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Characterization of Two Frit Ceramic Materials in Low Cost Fertilizers

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Abstract

Two frit ceramic materials were prepared from minerals (phosphate and feldspar) and other low-cost materials (bones and glass cullet). These powders can be used in agriculture as fertilizers since they are able to release the nutrient elements at a low rate. The above materials were characterized by X-ray Diffraction, Photoluminescence Spectroscopy, Scanning Electron Microscopy and Inductively Coupled Plasma Atomic Emission Spectrometry. The dissolution kinetic of macro and micro nutrients, components from frit materials, was also studied. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

The use of chemical fertilizers has increased the efficiency of the harvest, but their use leads to the contamination of the soil.[1,2] The washing away of the mentioned fertilizers, which occurs by the superficial water, gives also rise to the contamination of the phreatic layers.

In order to mitigate this problem a series of products, the so-called 'controlled release fertilizers', arose. These materials can liberate nutrients according to the needs and phases of growth of the plants, thus they must not be added in high amount. However, most of them are traditional fertilizers with a sparingly soluble coating,[3,4] though subsequently other researchers[5–7] prepared glasses with this aim from analysis grade reagents as starting materials. These latter works have been patented.

In this context the main objective of the present work consists of comparing and characterizing two glass–ceramic powders obtained from minerals (phosphates and feldspar) and other low-cost materials (bones and glass wastes) in order to determine: (i) their utility in agriculture as fertilizers since they are able to release the nutrient elements (P, K, Ca, etc) at low rate, (ii) other possible applications.

2 Experimental

2.1 Starting materials and processing

Starting materials were selected taking care of the contents in nutrient elements for the plants (phosphorous, potassium) and their low-cost. Then, waste materials (minerals of phosphorous and bones), cullet, etc., were used (Table 1).

Both compositions were melted in an aluminumsilicate crucible in a Superkhantal furnace with elevator at 1400°C, at a heating rate of 10°C min^{-1} for 30 min. The melts were subsequently poured into distilled water at room temperature in order to obtain a frit. The particle size obtained was $d_m < 2$ mm.

2.2 Experimental techniques

2.2.1 Chemical analysis and leaching attack

CBK and BPF glass–ceramics were milled in an agate mortar, then sieved to obtain powders with a particle size $0{\cdot}50\,\mathrm{mm} < d < 0{\cdot}80\,\mathrm{mm}$. These powders (0·20 g) were subjected to leaching attack with 200 ml of ammonium acetate buffer solution ($\mathrm{pH} = 5{\cdot}7$) for different time periods at a constant temperature of 25°C in a container which were shaken periodically. The lixiviated elements (Al, Ca, K, Na, P, Si) and their chemical analysis in the glass–ceramics were determined by ICP-AES and atomic absorption spectrometry.

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Table 1. Starting compositions to obtain the two glass–ceramic materials

Composition	*Starting materials*
CBK	Cullet (40 wt%) Bones (40 wt%) Potassium carbonate (20 wt%)
BPF	Bones (25 wt%) Phosphorite from Capinota, Cochabamba, Bolivia (25 wt%) Feldspar from Segovia, Spain (50 wt%)

Table 2. Chemical composition of the materials

	CBK		*BPF*	
Oxides	*Weight%*	*Mol%*	*Weight%*	*Mol%*
P_2O_5	17·1	8·33	14·6	7·27
CaO	26·3	32·4	18·9	23·8
K_2O	13·6	9·99	8·49	6·34
SiO_2	32·5	37·4	45·8	53·7
Al_2O_3	1·98	1·34	8·48	5·85
Fe_2O_3	0·19	0·08	1·02	0·44
Na_2O	6·19	6·90	1·73	1·96
MgO	2·00	3·43	0·24	0·42
MnO	—	0	0·08	0·08
Nd_2O_3	—	0	0·02	0·004

