}^3$  [12], in other words, the addition of  $\text{Pb}^{2+}$  atoms, will modify the glass structure by creating a non-bridging oxygen (NBOs) in the network[28]. The NBOs created were believed to alter the glass structure in a way that the packing of the molecules becomes denser as more network modifier ions (in this case  $\text{Pb}^{2+}$ ), attempt to occupy the interstices within the network[13]. The results are consistent with several studies by authors on the phosphate-based glasses [14, 15].

But in this study, the exceeding of PbO content more than 25wt%

revealed a decreasing in density. This can be explaining to, as the PbO content increase, sample may reach a saturation state which means that the liquid phases can consumption the contents then producing inrich PbO content samples. The exceeding of PbO content will segregates and retains bubbles leads to phase separation occurs then increasing in volume and consequently less dense.

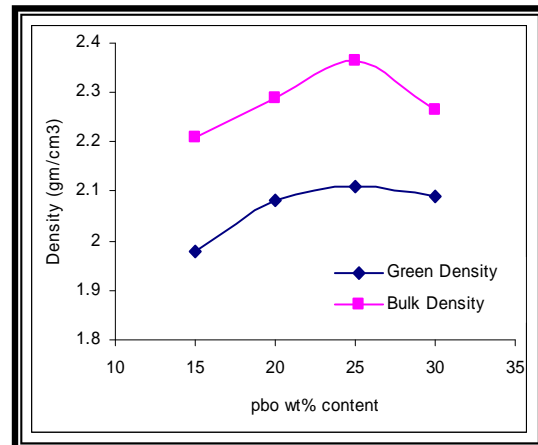


Fig. 1: The variation of green and bulk density as a function of PbO wt% additions.

## 2. X-Ray analysis

Samples that have 15 wt% PbO and 30 wt% PbO content were chosen to subjected to X- Ray diffraction analysis. The results were shown in Figs.2 and 3 respectively. PCPDFWIN program was used to estimate the presence phases. It can see clearly the appearance of several peaks related to the formation of crystal structures, Fig.2. The strongest peak related to silica oxide which has a position  $2\theta = 27.020 \text{ deg}$ . The other crystal phases formed were related to silica oxide ( $\text{SiO}_2$ ) and lead oxide ( $\text{PbO}$ ). The formation of these phases is due to the heat treatment that use in this work which helpful the glass composition to react and produce crystal structure of glass-ceramic with Hexagonal  $\text{SiO}_2$   $a=4.867$   $c=5.331$ . The other important information were illustrated in Table 1.

