Advances in Aeronautical Science and Engineering
ISSN: 1674-8190

Synthesis and Spectroscopic Analysis of Glass-Based Fertilizers

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ABSTRACT

Glasses in the phosphate system acting as slow release fertilizer were synthesized by melt- quenching technique. A new glass-material was prepared, which can be used as slowly soluble fertilizer for different type of plants. Glasses were melting at the temperature (800 – 950°C) with a soaking period of 1hr. which was earlier reported to be melted not below 1000^0c. Leaching study of these glasses with a maximum time period of 300 hrs. were conducted under Soxhlet distillation condition with distilled water. Fourier transform infrared (FTIR) spectra was recorded in the 400-4000 cm^{-1} range, revealed optical phonons specification for the phosphate matrix. FTIR studies show absorptions at 760, 879, 920, 1087, 1110, ~ 2193-2870 cm^{-1}, and ~3440-3500cm^{-1}. ^{57}Fe Mossbauer spectroscopy studies were presented. Mössbauer studies were done in order to analyze their structure. Amorphous nature of glass was confirmed by XRD (X-ray diffraction).The morphology of glass materials was analyzed by Scanning Electron Microscopy. SEM of some selected glasses were presented. X-ray Fluorescence (XRF) technique is used for elemental analysis and chemical analysis. The effect of different modifier ions like Na^+, Fe^{3+}, Mg^{2+}, Ca^{2+}, and K^+ in the basic phosphate networks on melting's and time of melting has been found to be evident. The model structure of glasses has been considered taking the role of some glass formers/ modifiers which ultimately has an effect on the chemical durability of these glasses. For GF (glass fertilizer) minimum solubility was measured for the sample containing Iron Oxide (Fe_2O_3) and maximum solubility for base sample and from GF (glass fertilizer) maximum solubility appeared for the sample with molybdenum oxide. The results of the experiments reported here demonstrate that is possible to adjust the release of phosphate from the fertilizer to phosphate demand of the plant.

***Keywords**: Phosphate glass, Glass Fertilizers, Leaching, Glass formers, intermediates and modifiers, SEM, FTIR, Soaking period, Mössbauer, XRD.*

I. INTRODUCTION

We are passing through an environmental crisis period. The protection of environment is very necessary in an industrial world. Using of fertilizers in agriculture can be very useful for food production, but on the other side it may be dangerous for environment. Hence only necessary amount of fertilizers can be used for successful vegetation. It means that we must use fertilizers, which are dissolved quickly as is nutrient requirement of plants. In this case it is not a contamination hazard for environment. In the year 1950 fertilizers comprised only a small percent of the nutrients needed for grain production, most of the supply being provided by the "natural fertility" of the soil and added manure. By 2020, more than 70% of the grain yield will have to depend on fertilizers. The world population is expected to increase by about 2.3 billion by 2020 and double by the year 2050. This situation will create a great problem: It will be lacking of food and water. In 2030 the world crop surface will increase only 7% respect to nowadays and there will be necessary to increase the use of fertilizers and irrigation water. This situation will also create a new problem: It will be an increase of soil and water pollution. So the world average cultivable land per capita (ha) gradually decreases in every year which is shown in Fig.1. This trend will require that crop production per unit of land continue to increases. The revolution which has resulted in a phenomenal increases in crop output per land and remarkably down the dimensions of food crisis; has its roots in two main sources –the evolution of innumerable new varieties of crop with high yield potentials and the ready availability of fertilizers which form the life line for the meeting their increased nutritional demands i.e. these yields increases will in turn require greater nutrient inputs [1].

Figure 1: Globally, arable land per capita is diminishing as population increases: while arable land remains constant, improved yield is required to meet the growing world food demand; [From: Phosphate Newsletter 23(2005)], [1].

The fertilizer elements are those which provided into three categories viz, major elements, i.e.; nitrogen(N), phosphorus(P), potassium(K);secondary elements i.e.; Ca, Mg and S and micronutrient elements, i.e., B, Co, Cu, Fe, Mn, Mo and Zn. With continuous application of sulfur free inorganic fertilizer and use of high yield variety seeds significant sulfur deficiency is observed. At recent Sulfur is accepted as the fourth major nutrient element that is essential for plant growth. High content phosphorus, potassium and sulfur glass capable of slow release of phosphorus, potassium and sulfur which particularly relates to the applications of the glass as fertilizer for agricultural applications and for any other plant [2].

