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Synthesis and Properties of Zinc Iron Phosphate Glasses Prepared by Microwave and Conventional Processing Methods

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Abstract: The synthesis and properties of zinc iron phosphate glasses, xZnO-(40-x)Fe_2O_3-60P_2O_5 where x = 0, 2.5, 5.0, 7.5, 10.0 (mol %) formed using domestic microwave oven and electric furnace are reported. In microwave glass melting, microwave absorber namely high purity magnetite powder has successfully coupled with microwave radiation at 2.45 GHz and completed the glass melting process at about 10 minutes radiation time. The properties of microwave samples are compared with equivalent samples prepared conventionally by melting the batches at 1300 ˚C for 2 hours in electric furnace. Although the mass loss trend is in agreement with the theoretical data, it is found that the microwave melted samples have slight increase in mass loss than conventionally melted ones and the mass loss is increased gradually with the increasing of ZnO contents. The powder density values of zinc iron phosphate glasses prepared using microwave method is found to be higher than the corresponding glasses prepared using conventional processing method. Identical trend of Fourier transform infrared spectra are recorded despite using different processing methods; it is clear that the addition of ZnO increased the cross-linking in the glass structure as well as improving the strength of the samples. Overall, the use of microwave radiation for the production of zinc iron phosphate glasses are promising and viable method as it gives comparable properties, faster glass melting and low energy consumption compared to conventional melting method.

Keyword: Zinc; Iron; Phosphate; Glass; Microwave; Conventional

1. Introduction

Phosphate glasses are significant in many industrial applications that require high thermal expansion coefficient, excellent UV transmission characteristic and low melting and softening temperatures [1]–[9]. However, the practical applications of these type of glasses are often limited due to their poor chemical durability *i.e.* phosphate glass could easily react with water at ambient temperature. This can be enhanced by the additional of one or more metal oxides for example Fe_2O_3. The addition of Fe_2O_3 enable the replacement of P-O-P bond with more moisture resistant P-O-Fe bond [4], [6], [7]. In this study, ZnO and Fe_2O_3 are introduced to the phosphate glass compositions and expected to improve the overall properties of the glasses for sealing and/or immobilisation of nuclear waste applications [10].

The most common method used in the production of zinc iron phosphate glasses is conventional processing that involves heat transfer mechanisms of conduction, convection and radiation. For this case, the surface of the raw materials will be heated from outside to inside of the sample; heat propagated from the heating element of the furnace to the surface of the sample. The existence of the thermal loss occurred by transferring the heat at multiple mediums causing the production of zinc iron phosphate glasses to be less economical and typically requires at least 5 hours melting time at ca. 1100 ˚C. This drawback encourages a new glass processing method that is more efficient in heating and overall cost effective.

The microwave processing method for the production of zinc iron phosphate glasses offers several advantages compared to the conventional processing. For example, the processing time of glasses can be reduced from hours to minutes, thus the energy consumption and the cost of preparing the zinc iron phosphate glasses can be significantly

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reduced [11,12]. To make useful direct microwave radiation in the production of glass, it is essential for the composition to include at least one microwave absorber component that can couple to the microwave field at frequency range of 900 MHz and 2.45 GHz; once coupled with microwave radiation, the heat will be generated from the molecular levels and heat up very rapidly [13,14].

In this communication, the work is focused on the synthesis and preliminary characterisations of the zinc iron phosphate glasses prepared using microwave and conventional glass processing methods. The aim is to prepare similar properties of zinc iron phosphate glass at much faster melting time using unconventional microwave method. The mass loss, powder density and molecular bonding of obtained glasses are compared and discussed accordingly.

2. Materials and Experimental

2.1 Raw materials and Glass Compositions

Zinc iron phosphate glasses with composition of xZnO-(40-x)Fe_2O_3-60P_2O_5, x = 0, 2.5, 5.0, 7.5 and 10.0 (mol%) were prepared using zinc oxide (ZnO - 99.0% pure, Alfa Aesar), magnetite (Fe_3O_4 – 97.0% pure, Alfa Aesar) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$ – 98.0% pure, Alfa Aesar) by microwave and conventional processing methods.

