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Alkaline and alkaline-earth silicate glasses and glass-ceramics from municipal and industrial wastes

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Abstract

Municipal (bottom ash and glass cullet coming from the municipal solid waste incineration and a community glass recycling program, respectively) and industrial (steel fly ash) wastes are particularly suitable to be subjected to a vitrification/devitrification process, leading to the production of alkaline and alkaline-earth silicate differently colored glasses with good chemical properties, capable to be transformed into surface nucleated basaltic glass-ceramics. These materials were investigated by means of differential thermal analysis, durability and release tests, X-ray diffraction and scanning electron microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recycling and valorisation of by-products and waste materials coming from municipal and industrial processes has become a problem more and more urgent for the next future. In the light of environmental norms aiming at limiting the use of the dump, the development of new recycling techniques capable also of exploiting the wastes into new marketable products acquires an increasing importance. Because of the complex chemical composition and the presence in some cases important than others of heavy metals in the wastes (dangerous special or special waste) the vitrification/devitrification technique, already used for nuclear wastes,[1,2] may represent a good opportunity. In particular, the properties that a glass should exhibit, such as good melting behaviour, homogeneity, durability, etc., are closely related not only to the chemical composition, but also to kind and quantity of raw materials used during the melting process. In this perspective, it is important that wastes of different origin are simultaneously submitted to vitrification, so that each of them may contribute to supply the appropriate quantities of vitrifying (SiO_2, Al_2O_3...), melting (Na_2O, K_2O....) and stabilizing (CaO, MgO, ZnO, PbO...) agents in the final glass and so that suitable physical-chemical features can be obtained.[3,4] The vitrification process simulates what already happens in nature: natural glasses produced by volcanic eruptions, such as obsidians (Na_2O–K_2O–Al_2O_3–SiO_2) and basaltic (CaO–MgO–Al_2O_3–SiO_2) rocks, are basically inert materials even when they contain toxic elements, because these are embedded in an extremely stable glassy matrix. The behaviour of basalt rocks is a good example to get an idea of the corrosive effect of atmospheric agents. The composition of these rocks can be simulated by mixing different kinds of wastes and their leaching rate never exceeds 1 mm in 100 000 years.[5] Consequently, waste glass, too, will interact to a negligible extent with the environment around, not releasing thus significant amounts of the toxic elements in it, even one thousand times less than those released by the same waste not vitrified. Through this last technique it is possible to obtain monolithic glasses which, by controlled thermal treatments, can be transformed into glass-ceramics, particularly of wollastonite ($CaO{\cdot}SiO_2$), diopside ($CaO{\cdot}MgO{\cdot}2SiO_2$), anorthite ($CaO{\cdot}Al_2O_3 2SiO_2$) and iron oxides ($Fe_2O_3$, Fe_3O_4) in order to obtain coating materials with high chemical and mechanical properties for building or thermomechanical applications.[6]

In this work, we investigated the possibility to obtain alkaline and alkaline-earth silicate glasses and glass-ceramics from bottom ash (special waste) coming from a municipal solid waste incinerator and/or steel plant fly

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ash (dangerous special waste). The incineration process, in countries where the population density is high and the availability of space for landfilling is limited, is becoming more and more in use; its objectives are:

- reduction of volume and mass of the waste in order to save the scarce and expensive space of the landfills;
- complete destruction of all organic matter in order to guarantee a total disinfection of the waste stream;
- detoxification of inorganic pollutants present in the waste;
- use of the energy contained in the waste stream.

On the other hand, this process produces a large amount of solid residues such as bottom ash (300 kg for 1000 kg of waste burnt), boiler ash and filter fly ash (30 kg for 1000 kg of burnt waste) and since the modern waste management system is based on avoidance, reuse and recovery strategies, the recycling of these materials is interesting both from a technological and an economical point of view.[7] As for the second kind of waste, that is steel fly ash, it is rich in Fe_2O_3 and ZnO and comes from the filtering of furnaces and waste gases on melting iron scraps and refining raw steel in electric arc furnaces and it is nowadays laid in dump.

2. Experimental procedure

As suggested by the results derived from a previous research,[8,9] in this work alkaline and alkaline-earth silicate glasses and glass-ceramics were obtained from the waste raw materials reported in Table 1. From the same table it is evident that:

a. municipal bottom ash contains the characteristic chemical constituents of glass;
b. steel fly ash could be introduced in a glass to increase the Fe_2O_3 and ZnO content in order to confer colour to a transparent glass, to increase the tendency toward crystallisation (Fe_2O_3) and to lower the melting temperature and the melt viscosity without affecting the chemical properties of the material (ZnO);
c. glass cullet could decrease the viscosity of the melts thanks to the Na_2O content.

