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Study of barium feldspar polymorphism as a function of temperature and calcium content

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A family of new glass-ceramic materials, of the general formula $(25\text{-}x)CaO \cdot xBaO \cdot yMgO \cdot zAl_2O_3 \cdot 50SiO_2$, where $x = 1, 2, 5, 10, 15, 20, 25$, $y = 20$ or 14 and $z = 5$ or 11 (mol %), has been prepared by melting raw materials in two parent glasses and performing heat treatments. The systematic substitution of BaO for CaO in the base glasses allows the effect of feldspars' isomorphism and polymorphism to be studied in a series of glass-ceramics where the structural environment around the bivalent cations, Ca^{2+} and Ba^{2+}, is systematically altered. Ba^{2+} has a large effect on the glass transition temperature and dilatometric softening point, causing a decrease with increasing BaO. The crystalline phases have been identified and found to be dependent on the preparation conditions, which are the BaO and Al_2O_3 contents, the heating rate and the soaking temperature adopted for the crystallization treatments. The infrared spectroscopy technique helped to identify the different polymorphs of barium feldspar, that were not clearly distinguishable by X-ray powder diffractometry due to preferred orientations. The kinetic parameters for the formation of the different crystals have also been determined and correlated with their thermal stability resumed in the well-known time–temperature–transformation curves.

1. Introduction

The barium feldspars are very interesting materials to study, both for their unique properties and for their complicated polymorphism. The low thermal expansion coefficient, high mechanical strength, chemical inertness, high melting temperature (near 1700 °C) and low dielectric constant are some of the properties which make it possible to use these materials in the ceramic, refractory and composite industries [1].

The three better known polymorphs of barium feldpars ($BaO \cdot Al_2O_3 2SiO_2$) are celsian and paracelsian, of the natural minerals, and hexacelsian as the synthetic form. The transformation temperatures may be represented as follows:

$$\underset{\text{Monoclinic}}{\text{Celsian}} \underset{\text{Slow}}{\overset{1590/1650\,^{\circ}\text{C}}{\rightleftharpoons}} \underset{\text{Hexagonal}}{\text{Hexacelsian}} \xrightarrow{1760\,^{\circ}\text{C}} \text{Melt} \quad (1)$$

It is important to note that according to some authors, the celsian–hexacelsian transition temperature shifts from 1650 to 1590 °C if hexacelsian is present as a solid solution with about 4% SiO_2 [2]. However, this transformation is so slow that hexacelsian is metastable at temperatures up room temperature. In the hexacelsian polymorph, a reversible transformation, at about 300 °C, involving the rotation of the hexagonal sheets of the two layers of the $(Al, Si)O_4$ tetrahedra with respect to each other, is also observed. This last transformation, which does not modify the fundamental framework, is not clearly visible in the XRD patterns, but the relative volume change, approximately 3%–4% [2], could produce degradation of the mechanical properties.

For all these reasons, it is evident how important it is to define suitable heat treatments so that the formation of unwanted crystalline phases, such as hexacelsian, can be avoided. In this paper we studied the thermophysical behaviour of a family of new glass-ceramic materials belonging to two systems of the quaternary glassy system $CaO \cdot MgO \cdot Al_2O_3 \cdot SiO_2$, where BaO has been progressively substituted for CaO. The two MgO-containing compositions were chosen on account of their tendency to crystallize in the form of calcium feldspar (anorthite) and/or pyroxene (diopside) [3]. The substitution of Ba^{2+} for Ca^{2+} was done to control the formation of the corresponding barium feldspar in the different polymorphs. The development of the crystalline phases was analysed using X-ray diffraction (XRD) and infrared techniques on samples heated and prepared differently.

2. Experimental procedure

2.1. Sample preparation

The series of glasses studied begins at the two $CaO–MgO–Al_2O_3–SiO_2$ quaternary system compositions [3] in which feldspar anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and pyroxene diopside ($CaO \cdot MgO \cdot 2SiO_2$) are present in ratios 1:3 (A) and 1:1 (B) and

