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A novel method to produce niobium phosphate glasses by microwave heating

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Niobium phosphate glasses were produced by microwave heating mixtures of Nb_2O_5, $(NH_4)_2HPO_4$, KOH, PbO, and $BaCO_3$. Not all tried compositions were melted during the microwave irradiation. Absorption of microwaves was checked for individual compounds to determine the best chemical form to be used. The presence of KOH is indispensable in the mixture to allow microwave coupling. Glasses were also prepared by melting the same mixtures in an electric furnace. Glasses produced by microwave heating shows concentration of Al lower than the ones for glasses melted in electrical furnaces because only the precursors are directly heated by the microwave energy, reducing the diffusion of elements from the crucible to the liquid. Glasses with dissolution rates in aqueous solution at 90°C of $8.6 \times 10^{-10}\ g \cdot cm^{-2} \cdot min^{-1}$were produced. The chemical durability of glasses increases as a function of the amount of PbO. The amount of water molecules, OH^- radicals, and CO_2 bonded to the glass structure decreases as the amount of Nb_2O_5 increases. © *2004 Kluwer Academic Publishers*

1. Introduction

Besides the fact that natural glasses can be found in the nature, such as the obsidians, glasses can also be artificially produced by melting raw materials using different heating sources such as electrical heating, gas burning, and induction furnaces. The dielectric heating of glasses has been reported, considering that the material had to be previously heated to transform itself into a sufficiently good conductor to accept power from the electromagnetic induction field. New designs and electronic systems have been introduced to allow the melting of glasses in an electromagnetic induction field by using an inductively heated metallic cylinder [1].

Microwaves are electromagnetic radiation in the frequency range of 300 MHz to 300 GHz. For heating purpose, microwaves of 0.915 and 2.45 GHz are preferable [2]. However, microwaves of 28 GHz are also used for sintering ceramic materials [3].

Microwaves are used mainly for radar, satellite communication, and cellular telephone transmission, but also in the processing of ceramic materials (drying, calcination, sintering, joining) [2, 4–6], curing of composite and polymers [2, 6–8], sintering of hydroxyapatite [9], processing of ceramic superconductors [10], mineral treatments [11], and synthesis of ceramic powder by combustion [12]. Microwaves turn the processing of materials faster and economic because this radiation is transferred directly to the material through the interaction of the electromagnetic field with the molecules, transforming it to kinetic energy [13]. In liquid solutions, the microwave energy is transformed to kinetic energy through the interaction of an oscillating electromagnetic field with dipolar molecules. In solid-state materials the heating is originated from the interaction of the electromagnetic field with conducting ionic or electronic species. In certain materials, heating occurs through the vibration of alkaline ions with positive charge trapped in an interstitial site surrounded by negative charges that acts as an oscillating dipole; in this case this is the main mechanism for microwave absorption [14].

The main obstacle for microwave heating is the response of different materials to the microwave exposure, since a large number of materials are transparent to microwave at room temperature. Commercial silicate glasses are generally transparent to microwave radiation at room temperature. However, at higher temperatures there is a structural relaxation that allows the absorption of microwave energy leading to an additional heating [14].

The use of microwave for processing alkaline silicate glasses has been previously reported. Since commercial silicate glasses are transparent to microwave radiation at room temperature, those materials had to be heated at 500°C to allow the coupling with the electromagnetic field. It was also noticed that the amount of alkaline elements affects the absorption of microwaves, and glasses with a combination of alkaline elements show less absorption of microwaves compared with glasses that contain just a single specie of these elements [14]. Microwave has also be used to vitrify radioactive wastes originated from a surrogate filtercake sludge [15].