2.2 Microwave Glass Melting

The batches for producing 3 g glass were mixed, ground in an agate mortar with pestle for approximately 15 minutes and pressed with the loads of 3 tons for 60 s to produce 20 mm diameter pellets. Each pellet was placed inside the vitreous silica crucible and irradiated in the Panasonic, model NN-ST342M - 2.45 GHz, 800 W nominal power domestic microwave oven (DMO) for 10 minutes after which being cooled at room temperature. The crucible was positioned as in Fig. 1 to ensure maximum absorption of the electromagnetic waves. After irradiation process, the obtained glass were taken out from the crucible and the samples were let dry for further characterisation.

2.3 Conventional Glass Melting

For comparison purposes, identical composition of zinc iron phosphate glasses to microwave samples were prepared by melting 30 g of the homogeneous batches in alumina crucible for 2 h at 1300 ˚C using box furnace (Protherm). The melted samples were quenched in air by pouring the melts onto a pre-heated steel mould to form blocks and annealed at 450 ˚C for 1 h. The samples were kept dry for characterisation.

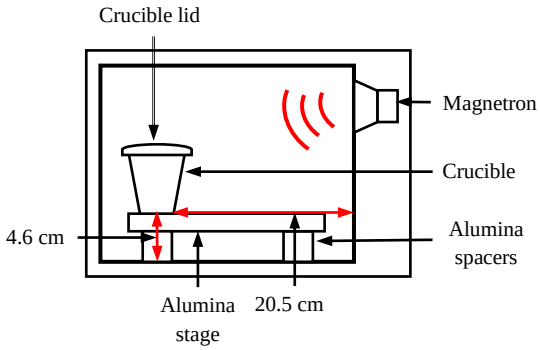

Fig. 1 Schematic diagram of the experimental setup inside the DMO

2.4 Characterisation Methods

The mass of the samples were calculated before and after heating. The mass loss of each sample was given by:

$$\%\ \text{mass loss} = \left(\frac{m_i - m_f}{m_i} \right) \times 100 \qquad (1)$$

where m_i is the initial mass and m_f is the final mass of the samples.

Powder density of the samples was measured using the Micromeritics AccuPyc II 1340 gas pycnometer. The samples was placed in the cell chamber and analysed using the AccuPyc II 1340 VI 05 software package.

FTIR spectra were recorded with a Perkin Elmer FTIR Spectrum 100 with 4 cm^{-1} resolution over 600-4000 cm^{-1} spectral range. Background spectra was measured prior to the samples and all of the spectra measurements were averaged to 20.

3. Results

In microwave melting, all zinc iron phosphate glasses were successfully completed the glass melting process within the 10 minutes radiation time. The mass loss of the samples prepared conventionally and microwave melted is shown in Fig. 2. The mass loss trend is in agreement with the theoretical data and there is a slight increase in the mass loss for samples prepared by microwave compared to conventionally melted ones. The mass loss also increases gradually with the ZnO content.

The powder density values of zinc iron phosphate glasses prepared using microwave and conventional processing decreased with the decreasing ZnO content as in Fig. 3. The powder density of the zinc iron phosphate glasses prepared using the microwave processing is found higher than the ones produced conventionally.

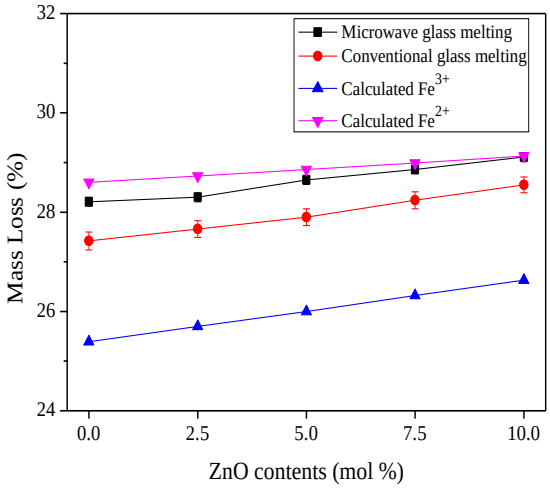

Fig. 2 Mass loss of zinc iron phosphate glasses.