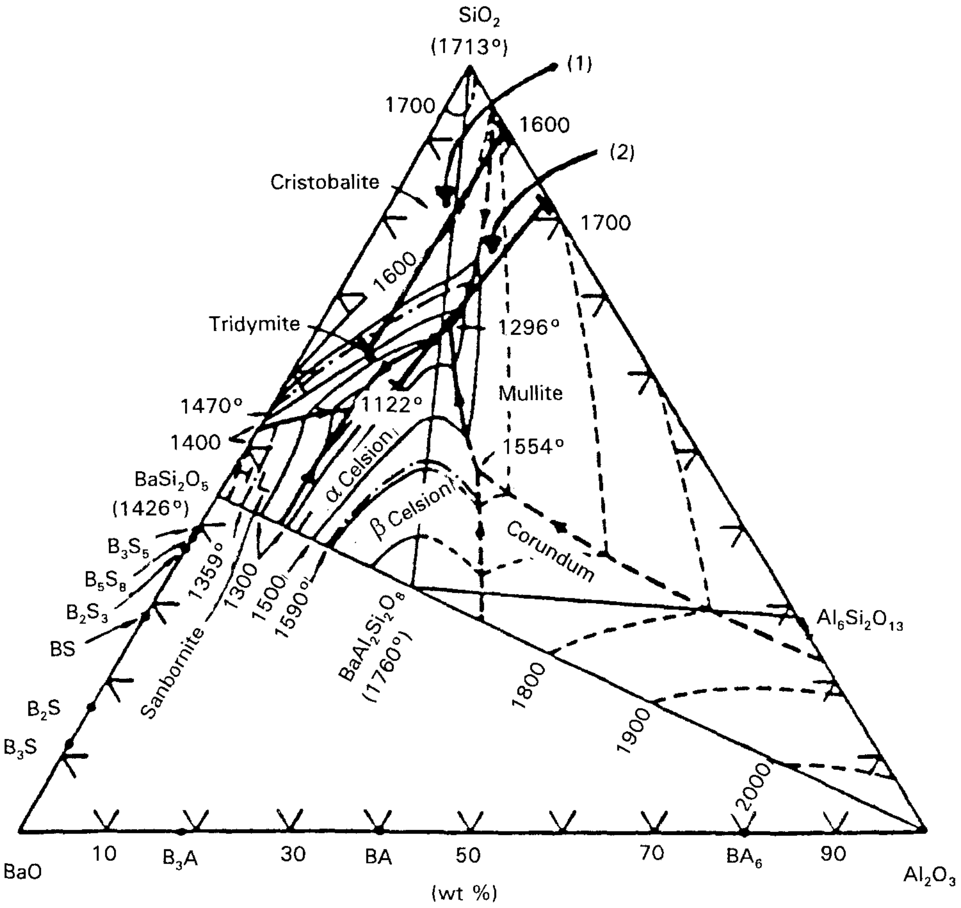

Figure 1 Compositional range of the investigated glasses of composition from (1) A to A–Ba and from (2) B to B–Ba on the ternary $BaO–Al_2O_3–SiO_2$ phase diagram, after Lin and Foster [4].

extends into the quaternary $BaO–MgO–Al_2O_3–SiO_2$ on two lines of constant 25 mol % CaO + BaO, as shown in Fig. 1. Barium oxide was substituted for calcium oxide to produce glasses containing 1, 2, 5, 10, 15, 20 and 25 mol % BaO (Table I). The raw materials, reagent-grade oxides and carbonates of high quality, were mixed together and ball milled for 20 min. No nucleating agents were added to allow the study of the natural trend towards the crystallization. The mixture was transferred to mullite crucibles and heated in an electric kiln following a three-step melting treatment: (1) a quick heating up to 1200 °C; (2) a slow heating up to about 1300 °C to homogenize the melt and to proceed with possible additions of new batch; (3) a quick heating at 1400 °C for 30 min. After this time, the glass melt was quenched either in water, to obtain the frits, or on an iron mould to obtain bars suitable for different thermophysical tests. No annealing treatment was performed, but, in some cases, a remelting of frits was necessary for good glass homogeneity. Element loss from the melt was negligible, and the glass composition was assumed to be identical to the original ones.

TABLE I Sample compositions (mol %)

Comp. name	Oxides		Comp. name	Oxides	
	BaO	CaO		BaO	CaO
A	0	25.031	B	0	25.031
A–1Ba	1	24.031	B–1Ba	1	24.031
A–2Ba	2	23.031	B–2Ba	2	23.031
A–5Ba	5	20.031	B–5Ba	5	20.031
A–10Ba	10	15.031	B–10Ba	10	15.031
A–15Ba	15	10.031	B–15Ba	15	10.031
A–20Ba	20	5.031	B–20Ba	20	5.031
A–Ba	25.031	0	B–Ba	25.031	0
	MgO	19.725		MgO	13.972
	Al_2O_3	5.146		Al_2O_3	10.931
	SiO_2	50.098		SiO_2	50.066

For consistency with previous studies, the glass-ceramic samples were prepared by crystallizing glasses in a one-step (nucleation and crystal growth together) thermal treatment at 1100 °C for 1 h, followed by natural cooling to room temperature.

2.2. Characterization

Differential thermal analysis (DTA) experiments were performed (Netzsch STA 409). The crucibles used were matched pairs made of alumina containing about 100 mg sample; calcined kaolin was used as the reference material. The DTA experiments were conducted at a heating rate of 10 °C min^{-1}, unless otherwise stated.

The thermal expansion coefficient of glass and glass-ceramic and the glass transformation temperature were measured using a conventional horizontal dilatometer (Netzsch dilatometer 402) by heating bars 3–4 cm long from 20–900 °C at the rate of

10 °C min^{-1}. Average thermal expansion coefficients were calculated over the range 30–500 °C. The glass transformation temperature was determined from the expansion curve using the standard intercept technique.