Fertilizer is simply a material added to soils or directly to plant tissues that contains nutrients essential to the growth and health of the plant or crop. Generally, this indicates fertilizer remaining N, P, and K. These basic elements are commonly in the form of chemical compounds that can be converted by the plant to access the needed elements [1]. Use of fertilizer in agriculture is very urgent to the plants or crops but at the same time it may be very dangerous for the environment. It may cause soil deterioration, greenhouse gas emissions, and water contamination. Slow-releasing fertilizers have long been recognized as the best solution to the various environmental problems caused by traditional water-soluble fertilizers [4,5]. With slow-release fertilizers, dosage requirements are lowered, fertilizer use efficiency is improved and environmental pollution problems are practically eliminated. Glass fertilizers (GF) are a new type of advanced and-release fertilizer made from glass matrixes containing the most useful microelements (K, P, Mg, S, Ca) for plants, and also incorporate some microelements (B, Fe, Mo, Cu, Zn, Mn) required for the correct growth and development of crops or plants[1,5,6].

The main advantages of new type of fertilizers against conventional fertilizers are increased grade of assimilation by plants, do not release insoluble compounds in soil, and remain in the soil during the entire period of plant development and do not pollute the phreatic water [7-10]. At the same time, these fertilizers have special peculiarities: controlled solubility in the time for many vegetable cycles, possibility to incorporate in the vitreous matrix of many useful microelements [11-12] do not contain toxic compounds and do not release insoluble residues [3].

The use of glass fertilizers offers a lot of advantages as a result of:

- Low or controlled solubility it avoid underground water pollution; the soil pH can be regulated by the pH of the glass matrix
- None release acid anions (Cl^-, SO_4^{2-}) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed.
- In a single type of fertilizer it can be embedded into almost all useful elements for plants.
- The controlled rate of solubility in water can be adjusted easily by changing the composition of glass matrix [1].
- A single dose of application of the glass fertilizer can supply the plant nutrients for very long time.

The main aim of this paper is to present the structural study and future development of glass fertilizer samples. The structure of the samples has been studied through XRD, SEM, XRF, Mössbauer and FTIR spectra.

II. EXPERIMENTAL DETAILS

. Materials and oxide composition

The glass sample ID, GF contains the major compounds necessary for crops and sample contain the same base oxides together with micro-elements oxides necessary for plant growth, 5 wt. % for iron (Fe), 5 wt. % for Zinc (Zn),5 wt. % for molybdenum(Mo) and 10 wt. % for boron(B) respectively over 100 %.Table1 presents the oxide composition of GF in weight%. The glass ID,GF5 contains four microelements together such as 15 wt.% of boron,10 wt.% of iron,8 wt.% of zinc and 6 wt.% of molybdenum respectively.

The glass batches used in the present work were prepared from the ingredients like Ammonium dihydrogen orthophosphate [$(NH_4)H_2PO_4$, AR grade, HI Media laboratory, Mumbai],Magnesium oxide (MgO, AR grade, Merck Life Science Private Ltd. Mumbai), Potassium dihydrogen phosphate (KH_2PO_4,AR grade, Merck Life science Private Ltd, Mumbai) and Calcium oxide (CaO, AR grade, Merck Life science Private Ltd. Kolkata) have been used as raw materials for macro-elements. Borax ($Na_2B_4O_7$, AR grade, RANKEM, New Delhi) ferric oxide (Fe_2O_3, AR grade, Merck Life science Private Ltd. Mumbai) Zinc oxide (ZnO, AR grade, Merck Life Science Private Ltd, Kolkata) and molybdenum trioxide (MoO_3, AR grade, E. Merck, Germany) were added in order to supply the micro-elements. Five glass compositions were prepared using the following precursor which has been shown in Table 1.