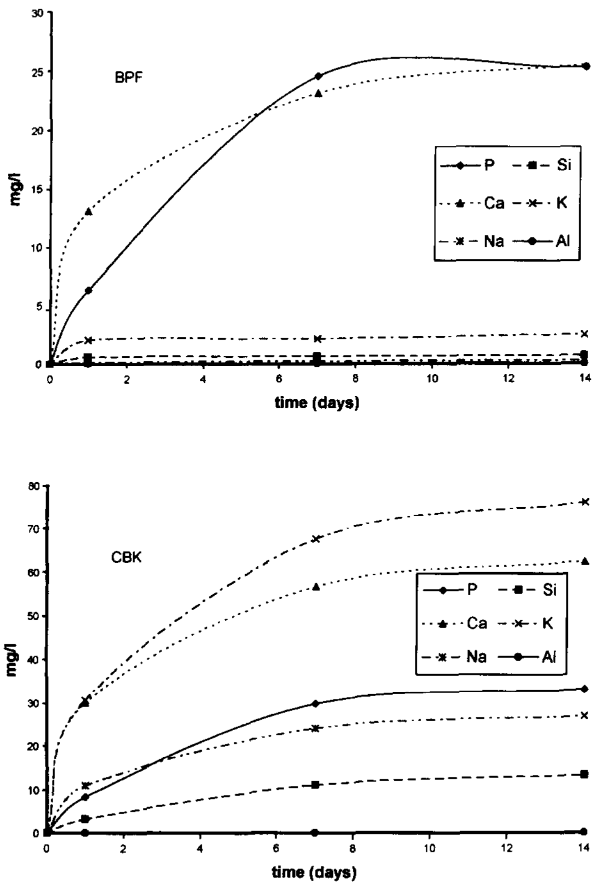

Fig. 1. Solubility of the BPF and CBK materials.

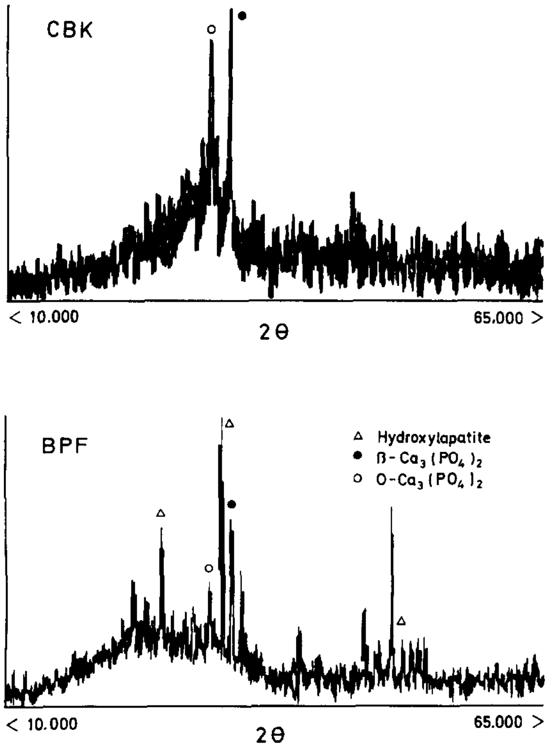

Fig. 2. XRD patterns for both materials.

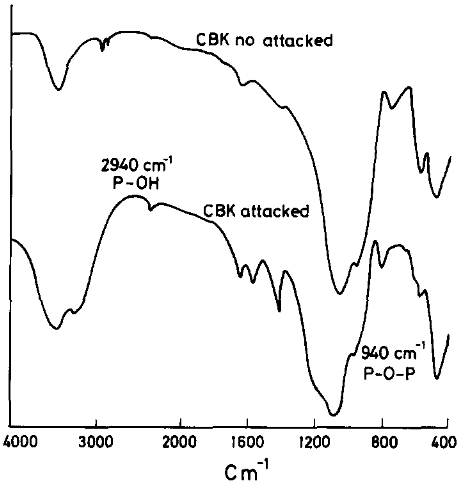

Fig. 3. FT-IR spectra of the CBK sample.

A Jobin–Yvon model JY-38VHR sequential spectrometer with an ICP source equipped with a high resolution monochromator (3600 grooves mm^{-1}) and a Perkin–Elmer model 2100 atomic absorption spectrophotometer, equipped with the HGA-700 graphite furnace, the AS-70 furnace autosampler and a deuterium background corrector were used in these determinations.

2.2.2 *X-Ray diffraction*

The XRD pattern of the glass-ceramics were obtained in a Siemens Diffractometer, D5000 Kristalloflex.

2.2.3 *FT-IR spectrophotometry*

The infrared spectra (FT-IR) of the CBK and BPF glass-ceramics were measured in a 1760X (Perkin Elmer) Fourier Transform–Infrared Spectrophotometer in the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. Ten scans were measured for each spectrum. The pellet method