Crystalline phases were identified by X-ray powder diffraction using an X-ray powder diffractometer nickel-filtered CuK_α (λ = 0.154 18 nm, Philips PW 1050) with a 2 s time constant and 1000 counts range in the 2θ range 10°–45° at a scanning rate of 1° min^{-1}. The powders were prepared in two different ways: the first produced preferential crystalline orientation by rubbing with an ordinary microscope slide the upper surface of the glass-ceramic powder, gently pressed inside the sample holder cavity. The second way of preparing the powders aimed at complete random orientation of the sample. This result was obtained by three different sample preparation methods: the first involved the drawing of some drops of the glass-ceramic slurry in water and exposing them to an ultrasonic stirrer for different times, before depositing them on a microscope slide. Another method was that proposed by Guillem Villar *et al.* [5], which consisted of compressing the powder in the cavity from the back. A third method was based on the packing of the powder between two glass slides, one of which was glued to the sample holder and constituted the back of the cavity, while the second was removable.

The infrared transmission spectra of glasses and glass-ceramics were recorded on KBr pellets in the range 4000–400 cm^{-1} with a Spectrointerferometer FT-IR Bruker IFS 113V. About 1 mg of well-dried and ground sample was mixed with 200 mg of well-dried IR-grade KBr and then sufficiently ground to obtain an homogeneous mixture of optimum particle size. The mixture, thus prepared to give an absorbance in the optimum range, was then mechanically pressed into a disc 13 mm in diameter. The force on the plunger was 10 ton, maintained for 10 s. This gave transparent, homogeneous pellets. In fact, many of the samples were scanned more than once with new pellets prepared. In most cases the reproducibility was > 99%. However, because of the very broad bands obtained for glassy samples and the intrinsic distortions associated with line shape in the spectra of powders, the accuracy in the peak position was probably no better than 5–20 cm^{-1}.

3. Results and discussion

3.1. Thermophysical measurements

The dilatometric behaviour of A composition glassy samples shows that the introduction of an increasing percentage of BaO caused a decrease in the glass transition temperature, T_g, from about 730 °C to about 710 °C. As far as the dilatometric softening point was concerned, the gradual decrease from 800 °C to 775 °C was clearly dependent on the increasing BaO content. This effect is usually observed when a cation, here Ba^{2+}, substitutes for a smaller one, Ca^{2+}. Completely amorphous B system bars were not always obtained, because of the tendency of most of these compositions to crystallize in the quenched state. In this case the effect of barium substitution could not be discussed.

The average linear thermal expansion coefficients (TEC) for glassy and glass-ceramic samples, recorded in the 30–500 °C temperature range, are shown in Fig. 2 for system A. The TEC of the glasses showed a gradual increase with an increasing amount of BaO, while for the corresponding glass-ceramics there was a scattered behaviour. However, for both the partial glassy and completely crystallized materials with composition B (Fig. 3) a minimum TEC value was found which corresponded to B–10Ba for the glassy samples and to B–5Ba for the crystallized bars.

It is important to note that the glass-ceramic's thermal expansion coefficients generally are lower than those of the corresponding glasses; the difference in the values can be correlated with the different nature and percentage of crystalline phases formed, celsian and hexacelsian for both A and B glass-ceramics at high barium content (see Section 3.3).

3.2. Thermal analysis

DTA curves were collected on completely amorphous samples, with grain size < 20 μm at 10 °C min^{-1}, for composition A with increasing BaO content. The curves showed one exothermic crystallization peak,

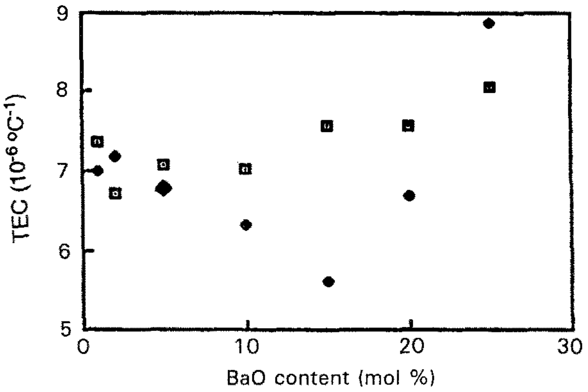

Figure 2 Dependence of the linear thermal expansion coefficient on composition, for (□) glassy and (◆) glass-ceramic samples belonging to A system, recorded in the 30–500 °C temperature range.

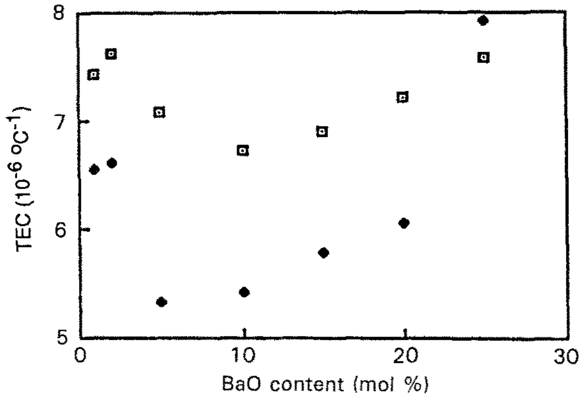

Figure 3 Dependence of the linear thermal expansion coefficient on composition, for (□) glassy and (◆) glass-ceramic samples belonging to B system, recorded in the 30–500 °C temperature range.

