Lead Iron Phosphate Powders Produced by Melting and Fast Cooling

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Abstract Lead iron phosphate glasses are potentially useful for nuclear waste immobilization, and others applications. Lead iron phosphate glass powders were obtained from a mixture of $NH_4H_2PO_4$, PbO and Fe_2O_3 melted in an induction furnace and fast cooled. After milling, the material was pressed in a die and finally sintered. The particle size distribution, specific surface area, density values and crystalline phases were determined. Three amorphous halos were observed with intensities depending on the particle size distribution. These halos were assigned to be from ferric metaphosphate $(Fe(PO_3)_3$, lead orthophosphate $Pb_3(PO_4)_2$ and lead metaphosphate $Pb(PO_3)_2$ compounds. It is proposed that ferric metaphosphate is the main compound on the surface of the particles and lead orthophosphate and lead metaphosphate are in the inner part of the particles. The milling process allows to exhibit these compounds which are then detected by the X-rays diffraction. Pre-sintered pellets were exposed to CsCl aqueous solution and the absorption of Cs has been determined by SEM. Crystallization temperatures were determined by thermal analyses, and it is noted that the maximum is displaced from 534°C to 543°C for samples containing CsCl. The surface area was determined to be 29 cm^2/g after milling.

Introduction

The production of glass powders is very important because they can be used to prepare enamels, glazes, sealant, and in others applications. They also can be used to immobilize industrial wastes if mixed, pressed and sintered together.

Nuclear wastes can be immobilized by glass powders after pressing and heat treating in order to reduce the porosity and to aggregate the waste particles. This process can be called vitrification of nuclear wastes, even though this term is commonly used when both glass and waste particle are melted together and cooled down in block shapes. Glass particles sintering has been shown to be useful because glasses are chemically stable, show high corrosion resistance, and do not degrade easily under radiation. The sintering process also avoids to submit nuclear wastes to commonly high temperatures of melting process. Hence the loss of contaminants by volatilization and chemical attack of the containers are reduced. The most common glass materials used in the vitrification processes are borosilicates with several different compositions being hot or cold pressed and finally sintered [1]. Porous materials have also been investigated in order to immobilize nuclear wastes in the liquid state. Examples are diatomite and shamote [2].

Lead iron phosphate glasses (LIP) were first developed for vitrification purpose in 1984, when they were mixed and melted together with nuclear waste compounds. These materials showed

low dissolution rate in water (10^{-8} g/cm^2. Min) revealing an important feature for a material that is intended application. The rate of dissolution decreases as the solution pH increases. In salted water solution the LIP dissolution rate is higher [3]. It was also noticed that these glasses could be used in other applications by modifying their basic composition. Glasses with thermal expansion coefficients of 18 x 10^{-6} /°C and relatively high refractive index could be obtained. These materials can be used potentially in the sealing of ceramics to metals, as laser hosts and optical fibers. Recently it has been suggested that these glasses can also be used as nuclear particles detectors [4, 5].

Chemical and structural properties of LIP depend on the glass composition. The P_2O_5 is considered the glass former and PbO is added to reduce the viscosity and consequently the melting point. By adding Fe_2O_3 it was possible to improve the chemical resistance and to decrease the crystallization rate [6]. The structure of LIP consists basically of a chain of oxygen atoms located in the corners of a tetrahedron containing in its center a phosphorous atom. Lead and iron are bounded to non-bridging oxygen atoms.

In the present work LIP powders were produced by melting and quenching the raw materials in order to obtain glasses as frits. This material was than milled and sieved to reach a suitable particle size distribution. The material so produced is intended to be used in the vitrification of liquid wastes. Powders are pressed and pre-sintered leading to porous pellets that will be impregnated with a liquid solution containing cesium chloride, and finally sintered.

Experimental Procedure

Lead iron phosphate glasses were obtained as frits by mixing and melting 43.49^P/$_o$ $NH_4H_2PO_4$, 46.64^P/$_o$ PbO and 9.87^P/$_o$ Fe_3O_3 and finally quenching to room temperature. Melting was performed in an alumina crucible placed in the center of an induction furnace coil. In order to heat the material, a graphite crucible was used externally to the alumina one. Argon was used as the working atmosphere so the graphite could be preserved. Initially the material was heated up to 450°C and soaked during 1 h in order to convert $NH_4H_2PO_4$ to P_2O_5. After that, the material was heated up to 1050°C at 17.5°C/min and soaked again during 1 h at that temperature. Frits were obtained by pouring the viscous liquid in a water tank. The selected composition was the same used in other works.