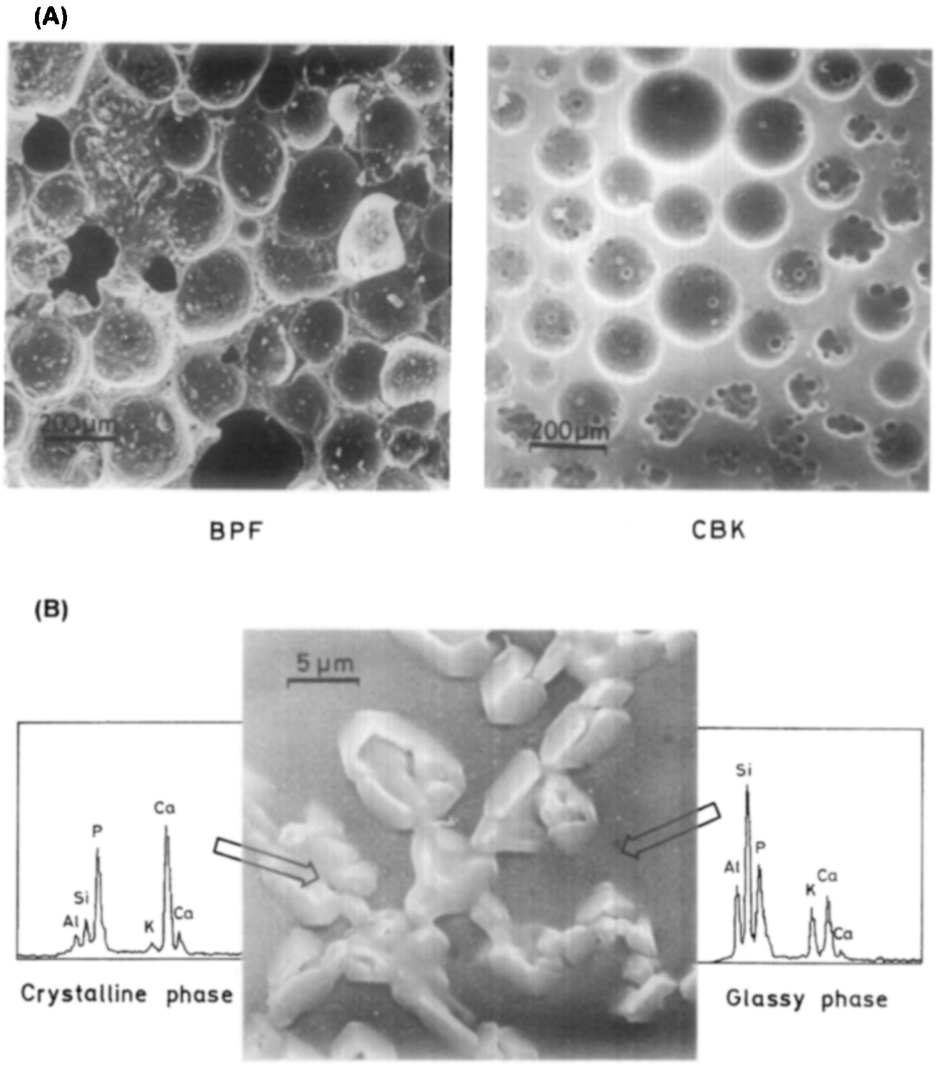

Fig. 4. SEM micrographs showing (A) the cellular structure (B) the presence and composition of crystalline phase and glassy phase.

was used where 1 mg of glass–ceramic sample and 300 mg of KBr were mixed thoroughly and quickly and then pressed at 8 Tm for 2 min under vacuum.

2.2.4 Scanning electron microscopy
The microstructure of the powders was studied by SEM/EDX with a ZEISS 950 MSD microscopy.

2.2.5 Photoluminescence spectroscopy (PL)
An apparatus (Laser Point), equipped with a 25 mW He–Ne Laser (NEC), a grating spectrometer (Jobin Ybon 640-HR) with a reciprocal dispersion of 2·4 nm mm^{-1}, a liquid-N_2 cooled germanium detector (North Coast E0817L), was used to obtain the glass–ceramic spectra.

3 Results and Discussion

The chemical analysis of the materials is shown in the Table 2. It can be seen the high content in P, K and other nutrient elements in both samples. All these elements are removed at a low rate as can be deduced from Fig. 1. From this figure it is also deduced that the solubility of the sample CBK is noticeably higher than that of BPF. P is more easily leached than Si (both elements are network formers). Thus it can be supposed in principle the following mechanisms: Si is leached by superficial dissolution according to the following equation:

$$c = kt$$

where *c = concentration*, *k = constant*, *t = time*. P and the other nutrients are leached by diffusion, according to the equation:

$$c = kt^{1/2}$$

The X-ray diffraction patterns of studied materials are shown in Fig. 2.

