Experimental Investigation of New Candidate Glass from Municipal Waste as Radioactive Waste Immobilizer

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Abstract: Up to 90 weight % of municipal waste were successfully vetrified into borosilicate and sodium borate glasses at ~1200^{o}C. The aim of preparing these glasses is to be used as a radioactive waste immobilizer, so the most important factor affecting such glass is its durability either in acidic or alkaline medium. Experimental durability data of the prepared glass immersed in ground water together with γ- irradiation was found to be affected according to the different irradiation doses. The damage occurred was correlated to their composition and irradiation dose. The results showed that glass containing higher amount of municipal waste possess high durability.

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1. Introduction

The international atomic energy agency (IAEA) defines immobilization as a conversion of a waste into a waste form by solidification, embedding or encapsulation. This facilitates handling, transportation, storage and disposal of radioactive wastes. Immobilization of HLW is achieved by chemical incorporation into the structure of a suitable matrix (typically glass or ceramics) so the HLW are captured and unable to escape [1].

Glass was one of the most successfully used materials as a host for HLW by melting virtification technology [2].

Vitrification also currently used for immobilization low and intermediate radioactive waste [3].

Vitrification involves melting of waste material of waste materials with glass forming additives so that the final vitreous product incorporates the waste contaminate in its macro and microstructure. Some of the hazardous waste constitutes are immobilized by direct incorporation into the glass structure. For example Si, B and P are included into the glass structure on cooling, while others such as (S, K, Na, Li, Ca, Pb and Mg) are confined as network modifiers.

Another part of radioactive wastes are immobilized by physical encapsulation, this is applied to elements and compounds with reduced solubility in the glass melt (they can not fit in the glass structure either as network formers or modifiers). As an example of this category of radioactive wastes, sulphates, chlorides, molybdates and noble metals such as Rh, Pd, also ref ractory oxides as PuO_2 [4].

The most common glasses used are borosilicate and phosphates because they have low melting temperature, can incorporate large number of elements and having the potential of high durable waste forms. Borosilicate glasses have shown indication that they have a unique blend of processing and product characteristics, which make them nearly ideal for this application. They shown to be as durable as basalt, have the ability to dissolve the full spectrum of nuclear wastes, have a respectively low melting temperature this make the corrosion rate of some materials (e.g. high chromium refractories) decrease exponentially as temperature decrease. Also is making it possible to allow the use of materials with high corrosion resistant but unstable at high temperatures [5].

Using glass as a safe and long term hosting matrix for hazardous wastes and for the immobilization of heavy metals and nuclear wastes become an attractive method [3], the most known glasses used as nuclear waste immobilizer are Pamela, SON68, and WAK [4]. There compositions are given in table 1, it can be noticed that all of them are borosilicate glass containing different amounts of Aluminum, Sodium and Calcium oxides. One of the most important factor affecting the use of glass as a nuclear immobilizer is its long term behavior, which is mainly determined by their resistance to aqueous corrosion. Corrosion of nuclear waste glass is a complex process which depends on many parameters; these strongly depend on the glass composition. Although glass composition is the most affecting factor in the glass durability but also ground water chemical composition, pH, time and temperature all these factors are affecting media, also some insoluble elements are able to form a passivating surface layer [5]. The other important parameter controlling the use of glass as an immobilizing nuclear waste is the effect of irradiation in long term stability of glass constituents [6]. The best approach is to determine the basic parameters governing the corrosion, so that a good evaluation can be made on the performance of the nominated glass.

The leaching processes of glass in water usually occur in two stages. At the first stage of corrosion is ion exchange which controls the initial cation release. The ion exchange inter diffusion of H^+ or H_3O^+ rather than diffusion of modifier [M^+] controls the kinetics. The ion exchange is ionic selective method, while hydrolysis of the glass network occurs only in the later stage and leads to glass congruent release of ions with time [7].