Preparation of glass batches and melting operation

Table 1: Different oxide composition (in weight %) of the prepared glasses

Glass ID	Composition (Wt. %)								
	$(NH_4)H_2PO_4$	MgO	KH_2PO_4	CaO	$Na_2B_4O_7$	Fe_2O_3	ZnO	MoO_3	Total
GF1	40	16	29	5	10	-	-	-	100
GF2	40	20	30	5	-	5	-	-	100
GF3	40	20	30	5	-	-	5		100
GF4	40	20	30	5	-	-		5	100
GF5	49	12	-	-	15	10	08	06	100

The raw materials used in the preparation of glass batches were accurately weighted by means of a four decimal electronic balance SATORIOUS (model BSA224SCW).All the ingredients in dry condition were taken in anagate mortars and mixed homogenously by a pestle for 1 hour. Acetone was introduced over the mixture of ingredients under continuous homogenization in chemical for 1 hour and then glass mixtures were dried. Both dry and weight mixes were done. The same process was performed for three times. Glasses were melted in phosphate system. Glass batches given in Table 1are synthesized in acetone medium. The mixture of raw materials prepared by the method describe above, were dried and taken in high alumina crucibles and fired in a muffle furnace fitted with programmer in the range 800-950^{0}c for soaking periods 1 hour under ambient condition. The melting duration was between four to six hours. In melting operation, the temperature and time of melting are the principle factors are to be monitored. The glass structure was confirmed from the XRD study. The melting operation was done in a programmable muffle furnace with window and temperature controller. The temperature and time of melting was varied. Table 2 shows the melting and time for different glasses.

Table 2: Melting point (ºC) and time of Soaking period for different glass compositions

Glass ID	M.P.(±2ºC)	Soaking period (Hour)
GF1	900	1
GF2	950	1

GF3	900	1
GF4	900	1
GF5	900	1

Grinding and sieving of glass batches

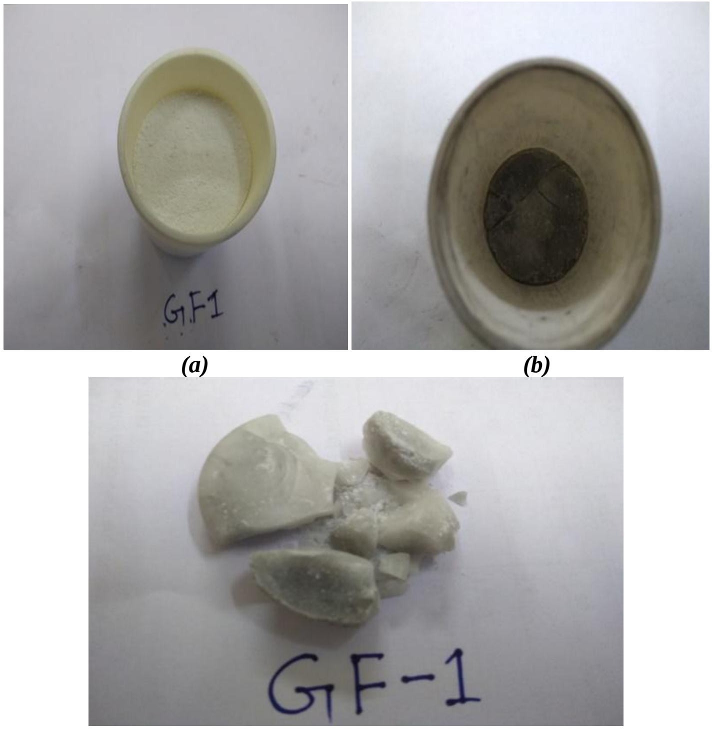
The glass to be analyzed is grinded in an agate mortar, then screened through two sieves with different mesh of 330-425 B.S. size. The fraction to be used is the one between the two sieves. The sieve mesh sizes are closer to each other, so the size fraction between them will be less dispersed and average size fraction will be constant from sample to sample. The procedure is repeated for all glass batches.

(a) *(b)*

(c) *(d)*

(e)

Figure 2: Picture of some powdered glass fertilizer samples (a) GF1 (b) GF2 (c) GF3 (d) GF4 (e) GF5



(a) *(b)*

(c)

Figure 3: Pictures of glass batch (Glass fertilizer) (a) before melting and (b, c) after melting.

Characterization of glass

XRD studies

The X-ray diffraction (XRD) experiments of glass were performed with a Bruker advanced D8 discovery X-ray Diffractometer for 2θ values from 10^o to 90^o using CuKα target at wavelength of λ =1.5406 A^0. X-ray diffraction (XRD) study of the glass sample was made to confirm its amorphous nature.

Mössbauer spectroscopy (MB)

Mössbauer study of the glass sample was made to analyze their structure. Mössbauer spectroscopic (MB) measurements of the glass samples were conducted in a transmission mode with the use of RENON MsAa-3 spectrometer equipped with the LND Kr-filled proportional detector and He-Ne laser based interferometer used to calibrate a velocity scale. A commercial 57Co (Rh) source kept at room temperature was applied for 14.41-keV resonant transition in ^{57}Fe. All the isomer shift data presented in this paper are relative to a-Fe. The Mössbauer absorbers were prepared by mixing ~80 mg of the powdered sample with epoxy resin. Spectra were recorded at273 K, and the isothermal scans were collected with 1023 points per each spectrum.