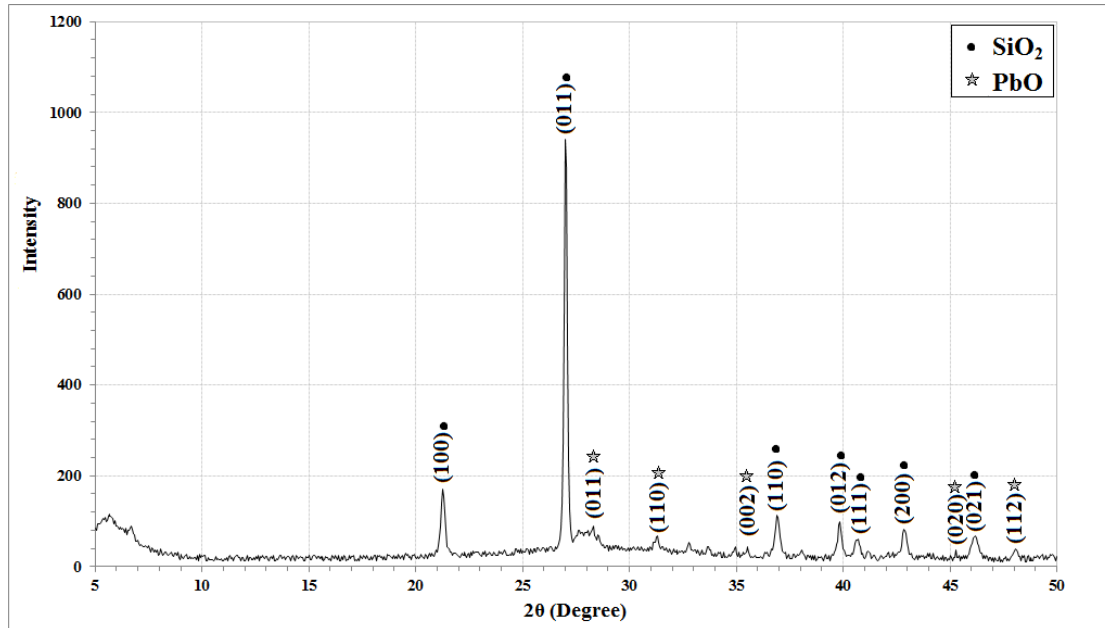


Fig.2: X-ray diffraction pattern and measurement done for sample contain 15 wt% PbO.

Table 1: The two theta, fill width half maximum, plane distance(Exp. &Std), grain size, apparent phases, and plan miller indices for sample contain 15 wt% PbO.

2θ (Deg.)	FWHM (Deg.)	$d_{hkl}$ Exp.(Å)	G.S (nm)	Phase	$d_{hkl}$ Std.(Å)	hkl
21.263	0.202	4.175	40.0	SiO <sub>2</sub>	4.2522	(100)
27.020	0.152	3.297	54.0	SiO <sub>2</sub>	3.3408	(011)
28.535	0.202	3.126	40.6	PbO	3.1391	(011)
31.263	0.253	2.859	32.7	PbO	2.8283	(110)
35.505	0.202	2.526	41.3	PbO	2.5327	(002)
36.919	0.253	2.433	33.2	SiO <sub>2</sub>	2.455	(110)
39.848	0.202	2.260	41.8	SiO <sub>2</sub>	2.2793	(012)
40.657	0.253	2.217	33.6	SiO <sub>2</sub>	2.2349	(111)
42.879	0.253	2.107	33.8	SiO <sub>2</sub>	2.1261	(200)
45.253	0.101	2.002	85.2	PbO	1.9999	(020)
46.162	0.354	1.965	24.4	SiO <sub>2</sub>	1.9783	(021)
48.030	0.202	1.893	43.1	PbO	1.8868	(112)

Fig. 3 show the X-ray diffraction of sample contain 30 wt% PbO by subject the same heat treatment condition. This pattern provide Hexagonal SiO<sub>2</sub> a=4.884 c=5.4000 with the same phases produce early for 15 wt% PbO with attention to appearance of K<sub>2</sub>O and decay of all crystal phases that obtained before.

This decay can be explain as the presence of large quantity of PbO in the composition of lead silicate at the same condition of heat treatment are unable to produce growth process of crystal structure. Important information for prepared sample contain 30wt% of PbO were illustrated in Table 2.