Phosphate glasses can be used, among other applications, in hermetic sealing of metallic and ceramic materials [16], nuclear waste immobilization [17], and optical applications [18, 19]. However, phosphate glasses are known to be low resistant to humid environment. To prepare phosphate glasses, raw materials, that also absorb humidity, are usually melted. Phosphate glasses can be prepared from ammonium phosphate dibasic ($(NH_4)_2HPO_4$), phosphate acid (H_3PO_4) and phosphate oxide (P_2O_5). Niobium oxide is added to improve the chemical durability. Typical features of the phosphate glasses preparation process are relatively high volatility of elements, low viscosity at the melting temperature, high tendency towards devitrification, and difficult removal of water from melt. To avoid the presence of water molecules in the glass structure and their influence in the final properties of glasses, novel preparation processes are investigated. Since the loss factor of phosphate glasses at room temperature is relatively low ($\tan \delta = 0.0046$ at 3 GHz) compared to materials that are recognized good microwave absorbers (for water, $\tan \delta = 0.1570$) [20], the coupling of microwave radiation with glasses at room temperature is unlikely. In the present work niobium phosphate glasses are obtained by melting suitable inorganic compounds in a microwave oven. A mixture of alkaline hydroxides, oxides, and ammonium phosphate is heated from room temperature to melting temperature, and fast cooled to produce durable phosphate glasses. This process is faster and more economical than conventional processing methods, and can reduce the amount of water molecules in the glass structure.

2. Experimental procedure

Phosphate glasses were produced by microwave heating mixtures of Nb_2O_5 (ceramic grade CBMM), $(NH_4)_2HPO_4$, KOH, PbO, and $BaCO_3$, in batches of 15–30 g, manually homogenized, in an adapted domestic microwave oven (Panasonic) with nominal power of 1,100 W during 30 to 50 min, 2.45 GHz. Alumina and silica crucibles wrapped by ceramic blanket (Fiberfax) were used to hold the liquid during the melting. A ceramic plate was used as support and it was allowed to rotate inside the oven to homogenize the radiation exposure. An alumina cover was placed over the crucible to reduce thermal losses. To avoid very fast heating rates, microwave absorbers were placed inside the oven, and removed gradually during the heating ramp. Not all the chemical compounds used in the mixture absorb microwave energy when exposed individually at room temperature. PbO, Nb_2O_5, and $BaCO_3$ are not good microwave absorbers, and consequently, do not self-heat at room temperature, as it was determined experimentally following the conditions of the present work. On the other hand, KOH and $(NH_4)_2HPO_4$, precursors of K_2O and P_2O_5, respectively, are good microwave absorbers. When KOH is exposed to microwave for times >1 min, it is noticed that the compound melts itself, there is self-ignition, and electrical discharges inside the resonant cavity. $(NH_4)_2HPO_4$ also is a good microwave absorber, and it decomposes itself during the heating.

Absorption of microwaves was also checked for NaOH, $Mg(OH)_2$, K_2CO_3, Na_2CO_3, and LiOH, to compare the response of different chemical forms of alkaline (Li, Na, and K) and alkaline earth elements (Mg). When NaOH is exposed to microwaves, it heats itself up to the melting point, as it was previously observed for KOH. $Mg(OH)_2$, LiOH, K_2CO_3, and Na_2CO_3 were also exposed to microwaves during 10 min., but no heating above 80°C was detected.

Mixtures of KOH + $(NH_4)_2HPO_4$ + $BaCO_3$ + PbO + Nb_2O_5 exposed to microwaves at room temperature, can reach temperatures in the range of 1000 to 1400°C, depending on the concentration of each compound in the mixture.

To check if glasses produced by microwave heating are homogeneous, chromium oxide powder was used as a dye, and a layer of this material was placed on the bottom of the crucible before melting. Two-third of the volume of the crucible was then filled up with the glass precursor compounds and melted inside a microwave oven. Care was taken to avoid mixtures of the chromium oxide with the glass components during the loading process. The final appearance of the glass does not show any visible feature that could be due to compositional variation. A green color was observed in the entire glass piece. Also, the chromium concentration was determined in different regions of the glass by EDAX, and no significant differences were observed. Therefore the microwave processing leads to homogeneous glasses.

Mixtures with the same compositions were also melted in an electric furnace, at 10°C/min. The liquid was kept at the maximum temperature during 1 h; then, poured in graphite or stainless steel molds at room temperature. Some glasses were also prepared by pouring the liquid in pre-heated graphite molds, followed by an annealing in the temperature range of 400–500°C during 1 to 2 h.

An optical pyrometer (Minolta) was used to monitor the liquid temperature inside the microwave oven. A hole 1cm in diameter was drilled on the top of the cavity to allow this measurement.

The nominal compositions of the materials are $0.30P_2O_5$-$0.25K_2O$-$0.15Nb_2O_5$-xBaO-$(0.30-x)$PbO, where x is the mole fraction and takes the values of 0, 0.06, 0.12, 0.18, 0.24, and 0.30. Samples were named BP X-Y, were X represents the concentration of BaO (mol%), and Y, the concentration of PbO (mol%).