Powders were processed by ball-milling during 30 h using alumina as grinding medium. The material was then uniaxially pressed in a 10mm diameter die at 1.0 ton/cm^2. The internal walls of the die were previously lubricated with zinc stearate in order to reduce the friction between the powder and the walls. Therefore a more uniform internal stress distribution could be reached and the resulting pellet could be easily pulled out from the die. After pressing some samples were pre-sintered at 400°C during 1 h, immersed in a CsCl solution (4.8M) from 2 to 600 s at room temperature and dried in air during 24 h. The final densification was performed at 750°C in air by using an electrical furnace. The heating and cooling rates were 20°C/min and 22°C/min respectively.

X-ray diffraction and scanning electron microscopy were used to identify crystalline and amorphous phases and to determine the Cs distribution in the LIP samples. A Philips X-ray diffractometer model PW 3710 and a Philips Scanning Electron Microscopy (SEM) model XL 30 were used for that purpose. The particle size distribution of the powder determined by using a Micromeritcs Sedigraph Model 5100 and the specific surface area of the material was determined by (B.E.T. method). In order to determine the crystallization and Tg temperatures thermal analyses were performed by using a T A Instrument model 2100 and a Netzsch Instrument model STA 409 C/7/E.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns from LIP powders before and after milling. No crystalline phases have been observed from these patterns. Three halos can be seen which correspond to amorphous phases typically found in LIP based glasses. Hence the procedure used in this work

was appropriated to obtain glass materials. Before milling the material has a ferric metaphosphate rich phase on the surface - $(Fe(PO_3)_3$ (see halo #1 on Fig. 1). Halos #2 and #3 are less pronounced in that spectrum. After milling, the material becomes more homogeneous and halos #2 and #3 related to lead orthophosphate $Pb_3(PO_4)_2$ and lead metaphosphate $Pb(PO_3)_2$ phases respectively become more pronounced.
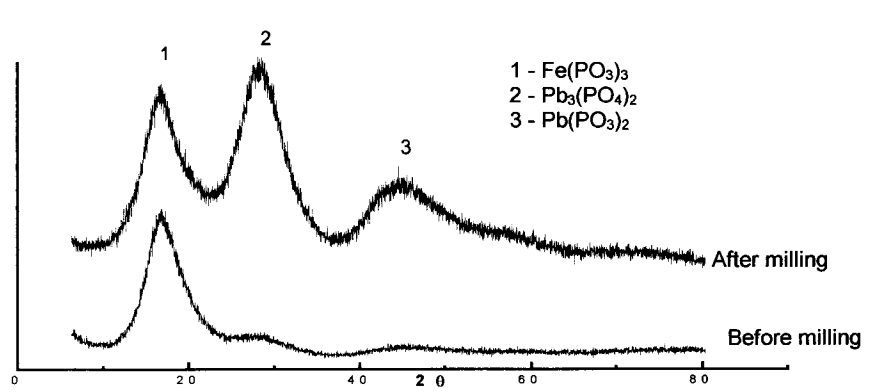

Fig.1: X-ray diffraction patterns from LIP powders before and after milling.

Table 1 shows LIP composition determined by X-ray fluorescence analyses.

Table 1. Composition of LIP in wt % determined by X-ray fluorescence analyses.

Samp Code	Starting Material (% wt)			Analyses (wt%)		
	$NH_4H_2PO_4$	PbO	Fe_2O_3	P_2O_5	PbO	Fe_2O_3
1	34.4	54.1	11.4	18.5	70.3	11.2
2	34.4	54.1	11.4	18.9	69.8	11.3
3	43.5	46.6	9.9	34.4	54.1	11.4

Samples # 1 and #2 were melted in air at 1050 °C in an electric furnace for 1 h and 2 h, respectively. Sample #3 was melted in argon at 1050 °C for 1h in an induction furnace.