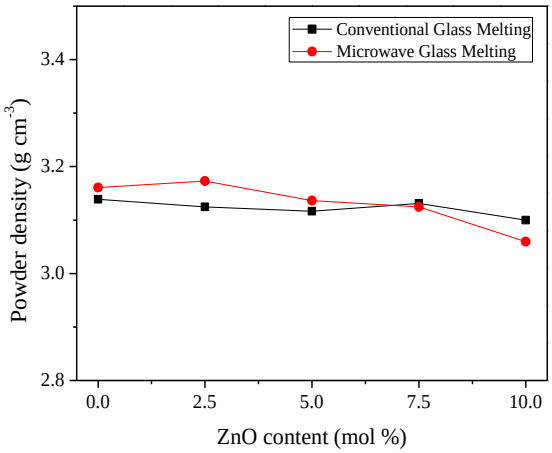

Fig. 3 Powder density of zinc iron phosphate glass

Identical trend of the FTIR spectra for the zinc iron phosphate glasses prepared using microwave and conventional processing are recorded in Fig. 4 and Fig. 5 respectively. In

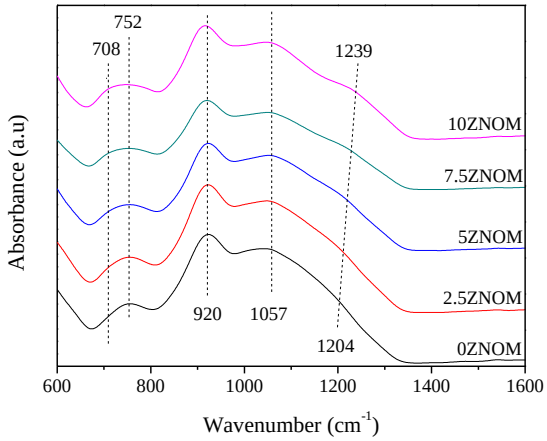

Fig. 4 FTIR spectra of zinc iron phosphate glasses prepared using microwave processing.

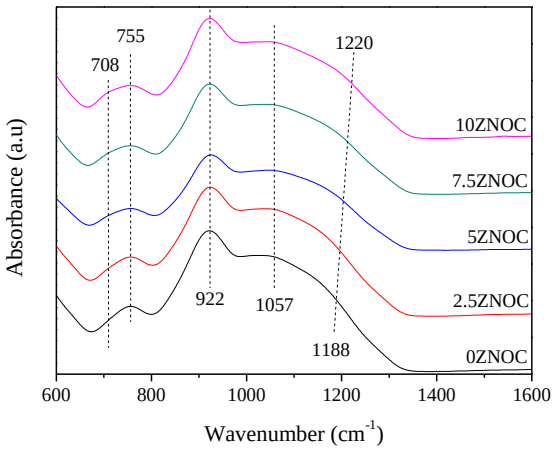

Fig. 5 FTIR spectra of zinc iron phosphate glasses prepared using conventional processing.

general, similar spectral changes and peak assignments can be seen in all zinc iron phosphate glasses indicating that the glasses having similar chemical functional groups. The peaks were shifted to the right with the increasing ZnO content at the wavenumber of 1204 to 1234 cm^{-1} in Fig. 4 and 1188 to 1220 cm^{-1} in Fig. 5. The peaks assigned to the specific bonding related to the zinc iron phosphate glasses are as follows: shoulder at 708 cm^{-1} in Fig. 4 and Fig. 5 may be due to the vibration of Fe-O-P bond [5]; 752 cm^{-1} in Fig. 4 and 755 cm^{-1} in Fig. 5 attributed to the

symmetric stretching vibration of P-O-P bridge [2]–[5]; 920 cm^{-1} in Fig. 4 and 922 cm^{-1} in Fig. 5 are due to the asymmetric stretching vibrations of P-O-P bridges [2], [4,5], [15]; 1057 cm^{-1} in Fig. 4 and Fig. 5 are assigned to the asymmetric stretching of the $(PO_3)^{2-}$ terminal group [4,5]; 1204 to 1239 cm^{-1} in Fig. 4 and 1188 to 1220 cm^{-1} in Fig. 5 attributed to the asymmetric stretching vibration of PO_2 in Q^2 units [5].