Glasses with ternary composition P_2O_5-K_2O-Nb_2O_5 were also prepared by microwave melting, keeping the molar ratio P_2O_5:K_2O equal to 6:5, and varying the amount of Nb_2O_5. The nominal composition can be expressed as $(1-x)\ [6P_2O_5\cdot 5K_2O]\cdot x Nb_2O_5$, were x is the mole fraction and takes the values of 0.1, 0.2, 0.3, 0.4, and 0.5. Samples were named as Nb Z, where Z is the mol% of Nb_2O_5.

These compositions are the starting composition. A loss of phosphorous and oxygen is usually expected during the melting process. To check this loss, elemental analyses were performed for two glasses. These analyses were performed by X-ray fluorescence spectroscopy.

For further analyses the sample Nb10 was discarded because it shows relatively low chemical durability in humid environments (dissolution rate $>10^{-4}$ g · cm^{-2} min^{-1}). The sample Nb60 also was discarded because it did not completely melt itself due to the limited response to microwave irradiation.

All materials were analyzed by X-ray diffraction (*Bruker—AXS model D 8—Advance*) using Cu K_α radiation in the range of 10–80°, step size 0.05°, time/step= 2 s. The chemical durability was evaluated from dissolution rate in deionized water at 90°C after 14 days. Soxlets were used for this purpose. Bulk samples with surface area of 2.4 cm^2 were ground with 240 grit SiC paper, washed in acetone with ultrasound, dried at 110°C/2 h, cooled inside a desiccator, and then weighed to ±0.01 mg. The dissolution rate (DR) was calculated from the measured weight loss, (Δm) (g), total sample surface area, S (cm^2), and the immersion time, t (min), using the following equation:

$$\mathrm{DR} = \frac{\Delta m}{St}$$

Density was determined by the Archimed's method.

Compositional analyses were performed on polished cross section at randomly selected locations by energy dispersive X-ray analysis (EDAX).

The glass transition temperature of the glass Nb40 was measured by DTA (Perkins Elmer) at heating rate of 10°C/min in a flowing synthetic air.

The Infrared Spectroscopy was performed using glass powder dispersed in dehydrated KBr pellets. Samples were also analyzed in a mineral oil (fluorolub), to avoid the interference of water from the atmosphere.

A comparison between the chemical durability of niobium phosphate glasses produced by microwave heating and iron phosphate glasses reported in the literature is done [17].

3. Results

Glasses produced by microwave heating show a relatively lower concentration of Al (<0.004 wt%), compared with glasses melted in electrical furnaces (6.1 wt%) using alumina crucibles. The diffusion of elements from the crucible is minimized because the time needed to heat the material to the melting temperature in microwave heating is shorter, and the temperature of the alumina crucibles is lower, since only the precursors are directly heated by the microwave energy.

Fig. 1 shows the density of glasses as a function of BaO concentration for glasses prepared in the microwave oven and in the electrical furnace. By decreasing the amount of BaO, and consequently, increasing PbO, the density increases. This fact is related to the higher molecular weight of PbO, compared to BaO, and possibly, denser amorphous structures are achieved due to stronger cross linking between phosphate chains.

No differences among density values of glasses produced by both methods that could indicate non-thermal effects caused by the interaction of the electromagnetic field with the material were observed.

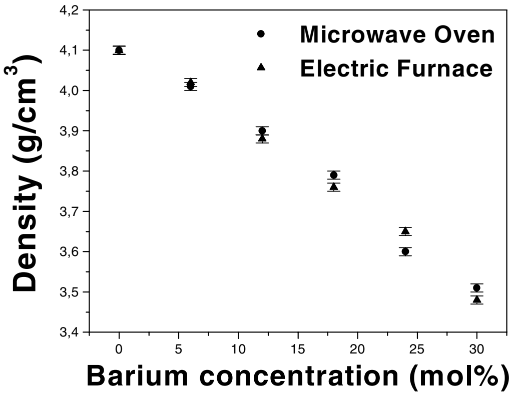


Figure 1 Density for barium niobium phosphate glasses.