Therefore, these raw materials were mixed together in the ratios reported in Table 2 also in order to point out the main differences with respect to the parent systems (S10 and V10).

It is important to note that for evaluating the colouring effect of steel ash on the glass, white glass cullet was used.

Table 1
Average chemical composition (wt.%) of the raw materials used

Oxide	Municipal incinerator bottom ash	Steel fly ash	Coloured glass cullet	White glass cullet
SiO_2	45.13	3.84	70.3	70.3
Al_2O_3	9.73	1.14	2.18	1.16
CaO	18.78	5.84	9.30	9.42
MgO	2.20	3.18	2.13	4.15
Na_2O	4.64	1.36	13.32	12.74
K_2O	1.29	0.76	1.19	0.33
Fe_2O_3	3.84	45.25	0.293	0.27
ZnO	0.32	25.44	0.12	0.10
TiO_2	0.93	0.08	0.068	–
MnO	–	3.11	–	–
Cr_2O_3	0.04	0.61	0.071	0.02
PbO	0.01	2.69	0.074	0.04
CdO	–	0.07	–	–
NiO	–	0.12	–	–
CuO	–	0.49	–	–
SnO_2	–	0.12	–	–
BaO	0.17	0.11	0.15	0.06
ZrO_2	0.29	–	0.06	–

Table 2
Wt.% components ratio in the studied compositions

Composition	Municipal bottom ash	Steel fly ash	Coloured glass cullet	White glass cullet
S10	100	–	–	–
S9	90	–	10	–
S9P1	90	10	–	–
V10	–	–	–	100
V9P1	–	10	–	90

The raw materials were dry mixed. Only for the municipal bottom ash a previous treatment of oven-drying and grinding was necessary in order to favour the homogeneity of the system. Glasses were obtained by melting in refractory crucibles at 1500°C in an electric furnace for about 5 h and by quenching in a graphite mould in air. They were subsequently annealed by holding them for 1 h at a temperature in the 570–650°C range depending on the composition. This temperature was chosen 10°C over the glass transition temperature, T_g, on the basis of DTA analysis. The samples were then slowly cooled down to room temperature in order to release stresses and to be able to cut suitable pieces for chemical and mineralogical analyses.

The experimental procedures performed on the above described glasses are:

1. Differential thermal analysis with a Netzsch DSC 404 equipment on glassy powders less than 25 μm in size and fired from 20 to 1400°C at the rate of 10°C/min in static air.

2. Durability tests in:
   a. Water (ISO 719) which requires 2 g of powder of the sample, 250–500 μm particle size, in 50 ml of water, all immersed in a boiling water bath for 1 h. Quantitative analysis of alkali release was in this case made by ICP (induction coupled plasma Varian Liberty 200).
   b. Acid (DIN) which requires bulk glass of known geometry in a boiling 6 mol/l HCl solution for 6 h. Leaching evaluation depends on the sample weight loss.
   c. Alkali (ISO 695) which requires a bulk sample of known geometry boiled for 1 h in an aqueous solution containing 1 mol/l of NaOH and 0.5 mol/l of Na_2CO_3. Same leaching evaluation method described in b).

3. Release test in acetic acid[10] for which a piece of glass is placed in 16 times the sample weight distillated water for 24 h, maintaining the solution at a $pH < 5$ with an HAc solution (0.5 M). Once extracted the sample, the volume is brought to 20 times the sample weight by adding distilled water and acidified by HNO_3 (65 wt.%) to obtain a concentration of 8 cc/l of the same acid. The quantitative analysis of the metallic micropollution is performed by ICP.
4. X-ray powder diffractometry with a Philips PW 3710 instrument in the 2θ 5–60° range to determine the devitrification tendency and the crystalline phases present in the heat treated glass samples of dimension $1\times1\times0.5$ cm.
5. Microstructural studies by means of scanning electron microscopy (SEM Philips XL 40) over Au/Pd sputtered coated samples, embedded in epoxy resin and subsequently polished with SiC and Al_2O_3 paste (0.5–0.3 μm).
6. Colour measurements (for the white glass cullet-containing series only) using a UV–Vis spectrophotometer with analytical software for colour measurements (Perkin-Elmer, Lambda 19) with CIELAB method, used in the ceramic practice and usually accepted to tell the color of a product. The method measures the absorption intensity in the visible region to obtain the L^*, a^*, b^* parameters, measuring brightness, red/green and yellow/blue color intensity, respectively.[11]