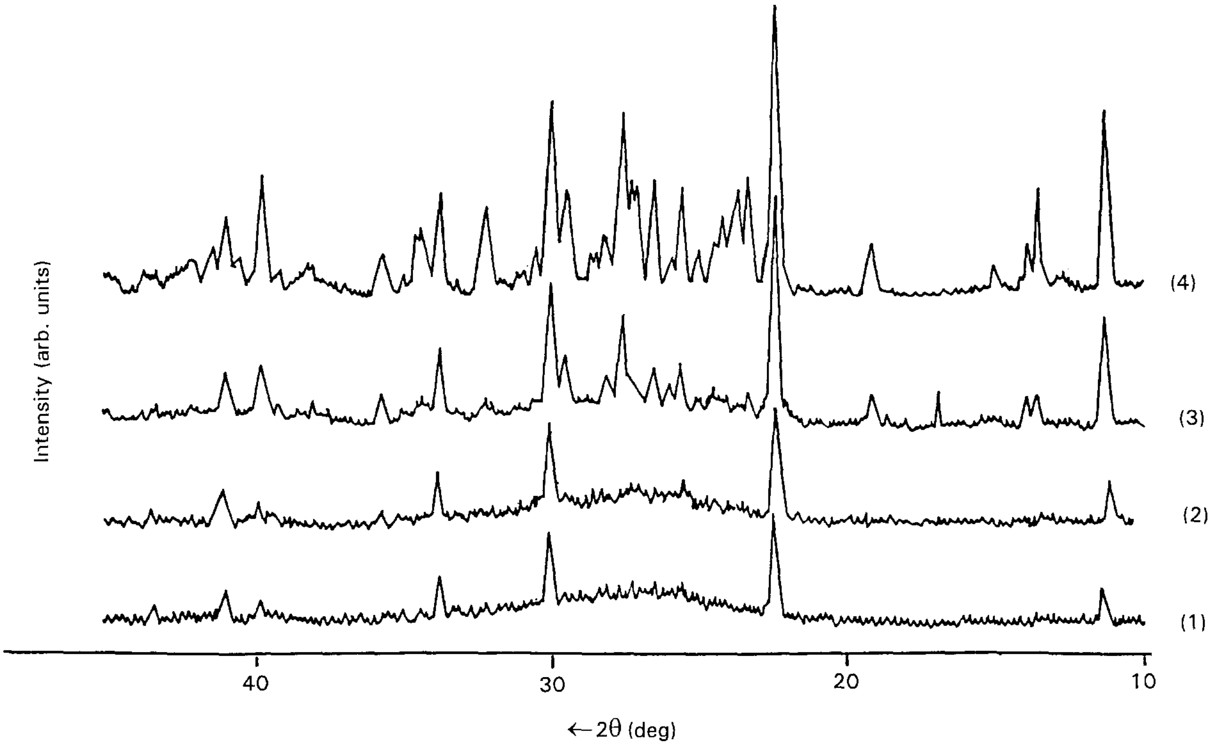

Figure 4 XRD patterns recorded on samples: (1) as-quenched B–Ba glass, and glass-ceramic heated at (2) 900 °C, (3) 1000 °C and (4) 1100 °C, for 1 h.

T_c, as well as a specific heat change corresponding to the glass transition, T_g, which agreed with that observed in the dilatometric curves. It was noted that there was an increase in the crystallization peak temperature from about 930–950 °C (Table II) for increasing amounts of BaO, up to 20 mol %. After this the peak splits into two peaks, one at a higher temperature, the second at a lower temperature (995 and 931 °C), indicating the presence of at least two different phases with characteristic temperatures, probably hexacelsian and celsian, respectively [2, 6].

On glass powders of composition A–Ba the DTA thermograms at different heating rates, 2, 5, 10 and 20 °C min^{-1}, were also performed in order to evaluate the activation energy using the so-called Kissinger equation. Because the nucleation mechanism was proved to be the surface catalysed by experimental evaluation [7], the expression of the applied equation was

$$\ln (\Phi/T_p^2) = -E_k/RT_p + \text{const} \qquad (2)$$

where Φ is the heating rate (K min^{-1}) at which the DTA curves were recorded, T_p(K) is the maximum temperature of the exothermic crystallization peak, E_k is the activation energy for crystallization process (expressed in cal mol^{-1} if R, the gas constant is expressed as 1.9872 cal mol^{-1} K^{-1}) [8–10]. The data collected were 113 and 98 and 85 kcal mol^{-1}, respectively, for A and A–Ba systems (note that for the second case we obtained two values corresponding to the two crystallization peaks). A good correlation was found with the literature data relating to different glass-ceramic systems: 86–313 kcal mol^{-1} for pyroxene crystals [11] and 130–132 kcal mol^{-1} for barium feldspar phases [12]. The lower activation energy of the barium-containing system can be related to its high tendency to crystallize (see TTT curves hereafter).

TABLE II Crystallization peak temperatures of 20 μm glassy powders from DTA curves collected at a 10 °C min^{-1} heating rate.

Comp. name	T_c (± 2 °C)
A	929
A–10Ba	939
A–15Ba	952
A–20Ba	951
A–Ba	931; 995

3.3. X-ray diffractometry

The X-ray powder diffraction allowed identification of the structure change from the glassy to the crystallized state and recognition of the different crystalline phases.