The basic mechanism for corroding silicate glass in water and the release of alkaline ions in solution is diffusion controlled ion exchange according to the following reaction [8]:

$$\equiv Si\text{-}O\text{-}M_{glass} + H_2O \rightarrow \equiv Si\text{-}O\text{-}H_{glass} + M\text{-}OH \quad (1)$$

Hydrolysis causing a release of the glass network, and leads to liberate the movement of glass constituents into water.

$$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \rightarrow 2 \equiv Si\text{-}OH \quad (2)$$

$$\equiv Si\text{-}O\text{-}Si\equiv + OH^- \rightarrow \equiv SiO^- + \equiv Si\text{-}OH \quad (3)$$

The hydrolysis reaction is not involving silica only but it may involve other network forming elements such as boron or aluminum.

The probable influence of irradiation in the glass corrosion stability is important for glass prepared for nuclear waste form. It is known that β and γ radiation are emitted in the nuclear waste glasses during the first hundreds of years [9]. The NBO hole centers are formed by radiation chemical reaction:

$$\equiv Si\text{-}O\text{-}M)_{glass} + \gamma \text{ irradiation} \rightarrow \equiv Si\text{-}O\bullet + M^+ \quad (4)$$

It is assumed that the NBO hole centers resulting from irradiation are first trapped at ≡Si-O-M site and then the alkali ions are free to diffuse away to a site of a trapped electron to stabilize its charge. Mobilization of alkalis in irradiated glass has been confirmed [10]. This means that the association with NBO limits the local motion of alkali; whereas the absence of NBO allows the alkali ion to undergo long range migration through the glass structure [11].

The main result of gamma irradiation in glass is the formation of point defects. For silicate glasses there are two types of point defects, oxygen deficiency and oxygen-excess defects [12]. In alkali silicate glasses, the most common point defect is the oxygen-excess centers, which are found in two types one of them is non bridging hole centers (NBO) and the other involves two NBOs on the same silicon [9]. The effect of radiation on borosilicate is more sophisticated than that of vitreous silica, possibly because of the two phase nature of many of borosilicate glass structure.

Thus we have planned to prepare glass containing large amount of municipal solid waste in its composition (70 – 90%) with the addition of some glass former oxides and examined the most important factors affecting the glass candidate to be used for the immobilization of nuclear waste such as effect of irradiation on durability, hardness, density and the pH of the solution, which are the main considerations of the produced glass.

2. Experimental procedure:

2.1. Glass preparation:

The composition of municipal waste after being burned at 700°C for five hours is shown in table 2. After being thoroughly mixed, the weighed powdered batches (table 3) were melted in platinum crucibles in an electric furnace at 1300°C ± 50°C for about 2 hours. The homogeneity of the melt was achieved by swirling of the crucibles containing melt several times at about 30 mints intervals and to make sure that the melt become free from bubbles. The glass melt was poured in stainless steel hot mold with dimensions of 1x1x0.2 cm, samples were immediately annealed at 500°C for two hours and left in the annealing furnace over night with a cooling rate of 25 ± 2°C/h to room temperature. The compositions of the prepared glasses were analyzed using dispersive X-ray analyzer as shown in table 4.

2.2. Corrosion procedure

The leaching experiments were carried out using cleaned glass slabs. Each sample was placed in 150 ml either acidic solution of 0.5N HCl or alkaline solution of 0.5 NaOH. The ratio of glass surface area to leachant volume (S/V) is 1.87m^{-1} ± 0.1, and the leaching was carried out at room temperature 25 ± 5°C. Glass samples were placed in a 200 ml polyethylene BD Falcon™ Conical Tube with Flip Top Cap, which allows the leaching solution (150 ml) to completely cover the whole glass surfaces of the specimen, and then the tube is tightly closed.

The weight loss was calculated by weighing the glass samples before and after being immersed in the leaching solution and irradiated. The glass samples were accurately weighed three times to minimize the error to be less than 0. 01%.