FTIR studies of the glasses

For Fourier Transform Infrared spectrometry (FTIR) measurements were made to identify the fundamental stretching vibrations. FTIR spectrum of the glasses GF1-GF4, was recorded by a Fourier Transform Infrared(FTIR) spectrophotometer (model Shimadzu IR prestige-21), with a resolution in the wave number range 400−5000 cm^{-1}at a resolution 4 cm^{-1} using 45 scans, using KBr pellet.

XRF (X-ray Fluorescence) analysis

The element determinations were performed by X-ray Fluorescence spectrometer .The instrument used for analysis of the glass was Bruker (model AXS ARTAX 800) micro-XRF spectrometer. The instrument is tripod-mounted and the X-ray tube and detector are mounted on an extended “arm” that allow all portions of the object to be accessed with no disruption to the object. The X-ray tube has ca. 80 μm spatial resolution. The X-ray detector is a silicon drift detector with a 10 mm^2 active area and energy resolution of ca. 142 eV for the Mn Kα at 100 kcps. Each area was analyzed at50 kV and 600μA for a life-time count of 30 sec.

Morphology studies (SEM)

Scanning electron microscopy (SEM) of some glasses was performed on a JSM6510 microscope (JEOL) (Thermo Scientific NSS coupled or linked) at a voltage of 20kv. Samples were previously fixed onto carbon stubs and coated with thin layer of gold in an ionization chamber (BALTEC Med. 020). SEM imaging was carried out using the secondary electron mode. SEM micrography was done to study the morphology of the glass product.

III. RESULTS AND DISCUSSION

XRD analysis

The structure and crystalline of glass fertilizer samples were studies. XRD pattern of the samples were recorded in the range of 20º ≤θ ≤ 80º. This pattern indicates that glass fertilizer samples are amorphous in nature and have non-crystalline structure. The X-ray diffraction of the glass fertilizer is shown in Figure 4.

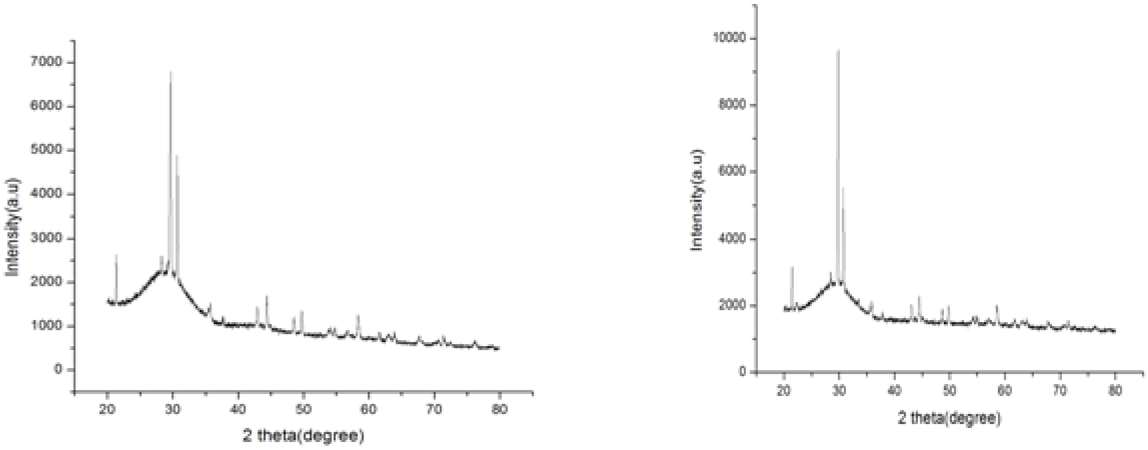


Figure 4: XRD Spectrum of glass fertilizer samples (a) GF1 (b) GF2.