As previously observed, soon after quenching, traces of crystallization were noted in the glasses starting from composition B–10Ba, increasing with increased BaO substitution. As a consequence, the glass B–Ba could not be submitted to the time–temperature–transformation (TTT) curve study because of its high degree of crystallinity. So it was heated at 900, 1000 and 1100 °C for 1 h, in order to analyse the development of crystalline phases with temperature. From the XRD patterns plotted in Fig. 4 the as-quenched glass and the 900 °C treated sample present the same peaks, hence the same crystallized fraction. The peak intensity and number of peaks had considerably increased for the 1000 °C treated glass-ceramic, and reached a maximum at 1100 °C. The identification of the crystalline phases led to various

TABLE III Crystalline phases identified by XRD in the samples heated at 1100 °C, 1 h (unless otherwise stated) by using Joint Committee on Powder Diffraction Standards files

Comp. name	Crystalline phases in glass ceramics[a]	Comp. name	Cryst. phases in as-quenched[a]	Cryst. phases in glass-ceramics[a]
A	D,A	B		A,D
A–5Ba	D,H,C	B–5Ba		D,C,H
A–10Ba	H,C,D	B–10Ba	C	C,D,H
A–15Ba	H,C,D,BaCaMgSi	B–15Ba	C,H*	C,H*,D,BaCaMgSi
A–20Ba	BaCaMgSi,C,BaMgSi,H	B–20Ba	H*,BaCaMgSi	H*,C,BaCaMgSi,BaMgSi
A–Ba	BaMgSi,BaAlSi,P,H,C	B–Ba	H*	(900 °C,1h)H* (1000 °C,1h) H*,P,C,BaMgSi (1100 °C,1h) H*,BaMgSi,C,BaSi,P

[a] D = Diopside ($CaMg(SiO_3)_2$) file no. 11-654.
A = Anorthite ($CaAl_2Si_2O_8$), file no. 12-301.
H = Hexacelsian (β-$BaAl_2Si_2O_8$), file no. 12-726.
C = Celsian ($BaAl_2Si_2O_8$), file nos. 18-153, 19-90.
BaCaMgSi = Barium calcium magnesium silicate ($Ba_2CaMg_2Si_6O_{17}$), file no. 32-61.
BaMgSi = Barium magnesium silicate ($BaMg_2Si_2O_7$), file no. 10-44.
BaAlSi = Barium aluminium silicate ($BaAl_2Si_2O_8$) file no. 26-137; (α-$BaAl_2Si_2O_8$), file no. 12-725.
H* = Hexacelsian + barium aluminium silicate.
P = Paracelsian ($BaAl_2Si_2O_8$), file no. 10-352.
BaSi = Barium silicate ($Ba_2Si_3O_8$), file no. 12-694.

TABLE IV Effect of sample preparation on the ratio of different crystalline phases deduced from XRD patterns of glass-ceramics prepared at 1100 °C, 1 h (error ± 5–10%)

Sample preparation	A–5Ba		A–10Ba		A–15Ba		A–20Ba		A–Ba
	H/C[a]	D/C[b]	H/C[a]	D/C[b]	H/C[a]	D/C[b]	H/C[a]	BaMgSi/C[c]	H/C[a]
Oriented	0.67	3.45	1.32	1.45	2.59	1.45	0.17	1.37	1.54
Ultrasonic 10 min	–	–	–	–	2.03	1.62	0.09	1.48	0.96
Ultrasonic 30 min	–	–	–	–	1.34	1.18	0.15	1.23	0.86
Ultrasonic 60 min	–	–	–	–	1.59	1.00	0.13	1.09	0.87
Random orient.	0.43	2.46	0.13	0.89	1.17	1.37	0.13	1.39	1.33

[a] H/C = Hexacelsian 0.776 nm/celsian 0.336 nm.
[b] D/C = Diopside 0.299 nm/celsian 0.336 nm.
[c] BaMgSi/C = Barium magnesium silicate 0.343 nm/celsian 0.336 nm.

barium aluminosilicates, listed in Table III, in different polymorphic forms. Moreover, a barium magnesium silicate was present at 1000 and 1100 °C, and a barium silicate developed at 1100 °C.

The effect of preferred orientation on the hexacelsian/celsian ratio was evident for glass-ceramics of composition A–10Ba and A–15Ba, for which the primary phase recognized was hexacelsian. As shown in Table IV, the other glass-ceramic powders are almost unaffected by sample preparation: both diopside/celsian and barium magnesium silicate/celsian ratios appeared uninfluenced by preferred orientation. This effect was deduced by Guillem Villar and Guillem Monzonis [13] who reported cleavage planes present only in hexacelsian form. The influence of the ultrasonic stirrer was also studied: peak intensity decreased with mixing time, and when the sample slurry was mixed for over 1 h, the peaks were almost undetectable.