3. Results and discussion

The thermal behaviour of the glasses studied is shown in Fig. 1(a) and (b). As for the bottom ash-containing samples [Fig. 1(a)], a slight decrease in the glass transition temperature is observed when a 10 wt.% of other kind of waste is introduced ($T_{\mathrm{g}}^{\mathrm{S10}}\sim650$°C and $T_{\mathrm{g}}^{\mathrm{S9,S9P1}}\sim635$°C), because of the effect of Na_2O and ZnO modifier oxides, while the crystallisation temperature shifts toward a lower value with the steel fly ash introduction only thanks to the iron oxide nucleating effect ($T_{\mathrm{C}}^{\mathrm{S10,S9}}\sim940$°C and $T_{\mathrm{C}}^{\mathrm{S9P1}}\sim870$°C). This last oxide is also responsible for a second exothermic peak near 990°C due to the formation of iron crystalline phases. In the white glass cullet-containing series [Fig. 1(b)], the addition of fly ash induces a beginning of crystallisation at about 800°C, absolutely absent in the sample V10, and this is again due to the increase in iron content. By the evaluation of DTA data, the ratio between glass transition and melting absolute temperature, $T_{\mathrm{g}}/T_{\mathrm{m}}$, was obtained. This ratio is, according to Zanotto[12] and James and Jones[13] an useful parameter to identify the crystallisation process. The crystallisation mechanism is bulk crystallisation if $T_{\mathrm{g}}/T_{\mathrm{m}} < 0.58$ and a surface crystallisation if $T_{\mathrm{g}}/T_{\mathrm{m}} > 0.58$ (in the studied glasses it always resulted to be > 0.60 and therefore surface crystallisation is favoured with respect to internal crystal nucleation). A further information that can be obtained from the thermal experiments is the devitrification activation energy. When DTA and DDTA can be simultaneously recorded, the method of the derivative differential thermal analysis (DDTA) for a surface mechanism is applicable[14] in

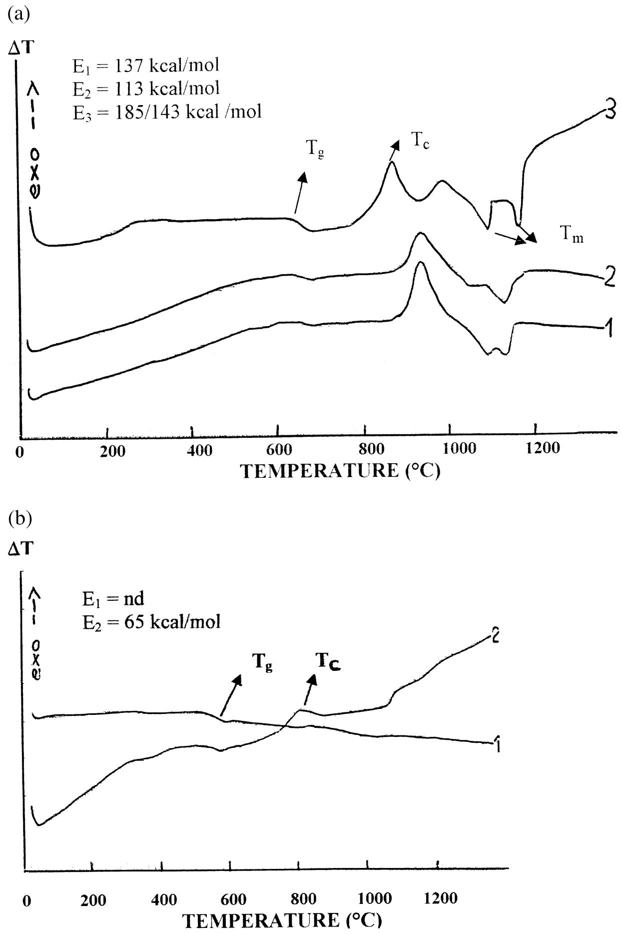

Fig. 1. DTA curves and devitrification activation energy values of glasses: (a) (1) S10, (2) S9 and (3) S9P1; (b) (1) V10 and (2) V9P1.