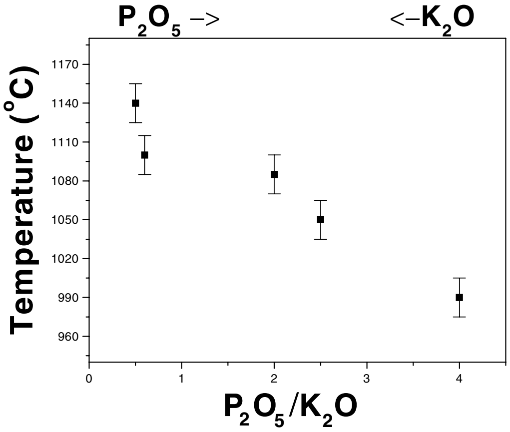
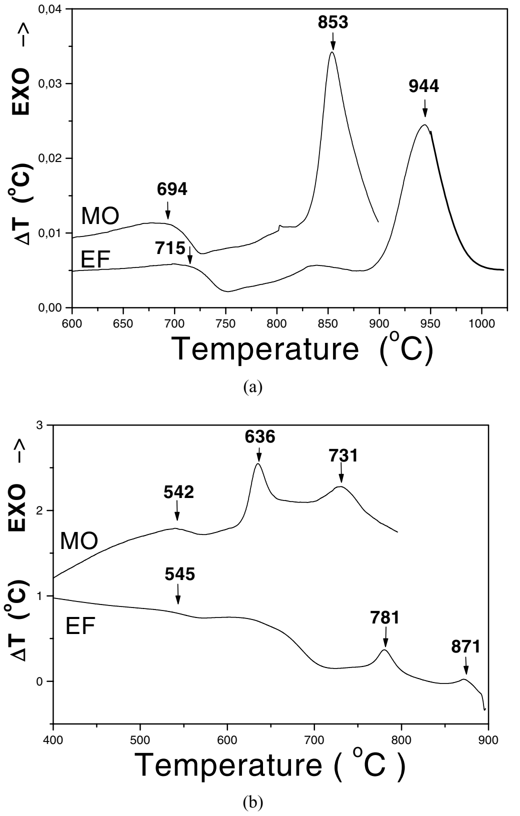


Figure 2 Maximum temperature measured during microwave heating of P_2O_5-K_2O-Nb_2O_5 (30 mol% Nb_2O_5) as a function of the molar ratio P_2O_5/K_2O.

Glasses with ternary compositions P_2O_5-K_2O-Nb_2O_5 were also prepared by microwave heating. Fig. 2 shows the maximum temperature reached by the liquid during microwave heating as a function of the molar ratio P_2O_5/K_2O. It is noticed that the maximum temperature decreases as the molar ratio P_2O_5/K_2O increases. For larger amounts of KOH (precursor of K_2O), the response of the mixtures to the microwave is better, and the chances to have thermal runaway also is higher, so the mixture is easily heated. The molecule KOH shows polar features, and therefore vibrates when exposed to microwave of 2.45 GHz. That is not the case for oxide molecules in the mixture.

Fig. 3 shows the DTA curve for the Nb40 glass (a) and BP 12-18 glass (b). Both glasses were produced by microwave heating and in an electric furnace. The glass transition depends on the production process because cooling rate is different. The glass transition temperature determined by DTA curves for the Nb40 is 694 ± 5°C and 715 ± 5°C, for the glasses produced in the microwave oven and in the electric furnace, respectively; a crystallization peak is also noticed at 853 ± 5°C, and 944 ± 5°C, respectively. The glass transition temperature determined for the BP 12-18 is 542 ± 5°C and 545 ± 5°C, for the glass produced in the microwave and electric furnace, respectively. In this case, two crystallization peaks are noticed for each sample at 636 ± 5°C and 731 ± 5°C, for the "microwaved" sample, and



(a)

(b)

Figure 3 DTA curves for: (a) Nb40 glasses, (b) BP 12-18, produced by microwave heating (MO) or in an electrical furnace (EF).

TABLE I Comparison of glass composition produced by microwave heating and in an electric furnace

Element	Glass composition			
	Nb40[a]	Nb40[b]	BP 12-18[a]	BP 12-18[b]
P[c]	20.61	17.82	25.04	24.38
P[d]	33.00	33.00	30.00	30.00
K[c]	32.51	30.82	29.83	31.29
K[d]	27.00	27.00	25.00	25.00
Nb[c]	46.88	51.36	26.27	24.82
Nb[d]	40.00	40.00	15.00	15.00
Ba[c]	–	–	7.69	8.83
Ba[d]	–	–	12.00	12.00
Pb[c]	–	–	11.17	10.69
Pb[d]	–	–	18.00	18.00

[a] Produced by microwave heating.
[b] Produced in an electric furnace.
[c] Determined by X-ray fluorescence spectroscopy.
[d] Nominal composition.