2.3. Irradiation procedure

The irradiation source is a ^{60}Co cell (2000 Ci), with a dose rate of 1.182 Gy/sec. The glass samples were placed in a certain place inside the cell to have the same irradiation dose.

2.4. Scanning electron microscope (SEM)

Scanning electron microscope is utilized to study the surface morphology of the specimen at high magnifications by means of high energetic electrons that scans the specimen surface and high-resolution image is screen on T.V monitor that shows the surface shape.

3. Results:

3.1. Glass corrosion

Figure 1 shows the effect immersing glass samples in 0.5N HCl for different intervals of time verses the weight loss, the results show that glass G2 is more durable than G1, where the amount corrosion represented by weight loss % . The results also showed that the rate of corrosion for both glasses still increase after three days of immersion.

Figure 2 shows that the amount of weight loss where is almost negligible when the glass samples are immersed in an alkaline solution of 0.5N NaOH except for the first day of immersing glass G1.

3.2. Effect of irradiation

Figure 3 represents the effect of irradiation on the glass corrosion where glass samples were immersed in 0.5N HCl after being irradiated with a dose of 100kGy. The results showed that when the glass samples are exposed to gamma irradiation the amount of corrosion decreased, while glass G2 still more durable than G1.

3.2. Scanning electron micrographs:

Figures 4 and 5 show the image of the scanning electron microscope of G1 and G2 before and after being leached at different irradiation doses. The images showed small isolated pits appeared at the first irradiation dose followed by larger pits appeared with dark center, as irradiation dose increased it appeared as if the glass surface covered by a corrosion crust.

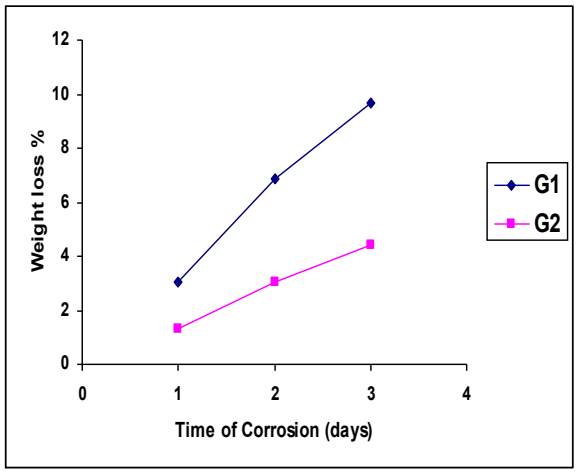

Figure (1) Weight loss % of nuclear waste glass (G1) & (G2) immersed in 0.5 N HCl.

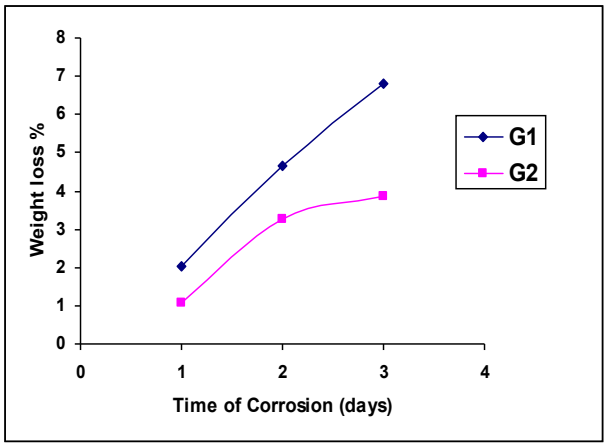

Figure (2) weight loss % of nuclear waste glass (G1) & (G2) immersed in 0.5 N HCl after gamma irradiation with 100 kGy.