It can be noticed that approximately 85 wt % of $NH_4H_2PO_4$ was converted to P_2O_5. Ammonia and water were also evolved. It is also noticed that the lead loss is higher when the melting is performed for 3 h in an electric furnace (sample #2) than when it is done in an induction furnace (sample #3). It is assumed that the lead is lost by volatilization. By using the induction furnace the heating rate is higher so it takes less time to reach the melting temperature and therefore the entire process lasts shorter than the one performed in an electric furnace.

Table 2 shows density values determined by helium picnometry. It can be noticed that the value spreading is due to lead volatilization (samples #1 and #2) and different composition (samples #1 and #3).

Table 2. Density values determined by helium picnometry

Sample Code	Temperature (°C)	Time (h)	Density (g/ cm^3)
1	1050	1	5.789
2	1050	3	5.449
3	1050	1	5.295

Table 3 shows the medium particle size and specific surface area values for LIP powders.

Table 3. Medium particle size and specific surface area for LIP powders.

Type of Furnace	Heat Treatment	Milling Time (h)	Medium Size (μm)	Specific Surface Area (cm^2/ g)
Electric	1050 °C / 2h	24	4.50	34.99
Electric	1050 °C / 2h	30	3.67	61.32
Induction	**1050 °C / 1h**	**30**	**3.23**	**68.82**

From these results it is suggested that powders obtained by melting raw material at 1050 °C/1h in an induction furnace, followed by quenching and milling during 30 h, are more suitable to be used in the sintering process because they show smaller medium particle size (3.23 μm) and higher specific surface area (68.82 m^2/g). In a recent work it has been shown that particle sizes and heating rates are relevant parameters for the sintering process of glass materials, hence these powders were used to prepare pellets [7].

Table 4 shows density values of glass pellets as a function of immersion time in a 4.8 M aqueous solution containing cesium chloride.

Table 4: Density values and treatment condition for pellets previously immersed in a cesium chloride aqueous solution.

Sample (code)	Immersion Time (s)	Heating Rate (°C/min)	Sintering Temp. (°C)	Density (%)
4	-	**20.0**	**750**	**99.0**
5	300	20.0	750	80.0
6	60	20.0	750	81.0
7	15	20.0	750	80.0
8	8	20.0	750	85.0
9	5	20.0	750	86.0
10	**2**	**20.0**	**750**	**90.0**

Glass powder density values determined by picnometry were used for comparison. As it can be seen from Table 4, density values increase as the immersion times decrease. These results are in accordance to the ones obtained in previous work [8] where it was proved that cesium is acting as crystallization nuclei. From Table 4 it is also noticed that samples submitted to lower immersion time show higher density values, probably because of the lower crystalline phase contents. Another fact is that pellets not submitted to immersion in cesium chloride solution always show higher density values than the ones immersed in the solution.

Fig.2 shows differential thermal analyses spectra obtained for LIP samples that have or not been immersed in a cesium chloride solution.
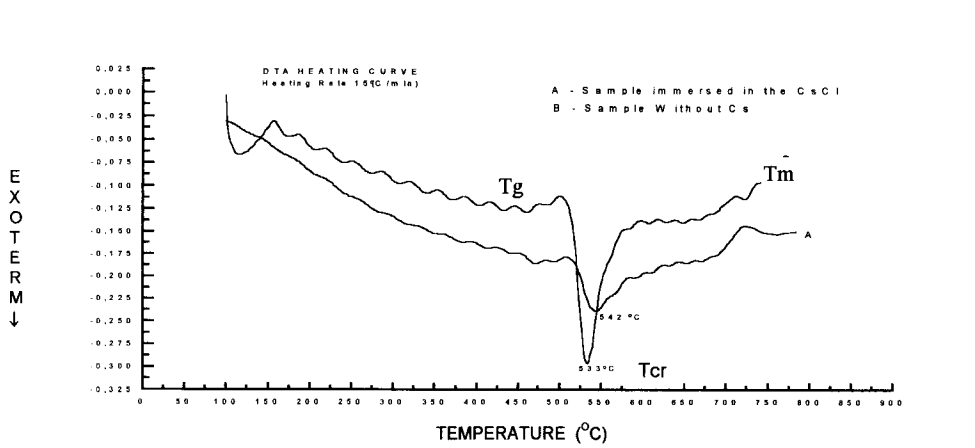

Fig.2. Differential thermal analysis spectra for LIP samples with and without immersion in the CsCl solution (4.8 M). These measurements were performed in a nitrogen atmosphere. The glass transition temperature T_g, the temperature of the maximum rate of crystallization T_{cr}, and the melting point T_m are depicted in the figure.