Mössbauer study

Ferric oxide has been used for incorporating iron ions into a structure. Nevertheless, not only Fe^{3+} but also Fe^{2+} ions usually exist in iron phosphate glass, due to $Fe^{3+} \rightleftharpoons Fe^{2+}$ equilibrium [13]. According to [13-14], it can be predicted that ferrous ions content varies from 10 to even 100% and it is strongly influenced by the synthesis conditions. It is also believed that tetrahedrally coordinated Fe^{3+} ions may act as a glass network former. Mössbauer spectroscopy is an effective tool which allows examining changes of ^{57}Fe nucleus energy levels that can be affected by even small deviations in local iron ions surroundings.

The Mössbauer spectrum of the glass (GF2) containing 5% Fe_2O_3 shows a clear doublet with isomer shift 0.37mm/sec.with a quadrupole splitting (QS) 0.76mm/sec. Such a value of isomer shift designate Fe^{2+} ions as is observed in Mössbauer spectrum. As the glass batch contains Fe^{3+} ions during melting process it undergoes a reduction of ferric ions (Fe^{3+}). Hence a reducing environment around the iron nucleus is quite obvious. The Mössbauer spectrum of the glass fertilizer is shown in figure 5.A doublet in MB spectrum signifies an asymmetric environment around the particular nucleus viz, nitroprusside (doublet) are in comparison to ferrocyanide (singlet).