In general, of the two phases present in the CaO-containing system, anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) and diopside ($CaO{\cdot}MgO{\cdot}2SiO_2$), the first disappeared with the introduction of 5 mol % BaO, being substituted by barium feldspathic phases, and the second disappeared for 15–20 mol % BaO. The calcium feldspar is substituted by different barium feldspars, listed in Table III for both A and B systems, in particular celsian in the glass-ceramics in B systems and hexacelsian in A systems, while the polymorphic form of paracelsian was present in the two BaO-containing quaternary systems. In the compositions with 15 and 20 mol % BaO, barium calcium magnesium silicate ($Ba_2CaMg_2Si_6O_{17}$) was also formed, and in 20 mol % BaO, a barium magnesium silicate ($BaMg_2Si_2O_7$) developed.

In the quaternary systems, A–Ba and B–Ba, a large number of the crystalline phases were identified, contrasting with the CaO-containing systems. In order to analyse better the effect on crystallization induced by Ca^{2+} and Ba^{2+} cations, the TTT curves of the A and A–Ba quaternary systems have been plotted in Fig. 5. The lines were drawn between the more representative points which separate amorphous samples and those which showed an initial crystallization, detected by

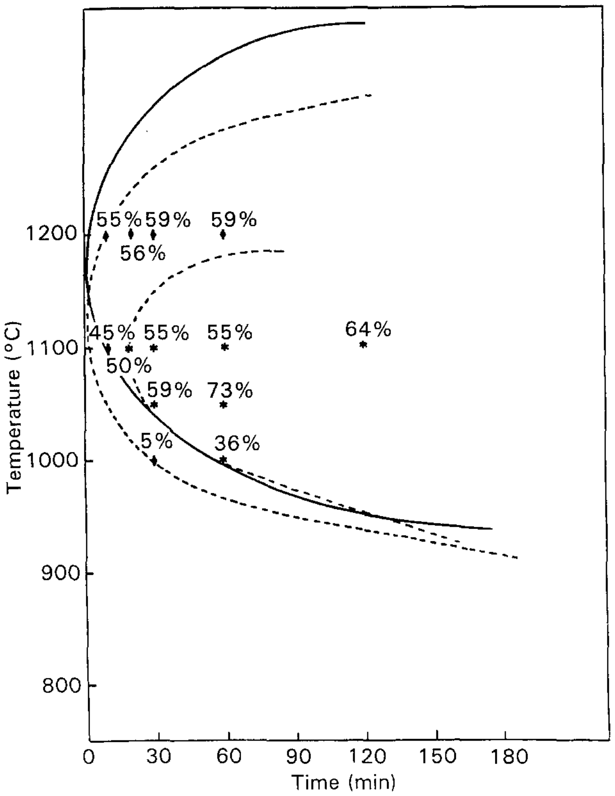

Figure 5 TTT curves of (——) A and (– – –) A–Ba quaternary systems, for (◆) barium magnesium silicate (JCPDS file no. 10-44, $d = 0.320$ nm, $I/I_0 = 100$) and (*) barium aluminium silicate (JCPDS file nos. 26-137, $d = 0.397$ nm, $I/I_0 = 85$, and 10-352, $d = 0.400$ nm, $I/I_0 = 100$).

XRD. The case of A–Ba composition shows two curves, one tracing the formation of the barium magnesium silicate phase and the second related to the stability area of the feldspatic form. The numbers represent a quantitative determination of the extent of crystallinity that was done using Ohlberg and Strickler's formula [14]:

$$\% \text{ crystallinity} = 100(I_g - I_x)/I_g \qquad (3)$$

where I_g is the intensity of the glass peak in the XRD pattern collected on the parent glass, and I_x is the intensity of the glass peak (corresponding to the same 2θ value) in the pattern of the heat-treated sample. As suggested by the Ohlberg–Strickler method, it is important to note that this quantitative determination is not suitable for measuring degrees of crystallinity lower than 10% because a small change in non-crystalline scattering cannot be measured accurately [15]. From the comparison between the A and the A–Ba systems, it was confirmed that the crystallization process started at lower temperature, when the Ba^{2+} cation was present and, up to 1050 °C, the crystallinity percentage was higher, 35%–75 % with respect to 35%–45 % for Ca^{2+} (Table V). On the contrary, when the temperature was raised to 1100 °C and above, the two systems presented different degrees of crystallinity: on average 75%–85 % for Ca^{2+} and 55%–60 % for the Ba^{2+} systems.

TABLE V Percentage of crystalline phase in glass-ceramics calculated using Ohlberg's formula

Heat treatment (°C) (min)	% cryst. of A comp.	% cryst. of A–Ba comp.
900 180	0	0
950 60	0	0
950 90	0	0
1000 20	0	0
1000 30	0	5
1000 60	0	36
1000 90	33	–
1000 180	33	–
1050 30	33	59
1050 60	46	73
1100 10	17	45
1100 20	42	50
1100 30	50	55
1100 60	75	55
1100 120	75	64
1200 10	75	55
1200 20	75	56
1200 30	83	59
1200 60	83	59

3.4. Infrared spectroscopy

This technique is well established for studying structures of glassy and crystalline materials. In this particular case, it provided a good method to determine the presence of the polymorphic form of hexacelsian, which is difficult to treat in powder diffractometry.

The original spectra are shown in Figs 6 and 7.