It can be deduced from them that the mean crystalline phase of the sample BPF is hydroxylapatite $(Ca_{10}(PO_4)6(OH)_2)$, $\beta-Ca_3(PO_4)_2$ and $\alpha-Ca_3(PO_4)_2$ being in less proportions. The sample CBK only contains the last two in similar proportion.

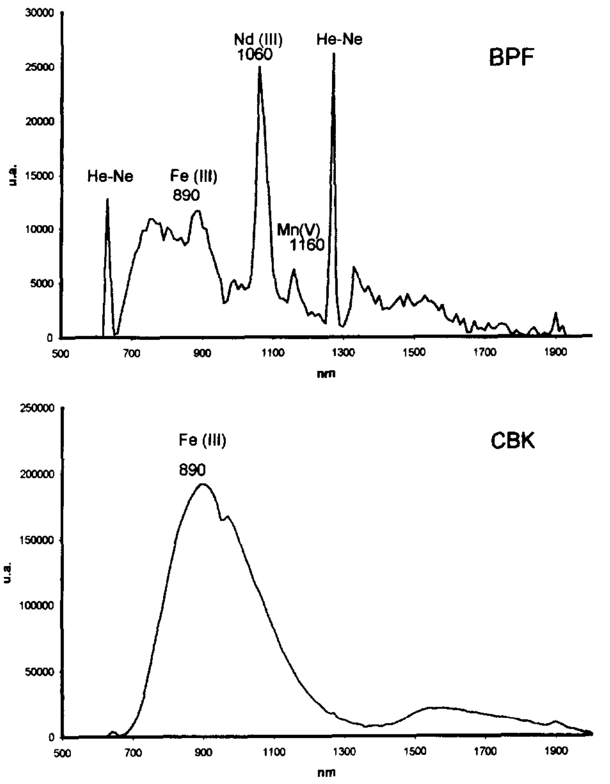

Fig. 5. PL spectra of the BPF and CBK materials.

The α– phase is the most soluble of the three phosphates as it was reported by Ducheyne,[8] and Lindsay[9]. According to the leaching data (Fig. 1) the sample CBK is more soluble than BPF one. This fact is due not only to the presence of α–$Ca_3(PO_4)_2$ but additionally to its higher content in alkalies in the glassy phase which makes it more accessible to the attack by the water.

Figure 3 shows the FT-IR spectra of the CBK sample, the ratio of the intensities of the bands at 910–940 cm^{-1} (corresponding to P–O–P bonds[10]) and 1065 cm^{-1} (of phosphates) is lower in the case of the attacked sample. This fact confirms that the attack breaks the oxygen bridge bonds. Thus, the band corresponding to the P–O–P bonds decreases. When more atoms of terminal oxygens are formed, the bands which lie between 1065 and 1200 cm^{-1} are better differentiated and the band at 2940 cm^{-1} due to the bond P–OH increases.

Figure 4 shows the micrographs and energy dispersion X-ray microanalysis of the materials. The microstructure of both samples is similar and shows big pores of a size of $d_m = 100\,\mu m$. This fact favors the attack by the water. It is also observed a glassy phase made up by alkaline phosphosilicates, more abundant in the sample CBK. Crystals of the phosphates embeded in the mentioned phase can be seen in this microstructure.

The PL spectra of the samples, recorded at room temperature are shown in Fig. 5. BPF spectrum exhibits in the 1000–1250 nm region an intense emission peaked at 1060 and a less intense band at 1160 nm. In agreement with previous work[11–13] we assigned the above bands to emission from Nd (III) and Mn(V) ions, respectively. These emissions are not observed for the CBK sample. This PL spectrum presents a wide band assigned to Fe(III) that can be resolved only at low temperature.[14]

The uncommon ion Mn (V) that was found in raw mineral material phosphorite[11] appears to survive mechanical and thermal treatments in the BPF glass-ceramic. This finding stimulates further investigation of physico-chemical behaviour of Mn(V), in order to synthetize new crystalline and amorphous materials with peculiar optical applications.

4 Conclusions

- Two glass–ceramic powders (CBK and BPF) has been designed and synthetized. Because of their composition, microstructure and elements leaching rate in water solution they could be used as controlled release fertilizers.
- The nutrient solubility of CBK material is higher due to their content in α–$Ca_3(PO_4)_2$ and their glassy phase, rich in alkaline phosphosilicate.
- The mechanism of dissolution of these materials is very complex because of the presence of various phosphates crystalline phases and a glassy phase with two network formers.
- Luminescence related to the Nd (III) and Mn(V) ions is observed in the BPF glass-ceramic and this could be interest in the field of solid state lasers.

Acknowledgements

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