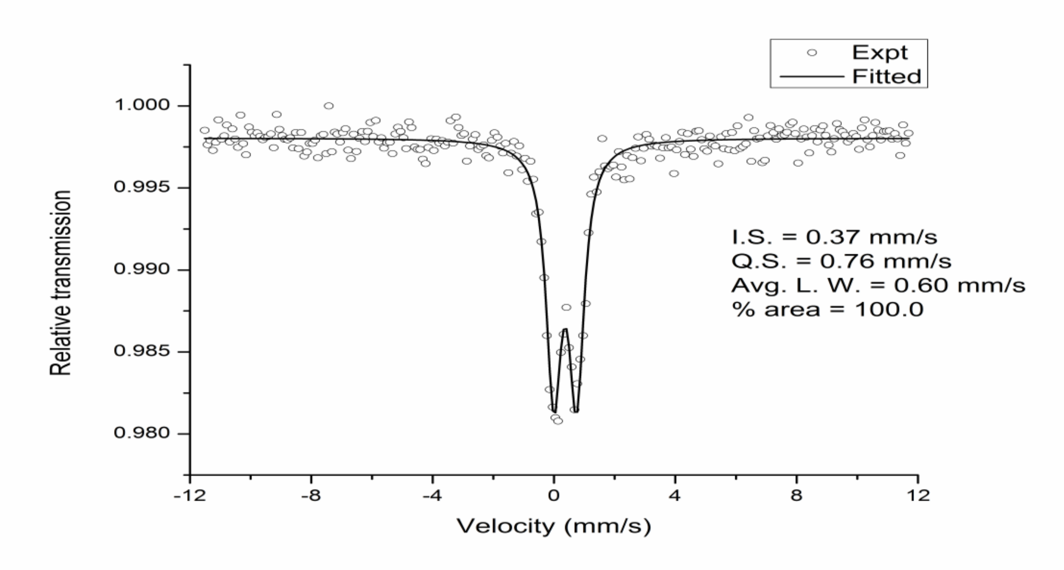


Figure 5: Mössbauer spectrum of glass fertilizer sample (a) GF2

FTIR analysis

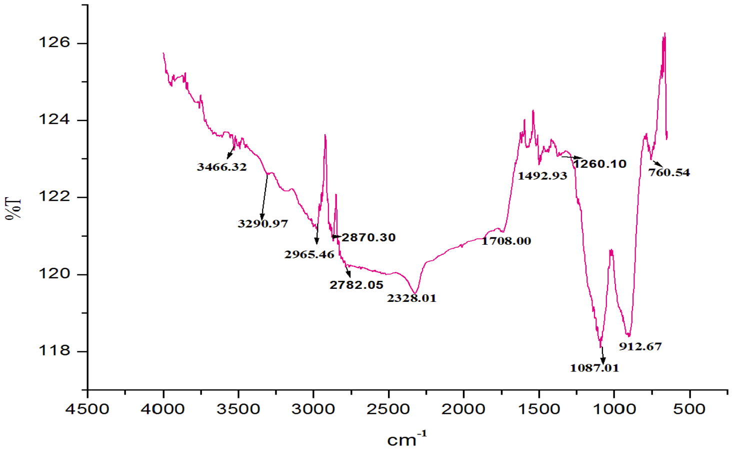


Figure 6: FTIR spectra of GF1

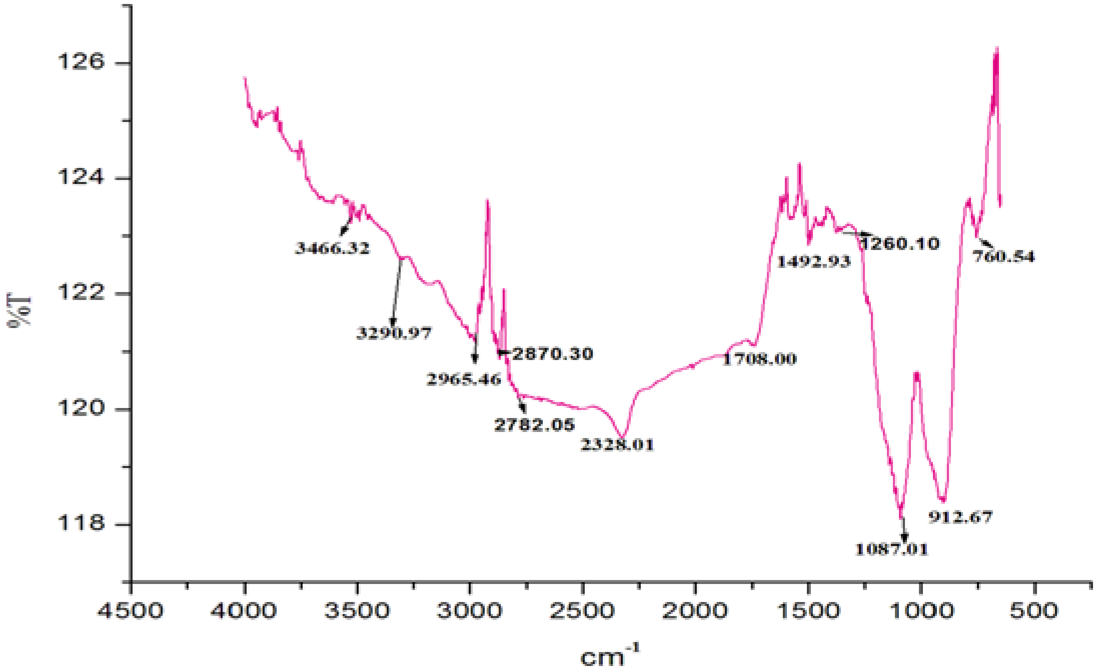


Figure7. FTIR spectra of GF2

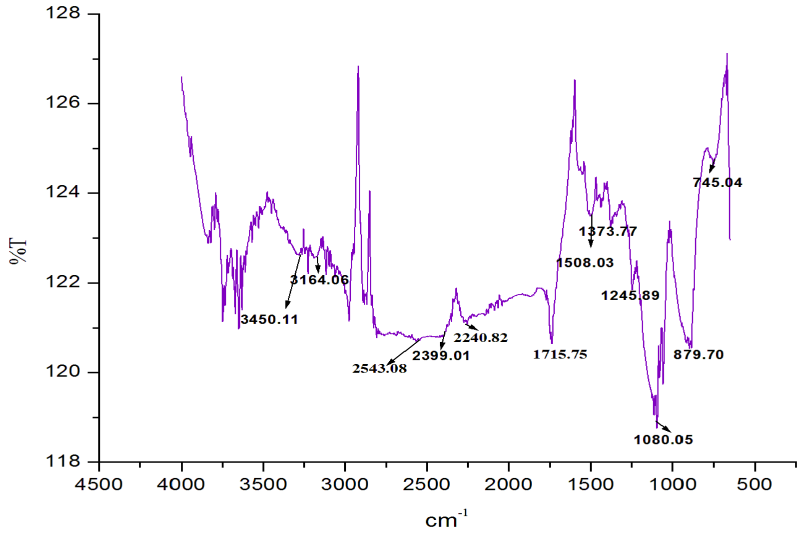


Figure 8: FTIR spectra of GF3

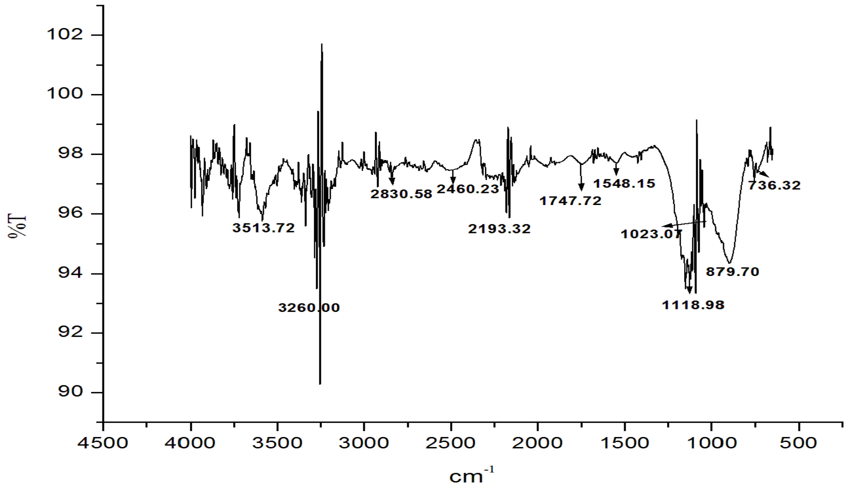


Figure 9: FTIR spectra of GF4

Figure 6-8 and Figure 9 shows the FTIR spectrum of glass fertilizer samples of different composition such as GF1, GF2, GF3 and GF4 respectively. In the IR spectra consists many bands for glass samples observed at ~720-3500 cm^{-1}.The IR bands at 736,745,752 and 760 cm^{-1} are attributed to the symmetric stretching of P-O-P group and the absorption band at ~879,912 and ~920 cm^{-1}corresponds to asymmetric stretching vibration of P-O-P attached with linear metaphosphate chain[15,16,17].The IR stretch at 1039,1080,1087 and 1110 cm^{-1} are related to asymmetric stretching between phosphorus and nonbridging oxygen, and an indication for the formation of the terminal phosphate groups PO_3^{2-} while 1245 and 1260 cm^{-1} are related to PO_2 asymmetric stretching vibration[17,18].The peak at 1665 cm^{-1} is related to the mode of vibration of OH bending. The IR stretch in the range 2193-2870 cm^{-1} is attributed to P-OH stretching[19] and the range 3440-3500 cm^{-1} is related to the OH stretching(phosphate glass absorbs moisture from air)[20].