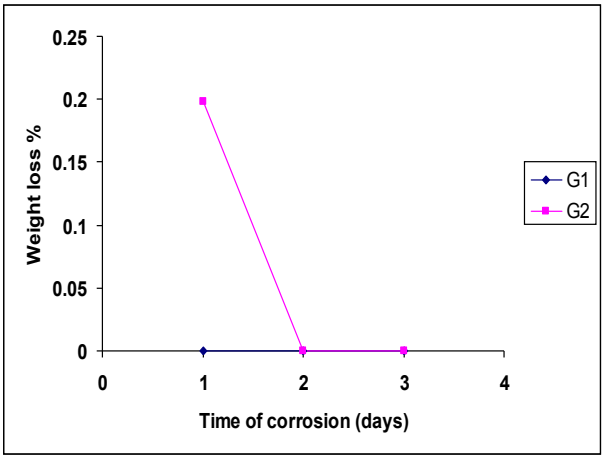

Figure (3) Weight loss % of nuclear waste glass (G1) & (G2) immersed in 0.5 N (NaOH).

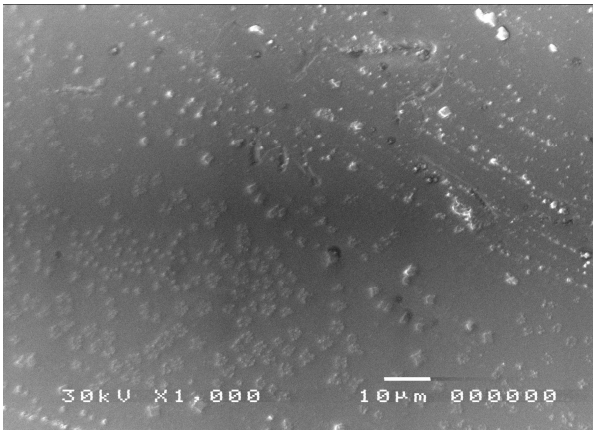

Figure (4) SEM micrograph of G1 before corrosion.

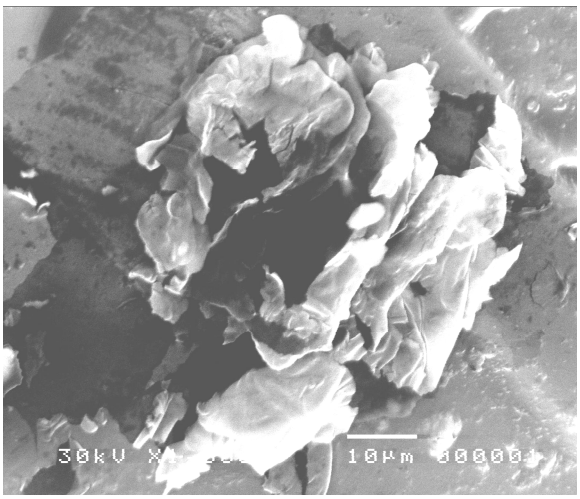

Figure (5) SEM micrograph of G1 after corrosion and irradiation with (10 kGy).

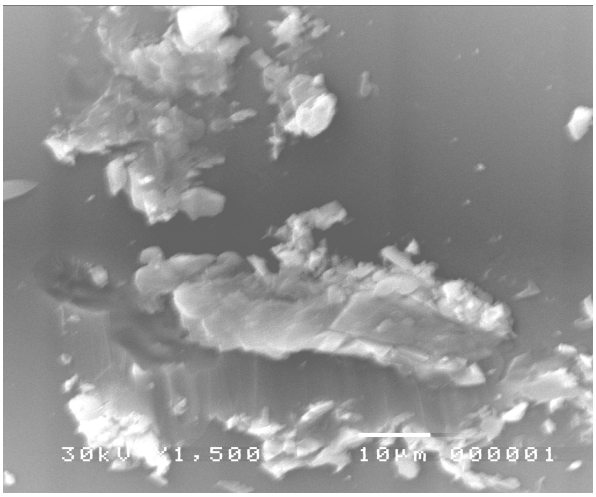

Figure (6) SEM micrograph of G1 after corrosion and irradiation with (100 KGy).