order to obtain the range of the devitrification activation energy values.[15] An interesting observation about the values obtained, reported in Fig. 1(a) and (b), is that the glasses belong to the range of the aluminosilicate (86–313 Kcal/mol[16]) and in particular the values are close to those characteristic of surface devitrification processes for basaltic glasses, belonging to the CaO–MgO–Al_2O_3–SiO_2 system, (77–131 kcal/mol).[17] A discussion about the single values obtained is too difficult because many and different crystalline phases are all present at the same time. For the white glass-cullet-containing series, the V10 glass activation energy was not calculated because this composition did not show any crystallisation peak, and the V9P1 value (lower with respect to the previous ones) is not reliable because of a too small crystallisation peak.

Since glasses which contain mobile ions, such as Na^+ or K^+, are subjected to leaching processes in which these ions diffuse into the surrounding liquid from the surface region, all the prepared glasses were subjected to durability tests. These tests divide glasses into categories and a low category number designates good durability. The results are listed in Table 3.

Table 3
Studied glass belonging class in three reaction environments

Composition	Water durability[a]	Alkali durability[b]	Acid durability[c]
S10	1	2	4
S9	1	1	4
S9P1	2	1	4
V10	3	1	3
V9P1	2	1	3

[a] 1, very high resistance, 2, high resistance, 3, medium resistance.

[b] 1, low alkali attack, 2, slight alkali attack.

[c] 3, slight acid attack, 4, high acid attack.

In the white glass cullet-containing series, water durability is improved by adding the steel fly ash (V9P1), because this addition causes a decrease of the content of those cations more subjected to the leaching action, viz. alkaline metals [$Na_2O_{(V10)} = 12.72$ wt.% and $Na_2O_{(V9P1)} = 11.27$ wt.%]; alkali and acid durability remains constant. As far as the bottom ash series is concerned, the addition of either glass cullet (S9) or steel ash (S9P1) improves the alkali durability with respect to the S10 composition, while the addition of steel ash worsens water durability. An important observation is that for all the prepared glasses acid durability is not very good because the test used is too drastic (boiling 6 mol/l HCl solution for 6 h).

Furthermore, by considering the particular waste nature of the raw materials, we also carried out the release test in acetic acid to simulate the behaviour of the waste incorporated in the glassy matrix when exposed to the leaching both of the rain and of the percolates from organic and inorganic mixed dumps. For all the glasses studied we obtained very low release values for metallic micropollutants, all in the range allowed by the Italian regulations, necessary condition for their reutilization as product of a inert waste.

All the materials, after quenching in air, showed to be completely amorphous and the subsequent conversion into the corresponding glass-ceramics was performed by the application of several different thermal treatments, decided on the basis of the composition. In general, the XRD patterns recorded on the above mentioned samples presented a change in the reflections to attribute to the different crystalline phases present depending on the glass-ceramic composition and thermal treatment performed (Figs 2 and 3), but the pyroxene (augite (AU)[Ca(Fe,Mg)-Si_2O_6] and/or diopside (D)[Ca(Mg,Al)$(Si,Al)_2O_6$]) resulted to be the thermodinamically most favoured phase, in