781 ± 5°C, and 871 ± 5°C, for the glass produced in the electrical furnace.

Not all compositions produced amorphous materials after cooling. Fig. 4 shows a compositional diagram and the types of phases determined by XRD for materials produced by microwave heating and fast cooled to room temperature.

Table I shows the concentration determined by X-ray fluorescence spectroscopy for the Nb40 and BP 12-18 glasses prepared by microwave heating and in an electric furnace, compared to the nominal composition.

For the BP 12-18 glasses the phosphorous loss is approximately the same for both experimental processes, microwave heating and electrical furnace. For the Nb40 glasses, it is noticed that the phosphorous loss is larger for the electrical heating than in the microwave oven.

Among all compositions tried in the present work, the presence of KOH was indispensable to melt the mixture during microwave heating. The maximum temperature of the liquid during the microwave exposure depends on the amount of KOH, and Nb_2O_5, keeping the ratio P_2O_5/K_2O constant. From Fig. 4, it is noticed that only certain compositions produce glasses. No effects that could be attributed to non-thermal effects caused by the interaction of the electromagnetic field with the material were observed. For glasses in the system K_2O-P_2O_5-BaO-PbO-Nb_2O_5 the maximum temperature reached by the liquid during the microwave heating does not depend on the amount of BaO and PbO.

Table II presents the dissolution rates for glasses produced by microwave heating and glasses produced in an electric furnace. The maximum temperature reached by the liquid during the microwave heating is also indicated.

The dissolution rate is reduced as the amount of PbO increases. This result is in agreement with the behavior of density: denser phosphate glasses are more chemical resistant.

From this table it is noticed that dissolution rate (DR) decreases as the amount of Nb_2O_5 increases, for

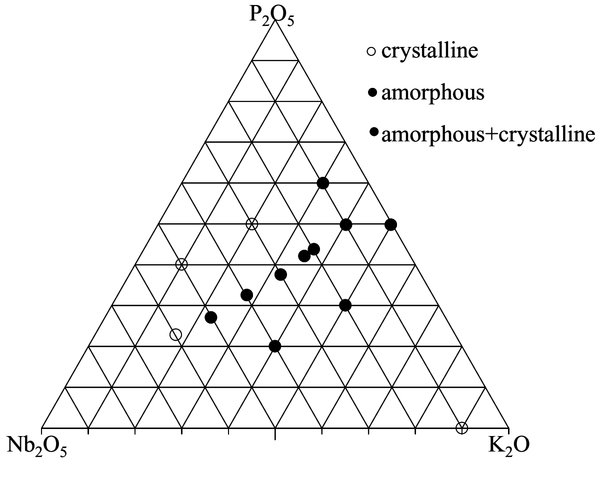


Figure 4 Compositional diagram for materials produced by microwave heating, and fast cooled to room temperature.

TABLE II Dissolution rate (DR) for glasses produced by microwave heating and in an electric furnace. Maximum temperatures reached during microwave heating are indicated

Sample code	DR ($g \cdot cm^{-2} \cdot min^{-1}$) (Microwave heating)	DR ($g \cdot cm^{-2} \cdot min^{-1}$) (Electrical furnace)	Temperature (°C)
BP 0-30	6.6×10^{-8}	1.1×10^{-7}	1206
BP 6-24	7.1×10^{-8}	3.7×10^{-8}	1200
BP 12-18	4.4×10^{-8}	2.6×10^{-8}	1212
BP 18-12	6.3×10^{-7}	–	1217
BP 24-6	7.8×10^{-7}	1.4×10^{-7}	1200
BP 30-0	2.1×10^{-6}	–	1198
Nb20	1.0×10^{-6}		1150
Nb30	9.3×10^{-9}		1158
Nb40	8.6×10^{-10}		1165
Nb50	1.2×10^{-9}		1187