4. Discussion

Microwave and conventionally melted zinc iron phosphate glasses resulted in similar physical properties hence it is suggested that the temperature reached during microwave processing is around 1300 ˚C. If ammonium dihydrogen phosphate is assumed to complete the decomposition process during microwave heating *i.e.*

$$2\left[NH_4H_2PO_4\right] \xrightarrow{\Delta Q} P_2O_5 + 2NH_3 + 3H_2O \quad (2)$$

Hence the theoretical mass loss was calculated based on two oxidation state of iron; all iron being present as Fe^{3+} *i.e*

$$4Fe_3O_4 + O_2 \xrightarrow{\Delta Q} 6Fe_2O_3 \quad (3)$$

Or all of the iron being present as Fe^{2+} *i.e*

$$2Fe_3O_4 \xrightarrow{\Delta Q} 6FeO + O_2 \quad (4)$$

In the mass loss data (see Fig. 2), the zinc iron phosphate glasses prepared using conventional and microwave processing still indicates the present of Fe^{2+}. Although theoretically all Fe_3O_4 from the batch should transform to Fe^{3+}. This is due to the complication of Fe^{2+} and Fe^{3+} ratios in the zinc iron phosphate glasses which indicates incomplete oxidation process during microwave melting.

The powder density values decreased with the increasing ZnO content and decreasing Fe_2O_3 content. This may be attributed to the replacement of Zn^{2+} with Fe^{2+} which decreases the cross-link in the density of the zinc iron phosphate glass [4]. This also in agreement with the increasing mass loss values of zinc iron phosphate glasses prepared using microwave and conventional processing.

No significance difference can be seen in the FTIR spectral between the zinc iron phosphate glasses prepared using the conventional and microwave processing methods; this confirmed that the glasses having similar chemical bonding. The FTIR spectra correspond to the linkage of P-O-P at wavenumber 752 and 920 cm^{-1} in Fig. 4; 755 and 922 cm^{-1} in Fig. 5. Wavenumber of 752 and 755 cm^{-1} in Fig. 4 and Fig. 5 respectively are related to the decreasing of P-O-P linkage as the Fe_2O_3/ZnO ratio increased, this suggested that the sample has a pyrophosphate structure [10]. The band at 920 cm^{-1} in Fig. 4 and 922 cm^{-1} in Fig. 5 attributed to the asymmetric stretching vibrations of P-O-P bridge shows that the P-O-P bond is strengthened as the O/P ratio increased. The peaks in microwave and conventional processing shifted to the right from 1204 cm^{-1} to 1239 cm^{-1} in Fig. 4 and 1188 cm^{-1} to 1220 cm^{-1} in Fig. 5 as the content of ZnO increased. This is due to the increasing of O/P ratio which leads to the breakage of more P=O bond and more Zn-O-P bond are formed, thus leads to the variation of glass structure [10].

5. Conclusions

The zinc iron phosphate glasses has been successfully melted in 10 minutes using the microwave glass processing method. The mass loss and FTIR data have shown that the glasses prepared via microwave processing tend to have similar physical and structural properties as the glasses prepared conventionally. It can be seen from the powder density investigation, the microwave processing has higher powder density values than the conventionally melted ones. The FTIR spectra of the studied compositions show that P-O-P bonds is replaced by the Zn-O-P bond thus enhancing the chemical durability and strengths of the glasses. The processing time is also reduced for the microwave melted samples compared to conventionally melted ones which required 5 hours melting time.

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