X-Ray Fluorescence (XRF) Technique (Elemental analysis)

X-ray fluorescence (XRF) spectrometry, a widely used and versatile technique, is well suited for *in situ*, non-invasive elemental analysis. X-ray fluorescence is created from a material that has been excited by bombarding with high-energy X-rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass and for research in geochemistry, forensic science and archaeology. Table3 and Figure 10 represent the analysis of the phosphate samples using the XRF technique. The data showed major elements Ca, Fe, Zn, Zr, Nb, and Cd (Qualitative Analysis).

Table 3: Results of analysis of the glass fertilizer samples using XRF-technique (Quantitative Analysis)

Element	Line	Conc./	Sigma/	RSD/ %	LLD/	Net area	Backgr.	Chi
K	K12	0.00	0.00		0.00	7862	687	1.29
Ca	K12	0.00	0.00		0.00	4269	597	0.89
Fe	K12	0.00	0.00		0.00	90951	486	27.95
Zn	K12	0.00	0.00		0.00	435	292	1.77
Zr	K12	0.00	0.00		0.00	5193	7309	46.98
Nb	K12	0.00	0.00		0.00	41071	8934	448.31
Nb	L1	0.00	0.00		0.00	446	642	40.99
Cd	K12	0.00	0.00		0.00	7036	4555	1.37
Cd	L1	0.00	0.00		0.00	107	645	1.25