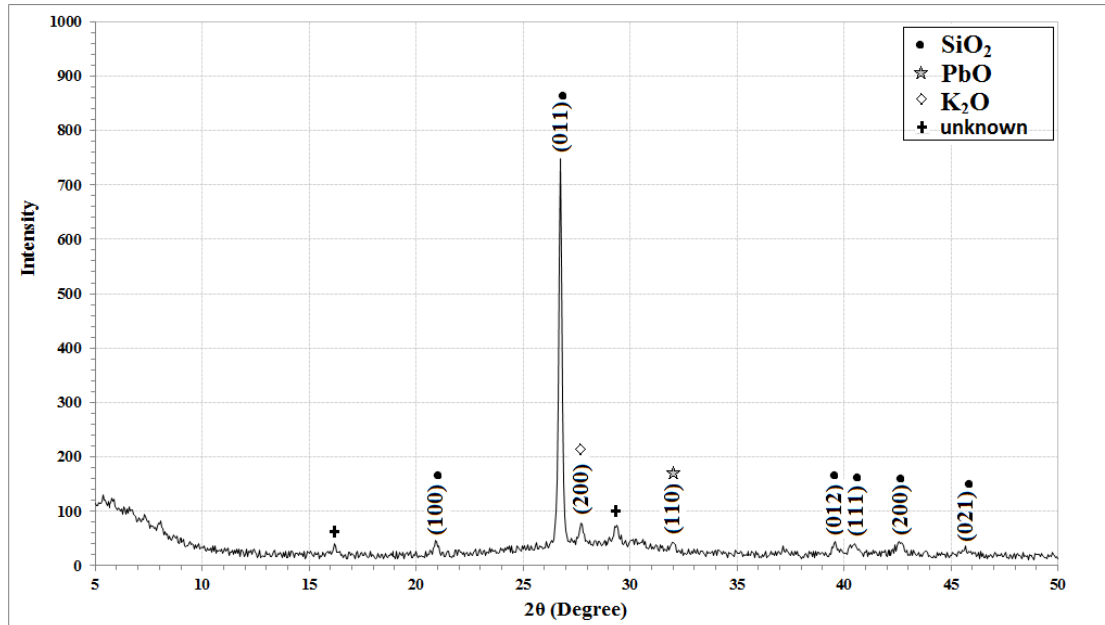


Fig. 3: X-ray diffraction analysis and measurement for sample contain 30 wt% PbO.

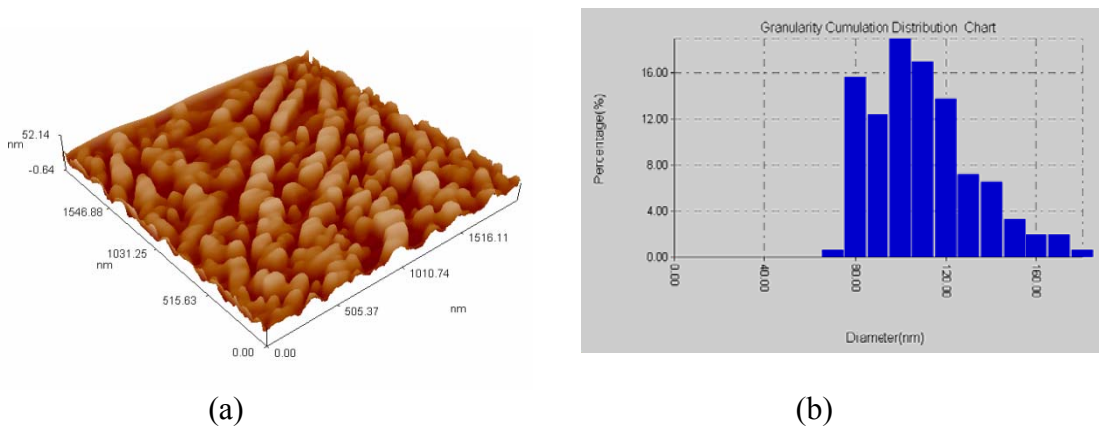
Table 2: The two theta, fill width half maximum, plane distance(Exp. &Std), grain size, apparent phases, and plan miller indices for sample contain 30 wt% PbO.

2θ (Deg.)	FWHM (Deg.)	$d_{hkl}$ Exp.(Å)	G.S (nm)	Phase	$d_{hkl}$ Std.(Å)	hkl
20.946	0.238	4.238	33.9	SiO <sub>2</sub>	4.2522	(100)
26.749	0.159	3.330	51.4	SiO <sub>2</sub>	3.3408	(011)
27.703	0.238	3.218	34.3	K <sub>2</sub> O	3.2180	(200)
31.995	0.159	2.795	52.0	PbO	2.8283	(110)
39.587	0.278	2.275	30.4	SiO <sub>2</sub>	2.2793	(012)
40.421	0.278	2.230	30.4	SiO <sub>2</sub>	2.2349	(111)
42.607	0.358	2.120	23.8	SiO <sub>2</sub>	2.1261	(200)
45.707	0.358	1.983	24.1	SiO <sub>2</sub>	1.9999	(021)