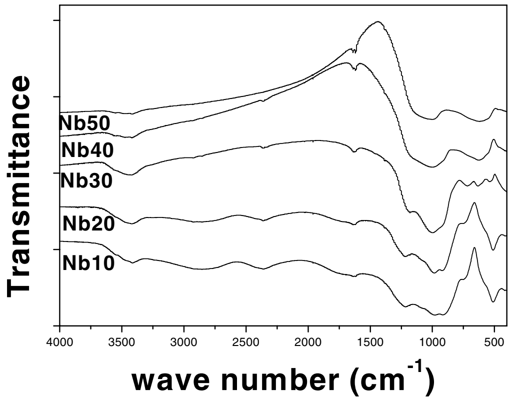


Figure 5 Infrared spectra of the glasses prepared in a microwave oven containing different amounts of niobium oxide (KBr pellets).

concentrations up to 40 mol%. The most chemical resistant glass is the Nb40, that shows DR comparable with the one for the phosphate glass with composition $40Fe_2O_3{\cdot}60P_2O_5$ (DR $= 2.5 \times 10^{-10}$ g $\cdot$ cm^{-2} $\cdot$ min^{-1}) [17].

Fig. 5 shows the infrared spectra of pellets of KBr containing phosphate glasses produced in a microwave oven with different amounts of niobium oxide.

Most of the IR bands have been previously identified, but some specific features can be inferred from Fig. 5. The bands located at 3430 and 1630 cm^{-1} are assigned to normal vibration modes (bond stretching) for either free water molecules or OH^- ions, and bond bending, respectively [21]. The band at 2850 cm^{-1} has been previously observed in phosphate glasses, and although attributed to OH^-, is not completely understood [21, 22]. A band located at 2360 cm^{-1} is attributed to CO_2 supposedly originated from the atmosphere. It is noticed that the intensity of these bands decreases as the amount of niobium oxide increases. Therefore, the amount of water molecules, OH^- radicals, and CO_2 decreases as the amount of Nb_2O_5 increases. When niobium gets into the phosphate network, atomic bonds get stronger and the glasses become more stable concerning to the water attack and inclusion of OH^-radicals and CO_2 molecules. IR bands located at 1228, 990, and 910 cm^{-1} have been assigned to P═O stretching, $(PO_4)^{3-}$ ionic group, P—O—H bending, respectively [21]. The intensity of the band at 910 cm^{-1} also decreases as the amount of niobium oxide increases, and it does not even appear for glasses containing 50 mol% of Nb_2O_5. A weak band located at 742 cm^{-1} for glasses containing 10 and 20 mol% of Nb_2O_5 is not clear for glasses containing higher amounts of niobium. For glasses containing 30 mol% of Nb_2O_5, a band located at 714 cm^{-1}is observed. Bands located at 740–714 cm^{-1} are assigned to P—O—P stretching vibration. Bands located at 584–630 cm^{-1} are assigned to O—Nb vibration; their intensity increases as the amount of niobium oxide increases. Bands located at 530–510 cm^{-1} are assigned to P—O—P stretching vibrations, or harmonics of bending O—P—O and O═P—O bonding [21].

The IR spectra were obtained also for niobium phosphate glasses in a mineral oil. The spectra are similar to the ones for the KBr pellets, except that bands due to the mineral oil are present. For phosphate glasses with lower amounts of niobium ($\leq$30 mol%) broad bands located at 2550 cm^{-1}, 3750–3500 cm^{-1} and 1625–1400 cm^{-1} are present. For higher amounts of niobium these bands are less perceptible.

4. Conclusions

Niobium phosphate glasses have been produced by microwave heating a mixture of inorganic precursors in alumina crucibles. Glasses with lower concentration of Al, compared with glasses melted in electrical furnaces were produced, since only the precursors are directly heated by the microwave energy, reducing the diffusion of elements from the crucible to the liquid.

Glasses with dissolution rates of 8.6×10^{-10} g $\cdot$ cm^{-2} $\cdot$ min^{-1} in aqueous solution at 90°C were obtained. Not all compositions were able to couple with the microwave energy, and melt themselves, as well, not all compositions produce glasses after cooling. KOH is indispensable in the mixture to allow the coupling with microwave energy. The chemical durability of glasses that contain BaO and PbO is better for materials with increased amounts of PbO.

The amount of molecules of water, OH ions and CO_2 bonded to the glass structure decreases for glasses with higher amount of Nb_2O_5.

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