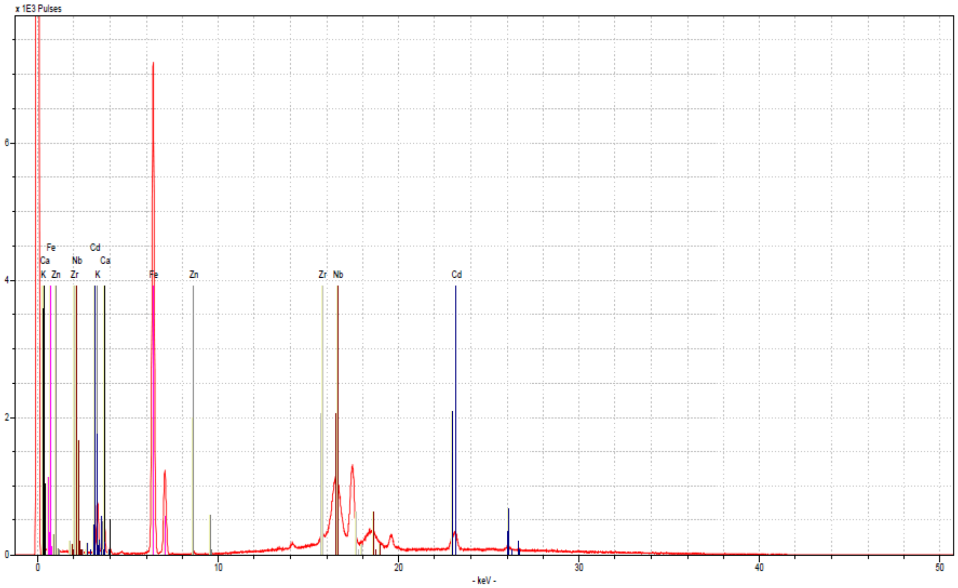


Figure 10: XRF spectra of glass fertilizer sample (a) GF2

SEM study

SEM images of some glass fertilizer sample were performed which has been shown in Figure 11. The picture indicate homogeneous nature of that the glasses formed.

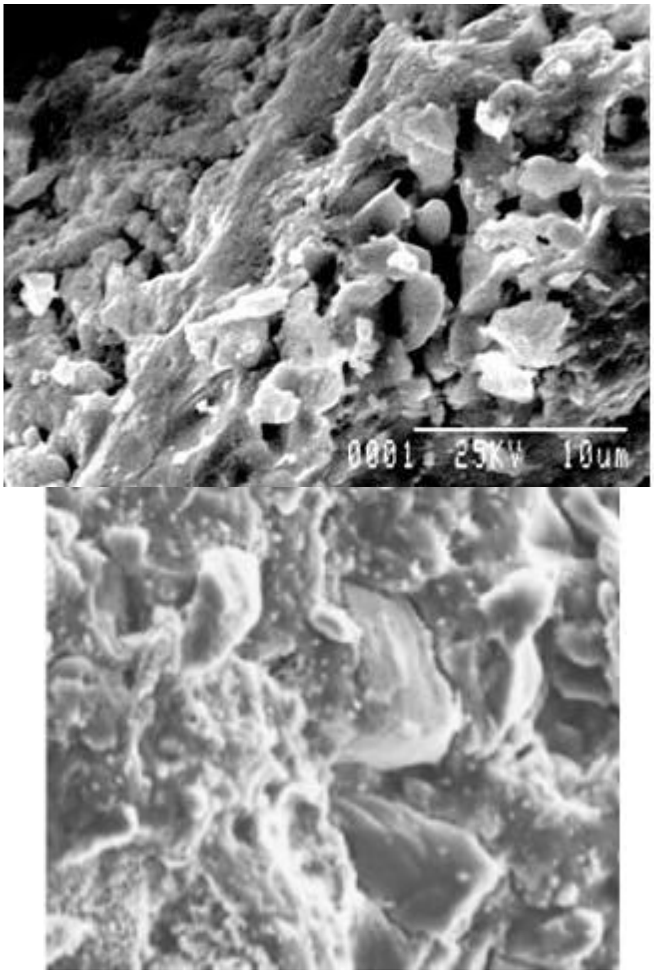


Figure 11: SEM structure of glass fertilizer samples

IV. CONCLUSION

This study revealed the preparation of glass fertilizer by melt. The structure of the samples has been studied through XRD, Mössbauer, XRF, FTIR spectra and SEM. The XRF analysis represents the major element in glass fertilizer samples. XRD study indicates that glass fertilizer samples are amorphous in nature and have non-crystalline structure. SEM images of some glass which indicate homogeneous nature of that the glasses formed. The study of the structure of glass fertilizer, FTIR spectra can be used for the investigation and other properties to development of glass fertilizer. Mössbauer spectroscopic performed in order to analyze their structure. Furthermore a structural study is required for the future development of glass fertilizer.

V. ACKNOWLEDGEMENTS

The authors thanks to Dr. J. Mukerji, retired scientist, $^{\text{CSIR}}$CGCRI, Jadavpur, Kolkata, for his constant encouragement and valuable suggestions. We acknowledged the service rendered by Dr. Dipankar Das, UGC-DAE Consortium for Scientific Research Kolkata Centre in performing the Mössbauer analyses.

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