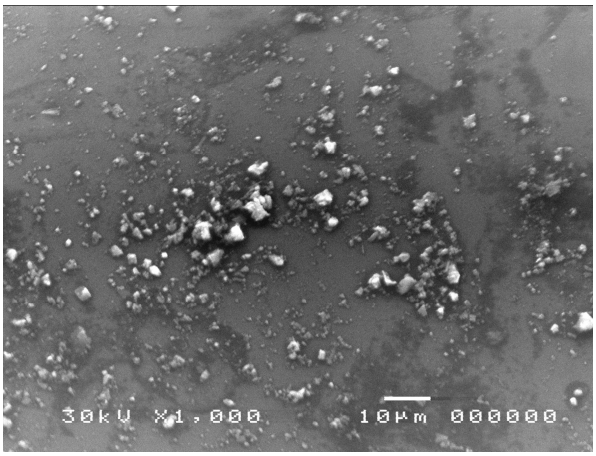

Figure (7) SEM micrograph of G2 before corrosion

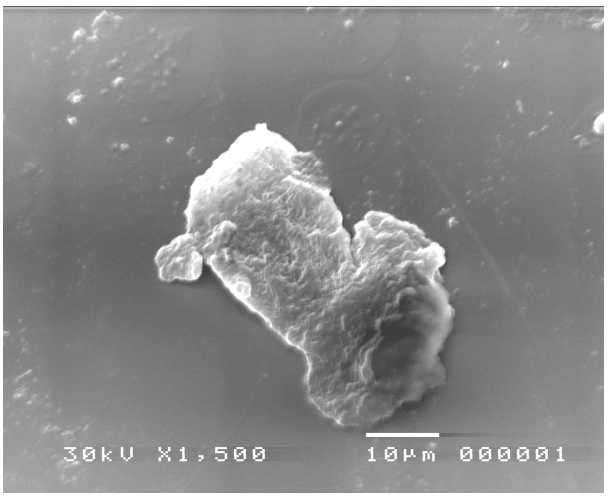

Figure (8) SEM micrograph of G2 after corrosion and irradiation with (10 kGy).

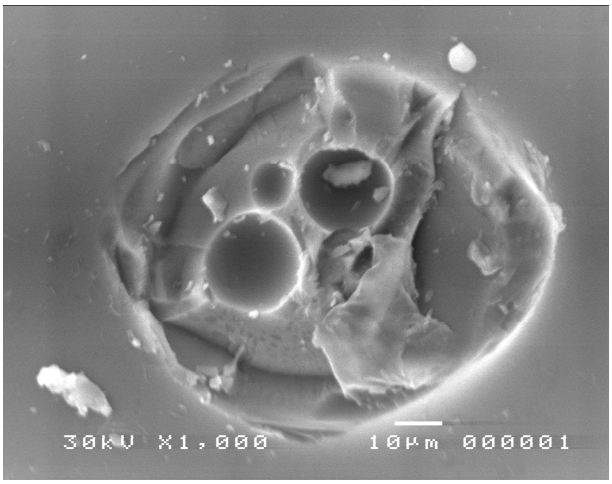

Figure (9) SEM micrograph of G2 after corrosion and irradiation with (100 kGy)

Table (1) Chemical composition of some borosilicate glasses matrices (basic glass) used for HLWC vitrification. Data are given in wt% [4]

Types of glass Components	PAMELA (SM513FR)	GG WAK 1	SON 68 FR
SiO2	58.6	60	54.9
B2O3	14.7	17.6	16.9
Al2O3	3.0	3.1	5.9
Na2O	6.5	7.1	11.9
Li2O	4.7	3.5	2.4
TiO2	5.1	1.2	-
CaO	5.1	5.3	4.9
MgO	2.3	2.2	-
ZnO	-	-	3.0