All the completely amorphous glasses generally exhibited three absorption peaks, with a main absorption peak at ~ 1000 cm^{-1}, a fairly broad strong peak at 470 cm^{-1}, and another weak variable peak at ~ 700 cm^{-1}. Besides these three, above 10 mol % BaO, two bands appeared at 640 and 620 cm^{-1} in the B glasses, and a band at 1400 cm^{-1} in B–Ba glass. It is not possible to attribute these modifications exclusively to the effect of the Ba^{2+} cation on the glassy state, because, as shown by X-ray diffraction, the new bands can be attributed to some crystals which are present even in the as-quenched glassy samples.

Correct assignment of vibrational frequencies in silicate structures is not at all an easy matter. It has been a subject of controversy for many years now [16]. The general agreement is that all these silicate glasses exhibit at least three bands in the 1100, 800, and 500 cm^{-1} regions, and in some cases another weak band appears at about 950 cm^{-1}. From literature data, the addition of alkaline and alkaline-earth oxides, produces shifts of the typical bands of the pure glassy silica toward lower wavelength values. This is due to the polarizing effect of these cations on the surrounding oxygens, which is so high that the oxygen–silicon bond in the tetrahedra is weakened. The normal vibrational frequencies of the SiO_4 tetrahedron shift from 1170 cm^{-1} to 1090–1060 cm^{-1} (asymmetrical stretching), from 1100 cm^{-1} to 960–930 cm^{-1} (symmetrical stretching), from 830 cm^{-1} to 700–680 cm^{-1} (O–Si–O ring deformation) and by only few wavelength numbers around the 470 cm^{-1} band (Si–O–Si bending) [17].

For A glassy systems, a shift of the Si–O–Si stretching, from 1015 cm^{-1} to 990 cm^{-1} passing from composition A to A–Ba, was observed, while for B

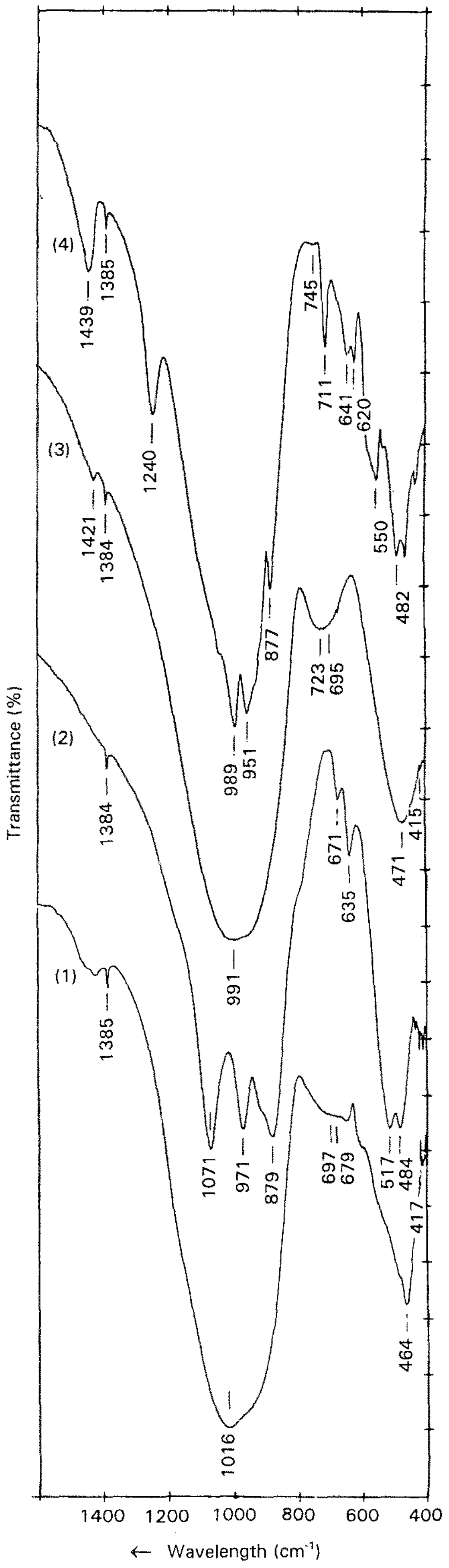

Figure 6 Infrared spectra for (1) A glass, (2) A glass-ceramic, (3) A–Ba glass, (4) A–Ba glass-ceramic. (Heat treatment 1 h at 1100 °C.)