It is noticed that for samples previously immersed in the CsCl the mass loss is higher than for samples not immersed in CsCl solution, even though that loss is very small. An initial mass loss is due to water evaporation. Above 550 °C there is again a mass loss which is suggested to be related to CsCl decomposition. From the DTA results it can be noticed that the temperature of crystallization is displaced from 534 °C to 543 °C.

Fig. 3 shows the Cs dot map obtained by energy x- rays dispersion analysis. It is noticed that Cs occupies specific positions which might or not be intergranular ones. It was not possible to distinguish these regions by electron microscopy because no etching was previously performed on the samples.

Fig.4 shows X-ray diffraction patterns from two LIP samples with and without immersion in cesium chloride. It is noticed that XRD peak heights corresponding to certain phases are higher for the sample exposed to CsCl during 300s (sample #9) than for the one not exposed (sample #4). A pronounced phase containing chlorine ($Pb_5(PO_4)_3Cl$) which is originated from the reaction between CsCl and the main LIP glass compounds has been identified. Phases containing Cs have not been detected. Lead iron phosphate phase has been identified for the sample not immersed in a cesium chloride aqueous solution.
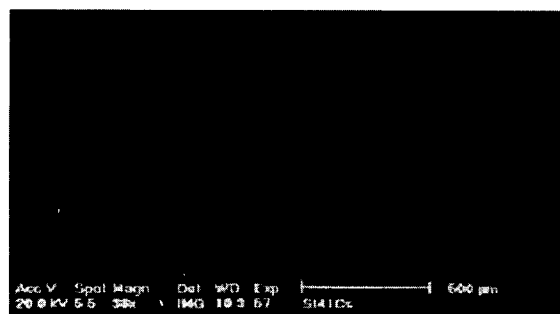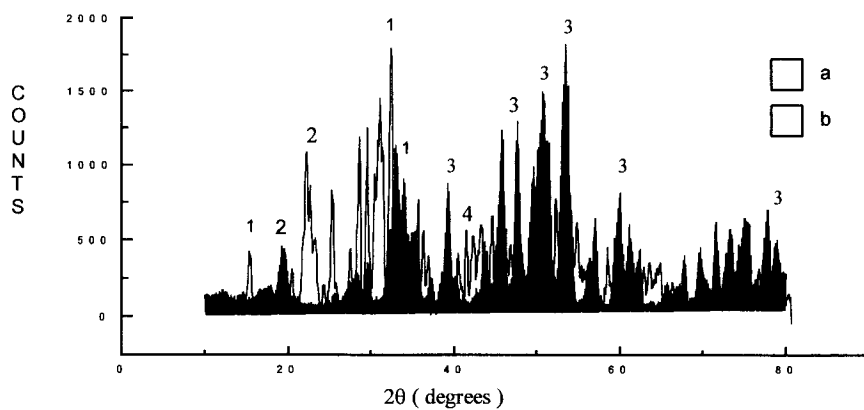

Fig.3. Energy X-Ray Dispersion Analysis for LIP pellets previously immersed in a cesium chloride aqueous solution (4.8 M) for 15 s.

−Fig.4. X-ray diffraction patterns from LIP samples with and without immersion in cesium chloride aqueous solution (4.8 M), sample #4 and sample #5:
1-$Fe_2Pb_3(PO_4)_4$; 2 - $Fe(PO_3)_3$; 3 - $Pb(PO_4)Cl$;
4 - $Pb_3(PO_4)_2$,   a - sample #4, b - sample #5

Conclusions

Lead iron phosphate glasses have been prepared as frits. Three amorphous phases have been detected, two of them more pronounced after ball milling. That is an indication that they are the inner part of the frit particles.

Pellets of LIP glasses prepared from suitable powders have been used to absorb CsCl from an aqueous solution.

Acknowledgements

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