Table (2) Chemical analysis of municipal waste

Element	Atomic % after the first heat treatment
O	13.15
Na	1.47
Al	7.83
Si	5.31
P	6.20
S	3.22
Cl	5.53
K	2.46
Ca	47.11
Ti	0.28
Fe	5.09
Cu	1.12
Zn	1.23
Total	100.00

Table (3) The prepared glass compositions

Number of Glass	Composition
G1	70% Waste + 10% B_2O_3 + 10% Na_2O + 10% SiO_2
G2	90% Waste + 10% Borax

Table (4) Chemical analysis of the prepared glass

Elements	Atomic %	
	G1	G2
O	21.43	21.50
Na	10.04	4.32
Al	0.34	2.50
Si	29.26	25.34
K	2.32	2.78
Ca	29.07	35.34
Ti	0.35	0.39
Fe	3.15	3.27
Cu	0.76	0.76
Zn	1.04	1.59
Total	100.00	100.00

4. Discussion:

Table 2 shows the composition of the municipal waste as obtained from the source, where it has been burned at 700°C. This table shows that the contents of the municipal wastes are mainly formed from oxides which can create glass with the addition of small amounts of glass former oxides.

4.1. Effect of composition in glass corrosion

According to Figures 1,2, It can be noticed that glass G2 is more durable than G1 and this can be understood taking into consideration the chemical analysis of glass surfuce shown in table 4, where glass G2 contains more percent of aluminum which are obviously more resistant to be corroded especially at the first stage of corrosion, and Ca ions which has large ionic radius causing blocking of the routes of exited sodium ions from diffusion. Also, glass G1 contains more percent of sodium, and as mentioned before the release of the alkali ions is the first step in the corrosion process of silicate glasses depending on the ion exchange process. So, it is easily expected that glass G2 will be more durable. The basic mechanism controlling the leaching of the glass with water at lower irradiation dose is the ion exchange including counter diffusion between cations in glass and protons (hydronium ions H_3O^+) from water which replace the cations released from the glass structure. The rate of release of cations into water during leaching is given by the magnitude of flux of cations through the surface of glass – water interface which depends on the cation concentration in the glass, the diffusion coefficient and temperature dependence [7]. While increasing the irradiation dose will give the chance for more free radicals to be formed, i.e. further ionization of glass modifiers will take place rather than alkali ions (which may be highly consumed), to form a defending layer precipitated in the glass surface formed from immiscible compounds. This layer is responsible for the observed decrease in the corrosion at higher doses.

4.2. Effect of irradiation in glass corrosion

Radiation affecting corrosion rate is assumed to be due to two factors, the first is the alteration of glass structure; the second is the changing of the pH of the leaching solution by the formation of corrosive radiolytic products [10,13]. From previous studies on the corrosion of γ irradiated glasses, it has been found that there was an incongruent dissolution of glass, especially for the in-situ γ irradiated corrosion tests of waste glass [14].

It is clear from Figures 1,2 that leaching is systematically larger when glass is leached without irradiation. The most important notice is that G2 is more durable than G1when leaching occurred without irradiation, while when the leaching process occurred after irradiation the glass become more durable, also G1 is more affected with radiation, where its corrosion rate decreased than G2 . This can be interpreted according to Sheng et al [15], where he assumed that the controlling step in the leaching mechanism is the solubility of various elements that precipitate during the course of reaction. He also assumed that the rate limiting step in the reaction is the removal of $Si(OH)_4$ group from the glass surface. According to the last assumption it can be understood that glass G1, which contains 10% SiO_2 has to be more durable than G2, where alkali ions are present inside the network structure of either Si or B lattice and their mobility is limited without the presence of the exiting irradiation. It only depends on the amount of hydrogen or hydronium ions formed during the leaching process.