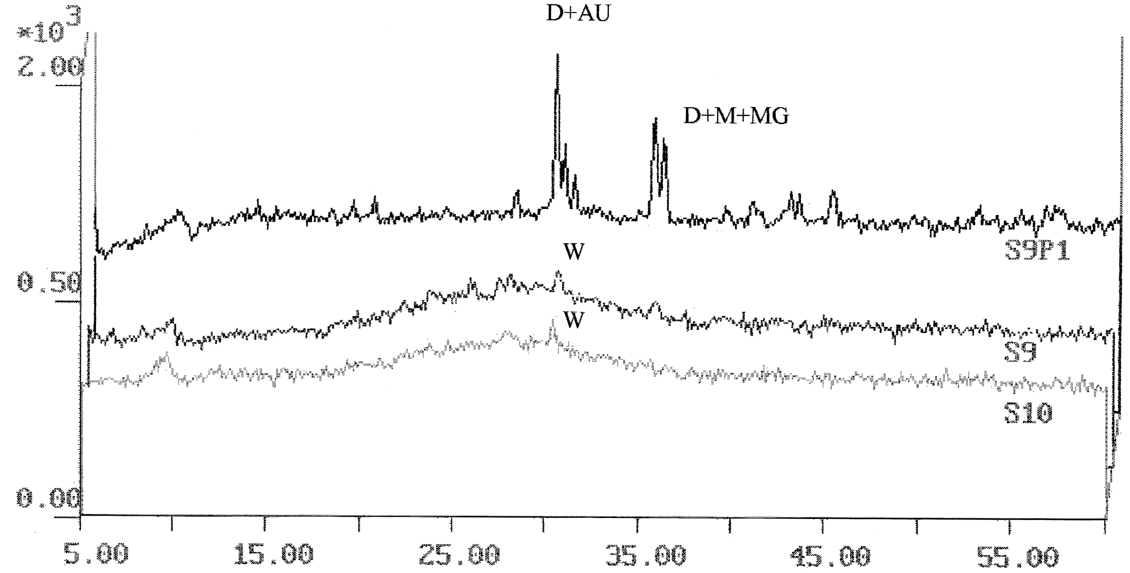

Fig. 2. XRD patterns recorded on S10, S9 and S9P1 glass-ceramics treated at 1000°C for 1 h.

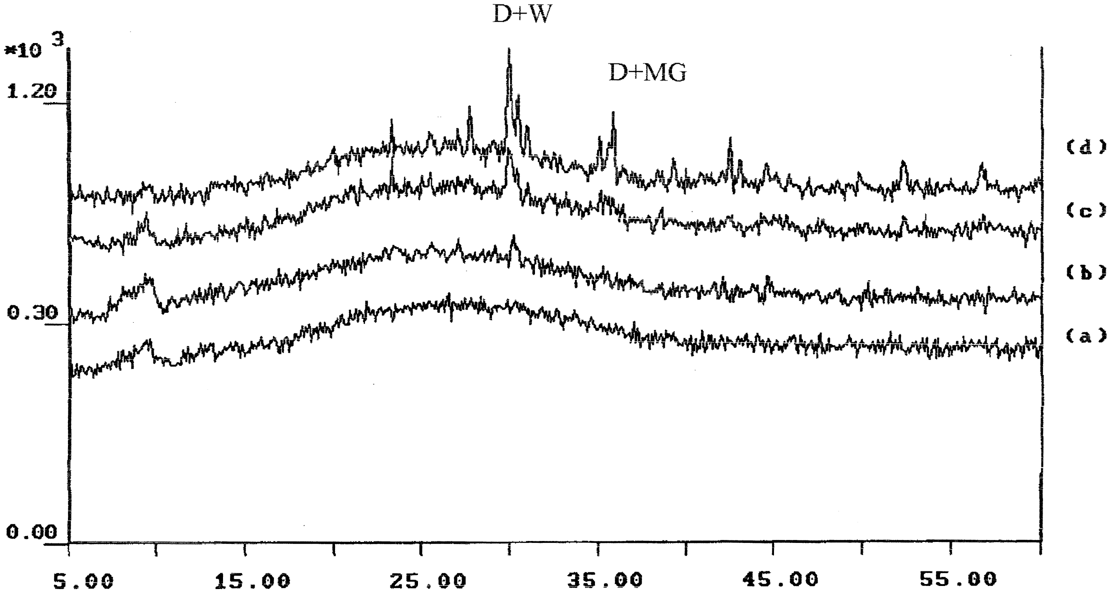

Fig. 3. XRD patterns recorded on the V9P1 glass-ceramics obtained by a thermal treatment of 900°C for (a)1, (b) 4, (c) 8 and (d) 16 h.

fact it is present in all the studied compositions (except for V10 since it does not crystallise). The steel fly ash effect is very evident in both the municipal bottom ash and white glass cullet-containing series, in which iron oxides such as (MG) maghemite (M)[Fe_2O_3] and magnetite (W)[Fe_3O_4] are present. As for the bottom ash series, in the S10 (constituted of municipal waste only) and S9 samples, the identified crystalline phases are anorthite sodian [$(Ca,Na)(Si,Al)_4O_8$], augite [$Ca(Fe,Mg)Si_2O_6$], diopside [$Ca(Mg,Al)(Si,Al)_2O_6$], and wollastonite (W)[$CaSiO_3$]; on the other hand, after the addition of steel fly ash (S9P1), iron oxides and franklinite [$ZnFe_2O_4$] replaced anorthite sodian and wollastonite. The degree of crystallisation was evaluated as a function of the composition for the same thermal treatment (Fig. 2). From the same figure, it appears evident that the steel fly ash acts as a catalyst for the crystallisation process.