### 3. AFM analysis

The microstructure of selected sample (has 15 wt% PbO) was analysed using AFM (type scanning probe microscope CSPM) Fig. 4. The surface morphology revealed the presence of homogeneous crystal growth tend to have a certain direction Fig. 4a . This state raises attention to

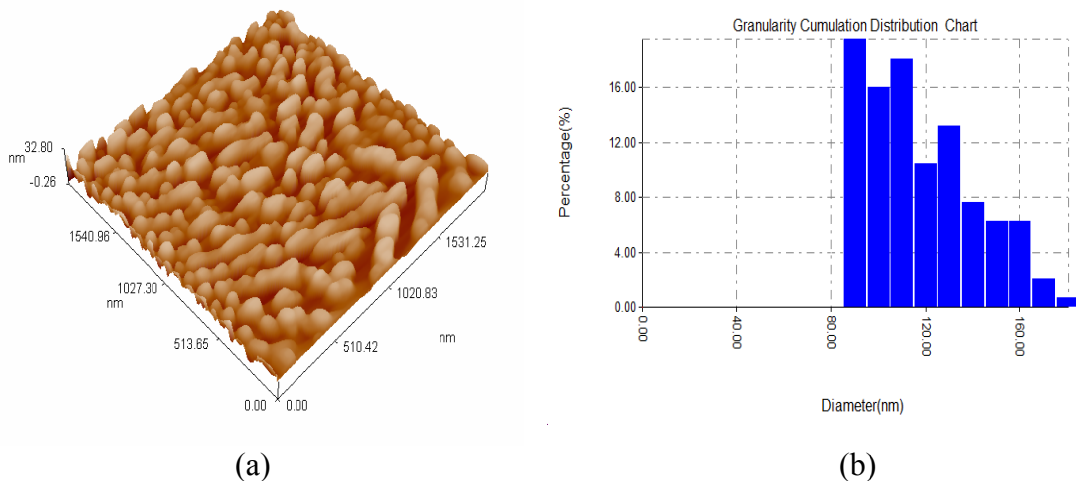
the growth tendency of specimen to a favorite direction. The important feature is, although, the method used in the manufacture of the specimen is the traditional way of glass, it was obtained a sample with an average diameter: 104.33 nm which mean a good result. The granularity normal distribution chart was shown in Fig.4b.



**Fig. 4:** The AFM analysis for prepared sample contain 15wt% PbO, (a) the 2D surface feature, (b) the granularity normal distribution chart.

Surface morphology for sample contain 30 wt% of PbO was shown in Fig.5. The surface revealed a homogeneous crystal growth tend to

have a prefer direction like zigzag Fig.5a. Average diameter: 112.49 nm, the granularity normal distribution chart was shown in Fig. 4b



**Fig.5:** The AFM analysis for prepared sample contain 30wt% PbO, (a) the 2D surface feature, (b) the granularity normal distribution chart.

#### 4. FTIR analysis

Fourier transform infrared (FTIR) technique is one of the most sought spectroscopic investigations to probe the structural units present in the glass matrix. The structure of glass not only depends on the Glass forming oxides, but also on the moodier oxides present in the glass compositions. The FTIR vibration spectra f the present glasses were recorded at room

temperature using KBr pellet technique in the wave number range  $400\text{--}4000\text{cm}^{-1}$  using SHIMADZU spectrometer which has a resolution of  $1\text{cm}^{-1}$ .

Figs.6 and 7 shows the infrared spectrum for samples contain 15 and 30 wt% PbO respectively. PbO may act as a network modifier in the same way as alkali oxide disrupting the bonds connecting neighboring  $\text{SiO}_4$

group. The ionic cross-links provided by lead ions ( $\text{Pb}^{2+}$ ) are stronger than those provided by alkali ions. On the other hand,  $\text{PbO}$  can be incorporated in to the glass as network forming  $\text{Pb-O}$  groups ( $\text{PbO}_4$  and  $\text{PbO}_3$ )[16]. The formation of  $\text{SiO}_4$  groups proceeds at the rate of two Tetrahedral oxygen. This formation of tetrahedral is reduced with increasing the content of  $\text{PbO}$  above 20% because some of the lead atoms will participate in the network as  $\text{PbO}_4$  pyramids with the  $\text{Pb}$  atom forming the apex of the pyramid[17].