Also it must be taken into consideration that Si ions show lower release rates, while the dissolution rate of B from borosilicate glass is usually much higher than Si ions although both of them are network former. This may be due to the presence of Si in a form of SiO_4 tetahedra while B is found at least partly as BO_3 triangles, as well as due to the higher mobility of B in aqueous media [7]. The observed deterioration in the durability of G1 upon irradiation can be referred to radiation ability to initiate ionization, which encourages the increase of ion exchange and since the alkali ions (i.e most of Na and k ions shown in table 4) are the highest released elements, besides it is well known that for the in-situ γ irradiated corrosion tests large amounts of hydrogen and hydronium ions will be formed causing the fast release of alkali ions before the formation of any depleted layer, causing the observed increase in the weight loss.

Figures 4-8 show the optical micrographs of thin section of the glass surface, containing large voids and layers and showing some whirling and ripple like corrugations. Shot particles (i.e. teardrop-shaped and spheres) and large voids are found scattered through out the material. Large voids are believed to have formed in regions where small ions bridged together with sufficient strength to resist the consolidation stresses. Plane was strongly cross linked in a complex way and had approximately random orientations in the glass surface [16].

Conclusions

The addition of high percentage of municipal solid wastes (70-90%) as a source for different glass modifier with the addition of some glass former oxides made a promising glass. This glass may be used for the immobilization of radioactive wastes, with low irradiation doses, where the results showed that the highest corrosion occurred for the two prepared glassesG1 then G2. The results also showed that glass G2 which contains higher amount of waste has higher durability.

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References

[1] Ojovan, M.I and Lee, W.E "An introduction to nuclear waste immobilization" , Amaterdam Elsevier Science (2005).
[2] Colombo, P., Brusatin G., Bernardo, E., Scarinci G., Cun. Opn. Solid state Mater . Sci, 7 (2003) 225-239
[3] Soboler, I.A., Dmiture, S.A., Lijanvo, F.A., Kobeler, A.P., Stepnoreky, S.V., Ojovan, M.I, Glass Technol. 46 (2005) 28-35.
[4] Jouan, A. Proc. Int. Cong on Glass, Edinburg UK, 1(2001) 286-291.
[5] Sheng J. and Luo S., J. Nucl. Mater., 57 (2001) 297-
[6] Park YJ., Heo J., J. Hazard. Mater. B, 91 [2009], 83-89.
[7] Roth G., Weisenburger S., Vitrification of high-level waste: glass chemistry, process chemistry and process technology, Nuclear Engineering and Design, 202 (2000) 197-207.
[8] Frugier P., Martin C., Ribet I., Advocat T., Gin S., J. Nucl. Mater. , 346(2005), 194-207.
[9] Jollivet P., Parisot G., J. Nucl. Mater. 345 (2005), 46- 64
[7] Ojovan M.I., Pankov A., Lee W.E., J. Nucl. Mater., 358(2006) 57-68.
[8] Antropova T.V., J. Non-Cryst. Solids, 345(2004) 270-275.
[9] Weber W.J., Ewing R.C., Angel C.A., Arnold G.W., Cormack A.N., Delaye J.M., Griscom D.L., Hobbs L.W., Navrotsky A., Price D.L., Stoneham A.M., Weinberg M.C., J. Mater Res. 12(1997) 1948- 1978.
[10] Ojovan M.I, Lee W.E., J. Nucl. Mater., 335 (2004) 425-432.
[11] Cormack A.N., Du J., Zeitler T.R., J. Non-Cryst. Solids, 323(2003) 147-154.
[12] Skuja L., J. Non Cryst. Solids, 239 (1998) 16-48
[13] Ojovan M.I., Hand R.J., Ojovan N.V., Lee W.E., J. Nucl. Mater. 340 (2005) 12-24.
[14] Lemmens K., Van Iseghem P., Mater. Res. Soc. Symp. Proc.663 (2001) 86-
[15] Sheng J., Luo S., Tang B., Waste management, 19 (1999)401-407
[16] Doremus R.H. and Lanford, W.A**;** J. Non_ Cryst. Solids 54 (1983) 139.