When the steel fly ash is added to the white glass cullet, which does not crystallise by itself, it acts as a devitrification promoter (wollastonite, maghemite and diopside) as evident from Fig. 3 which shows the tendency towards crystallisation of different specimen of the V9P1 composition that were treated at 900°C for different times.

In order to confirm DTA and XRD data and to draw more information about the crystallisation mechanism, microstructure and crystals dimension, SEM analysis on a polished section of a glass-ceramic piece was performed. Fig. 4 shows the microstructure of a glass-ceramic, heat-treated at 1000°C for 8 h, belonging to the bottom ash-containing series. First of all, the surface mechanism was confirmed, in fact crystallisation starts from the glass surface and grows toward the inside of the glassy matrix.

From the same micrograph, it is possible to note that two different microstructures are present, one acicular, characteristic of the wollastonite phase, and the other one dendritic, characteristic of pyroxene, and the different kind of crystals are very different in size, from 5 up to 50 μm. In the white glass cullet-containing samples, acicular crystals rich in silicon and calcium, i.e. wollastonite, are also present [Fig 5(a) and (b)], but rhombic-shaped crystals slightly richer in iron and zinc [Fig. 5(c) and (d)] grow from the glassy matrix. It is possible to note that in this series more residual glassy phase is present with respect to the previous series, confirming the XRD data which point out a stronger tendency toward crystallisation in the bottom ash samples.

The colour analysis results, limited to the white glass cullet-containing series and reported in Table 4, indicate

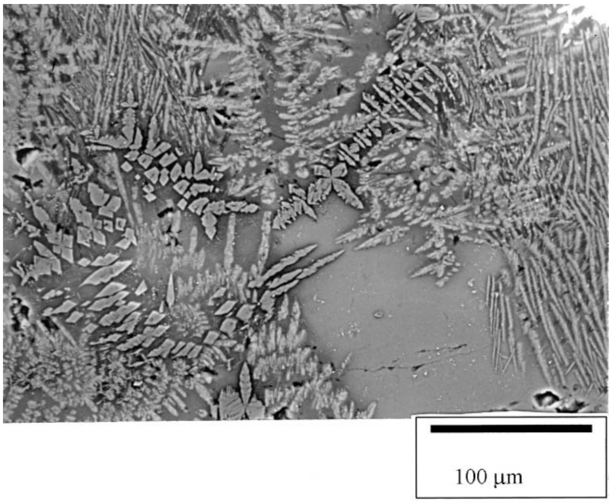

Fig. 4. SEM micrograph (300×) of S10 glass-ceramic heat-treated at 1000°C for 8 h.