The peaks corresponding to the infrared bands observed in these glasses are given in these figures. The background spectrum includes the contribution from any ambient water (these bands lies in the range from 3200 to 3640 $\text{cm}^{-1}$ , and about 1600  $\text{cm}^{-1}$ ) This band is ascribed to OH stretching of the adsorbed water, related to the bridged hydroxyl group with stretching vibrations of adsorbed water molecules or with other OH groups, and to isolated OH groups[18] and carbon dioxide doublet at 2360  $\text{cm}^{-1}$  [19].

The comparison between these figures illustrate the broadening absorption peak at 3, 450 $\text{cm}^{-1}$ . It can conclude that the increasing of  $\text{PbO}$  content to 30wt% causes an increase in intensity of this broad. This increases may be due to the moisture adsorbed during the test or its related to formation of more adsorbed structure with increasing  $\text{PbO}$  percentage, as well as the presence of  $\text{K}_2\text{O}$  which is characterize as highly absorbance material as demonstrated in XRD Fig.3.

Infrared spectrum is characterized by the presence of large absorption band between 1200 and 900 $\text{cm}^{-1}$  and have

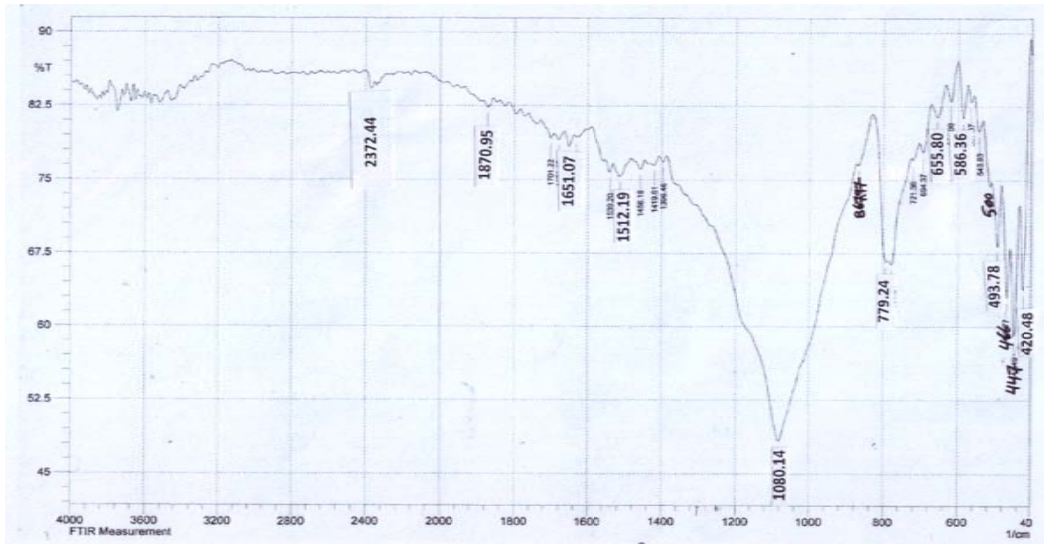
its maximum at 1080  $\text{cm}^{-1}$  which is typical to stretching vibrations of  $\text{Si-O-Si}$  bonds [20, 21]. For comparison, Verweij (1979b) observed a broad depolarized band near 1080  $\text{cm}^{-1}$  for  $\text{K}_2\text{Si}_2\text{O}_5$  and  $\text{Na}_2\text{Si}_2\text{O}_5$  glasses and Furukawa et al. (1981) observed a depolarized band near 1080  $\text{cm}^{-1}$  between silica and the disilicate composition for the Na-series, whose depolarized band maximum decreased sharply to near 1050  $\text{cm}^{-1}$  between the disilicate and metasilicate [22].