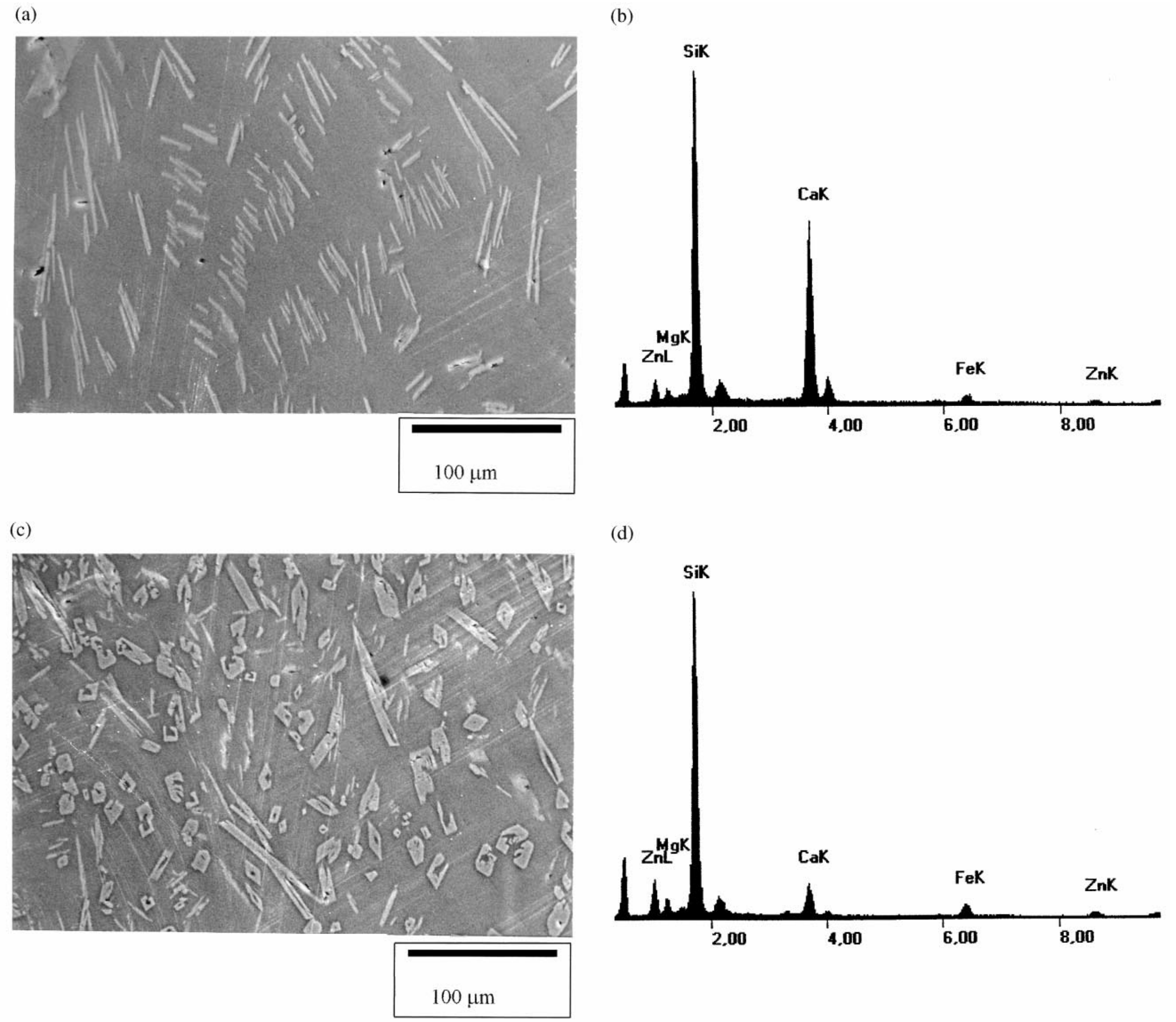

Fig. 5. SEM micrograph (300×) of V9P1 glass-ceramic heat-treated at 900°C for 16 h: (a) acicular crystals with (b) respective EDS analysis and (c) rhombic crystals with (d) respective EDS analysis.

Table 4
CIELAB L^*, a^*, b^* parameters for white glass cullet-containing glasses

Composition	L^*	a^*	b^*
V10	85.33	−0.88	−1.40
V9P1	42.93	−2.36	6.15

the highest brightness and the almost total absence of colour development in the V10 sample. In particular, from the V10 to the V9P1 glass the L^* value, which extends from absolute white ($L=100$) to absolute black ($L=0$), decreases; the values of the a^* and b^* parameters in relation to the scale extending from green ($-a^*$) to red (a^*) and from blue ($-b^*$) to yellow (b^*), respectively, shift towards lower a* and higher b^* indicating the appearance of the green/yellow colour in the V9P1 sample.

4. Conclusions

The experiments performed confirm the usefulness of the simultaneous vitrification of wastes of different origin to obtain low cost and common (alkaline and alkaline-earth silicate) glasses able to immobilise hazardous elements and to be transformed into glass-ceramics containing crystalline phases (wollastonite, diopside, anorthite and iron oxides) with well-known high chemical and mechanical properties. An accurate selection and proper ratios of the used wastes allows to produced glasses with suitable properties and suggests a possible way for waste recovery.

The municipal incinerator bottom ash belongs to the Si–Al–Ca system and so it is easily capable to give glass. In order to decrease the viscosity of the melts (visible as a lowering of the glass transition temperature in DTA), glass cullet can be added to the batch for increasing the Na_2O content. The transformation of these amorphous materials into the corresponding glass-ceramics is possible, but can be catalysed by the presence of steel fly ash. The nucleating effect of this Fe_2O_3 and ZnO-enriched by-product is particularly evident when it is added to the glass cullet because it promotes the devitrification process. Furthermore the same fly ash is able to confer colour to a transparent glass.

In general, all the compositions studied give stable glasses (with a negligible leaching) with good chemical durability both in alkali and in water, and develop basaltic glass-ceramics by a surface devitrification mechanism.

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