The broad bands in the range 800–1, 300  $\text{cm}^{-1}$  indicate different structural orderings of the glass network due to overlapping of stretching vibrations of various silicate units. This behavior can be influenced by quantities of  $\text{PbO}$  and  $\text{Na}_2\text{O}$  in the glass composition. The bands noticed in the range 400–500  $\text{cm}^{-1}$  were attributed to  $\text{Pb-O-Pb}$  and  $\text{Pb-O-Si}$  bonds according to previous observations [23,24].

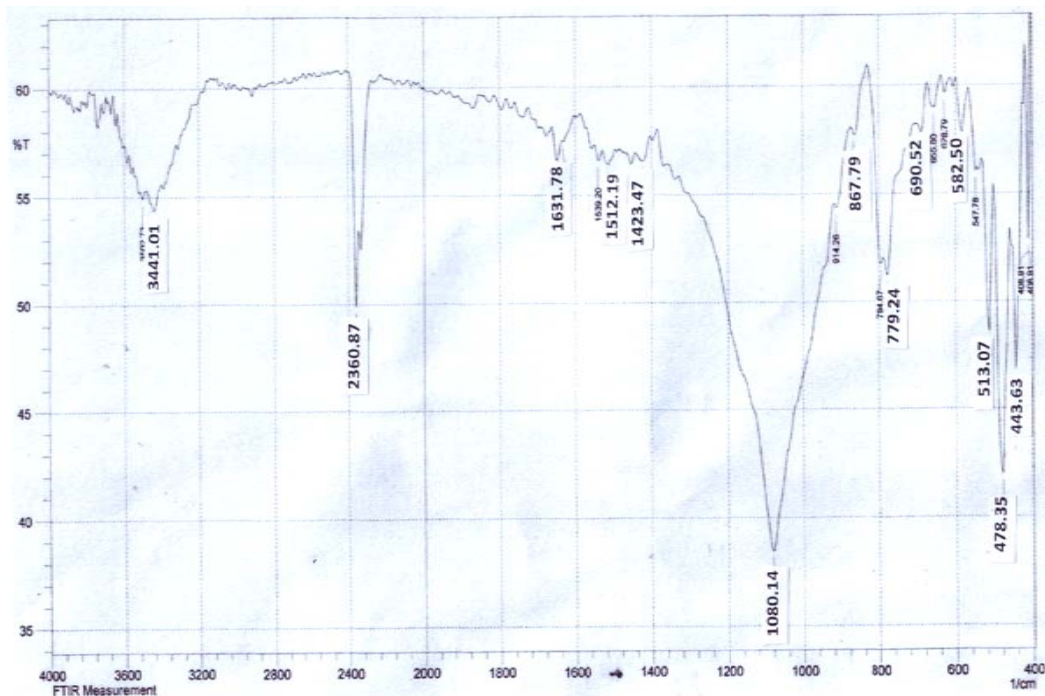
There are also absorption bands in the area of 900– 850 $\text{cm}^{-1}$  typical for  $[\text{AlO}_4]$ -tetrahedron, and the maximum at 867  $\text{cm}^{-1}$  pertinent to  $\text{Si-O-Al}$  bond. The characteristic band of the cordierite phase with absorption maximum at 779  $\text{cm}^{-1}$  pertinent to  $[\text{Si}_5\text{AlO}^{18}]$  is a peculiarity of refractory IR-spectrum[20].

weak, sharp peak which also appear polarized is observed at 600  $\text{cm}^{-1}$ . The origin of these weak peaks is controversial. It was originally attributed to structural defects in vitreous silica associated with broken  $\text{Si-O-Si}$  bonds [22].

the peak around 470  $\text{cm}^{-1}$  was related to  $\text{Pb-O}$  bond vibrations [25], and around 462  $\text{cm}^{-1}$  for  $\text{Al-O-Al}$  bending vibration [26].



*Fig. 6: FTIR for sample contain 15 wt% of PbO.*



*Fig. 7: FTIR for sample contain 30 wt% of PbO.*

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