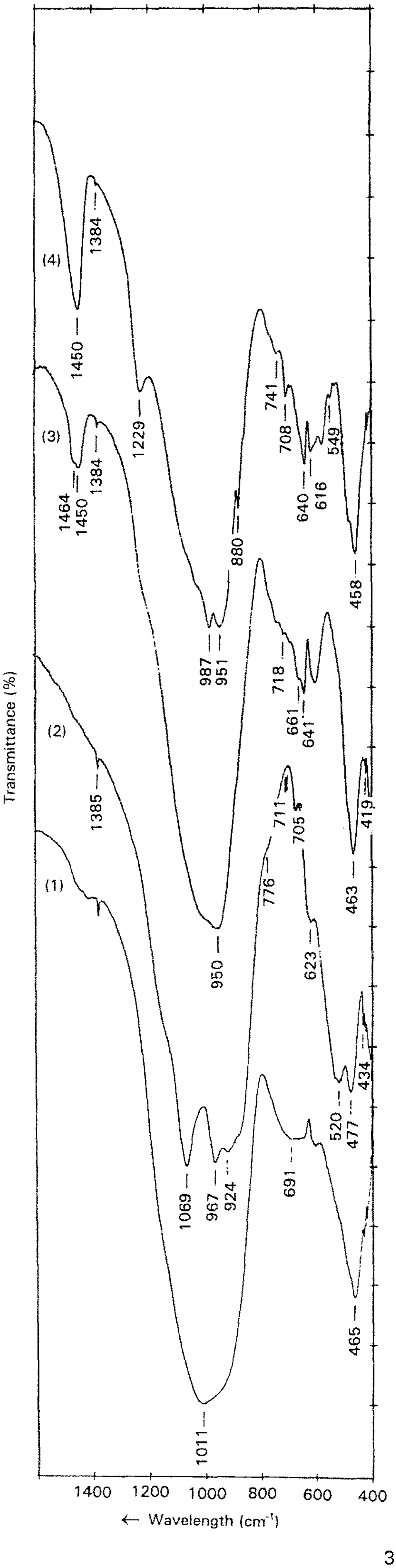

Figure 7 Infrared spectra for (1) B glass, (2) B glass-ceramic, (3) B–Ba glass, (4) B–Ba glass-ceramic. (Heat treatment 1 h at 1100 °C.)

glasses the shift was from 1010 cm^{-1} (CaO-containing system) to 950 cm^{-1} for B–Ba. These experimental results agree well with the aforementioned polarizing effect.

As a general trend, the bands of the glass-ceramics, as in any ordered solid structure, are well defined and sharp. These bands arose from those of the parent glasses, and present a higher resolution in the range of 1100–800 and 700–400 cm^{-1}. The assignment of these bands was discussed in a previous work [18] and attributed to the presence of different mixtures of diopside and anorthite crystals.

The glass-ceramics infrared spectra were significantly different when 10–25 mol % of BaO were added, because some new peaks appeared at about 1450 cm^{-1}, for A–Ba and B–Ba, and 1230–1210 cm^{-1}, from A–10Ba to A–Ba and from B–20Ba to B–Ba. The presence of 1230 cm^{-1} absorption bands attributable to hexacelsian [13] in the spectra of the majority of A samples can be explained by the assumption that this crystalline phase was the main phase present, thus confirming the XRD results. The other absorption bands in the Si–O–Si stretching region and at 600–450 cm^{-1} were due to celsian. The position of the third band, 1450 cm^{-1}, enabled us to assign it to the new crystals present in the quaternary barium compositions, for which the XRD patterns showed paracelsian and barium magnesium silicate phases. The slight displacement of the maximum of the asymmetric stretching band in the order calcium and barium to lower frequencies, cannot be reasonably explained by the effect of the difference in ionic radii of the two cations in their feldspatic crystals.

These results support those already discussed in the paragraph about diffraction, showing particular agreement with data collected on randomly distributed powder samples.

4. Conclusion

The comparison between the thermophysical measurements and X-ray powder diffraction results proved to be very interesting, because the greatest changes in the thermal expansion coefficient from glass to glass-ceramic corresponded to the appearance of particular crystalline phases, such as celsian which is characterized by a low thermal expansion coefficient.

The substitution of BaO in place of CaO in the two investigated glassy compositions led to the appearance of barium feldspar polymorphism. Of the many crystalline phases formed, the barium feldspars were the most kinetically and thermodynamically favoured, so much so that they were sometimes present even in the as-quenched glass.

Acknowledgement

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References

1. C. H. DRUMMOND III and N. P. BANSAL, *Ceram. Eng. Sci. Proc.* **11** (1990) 1072.
2. C. H. DRUMMOND III, W. E. LEE, N. P. BANSAL and M. J. HYATT, *Ceram. Eng. Sci. Proc.* **10** (1989) 1485.
3. C. LEONELLI, T. MANFREDINI, M. PAGANELLI, P. POZZI and G. C. PELLACANI, *J. Mater. Sci.* **26** (1991) 5041.
4. H. C. LIN and W. R. FOSTER, *J. Am. Ceram. Soc.* **53** (1970) 550.
5. M. C. GUILLEM VILLAR, C. GUILEM MONZONÌS and J. ALARCÒN NAVARRO, *Trans. J. Br. Ceram. Soc.* **82** (1983) 69.
6. J. S. MOYA CORRAL and A. GARCIA VERDUCH, *Bol. Soc. Esp. Ceram. Vidr.* **15** (1976) 379.
7. L. BARBIERI, C. LEONELLI, T. MANFREDINI, M. PAGANELLI and G. C. PELLACANI, *J. Thermal Anal,* **38** (1992) 2639.
8. K. MATUSITA, S. SAKKA and Y. MATSUI, *J. Mater. Sci.* **10** (1975) 961.
9. K. MATUSITA and S. SAKKA, *Phys. Chem. Glasses* **20** (1979) 81.
10. *Idem, J. Non-Cryst. Solids* **38-39** (1980) 741.
11. N. K. CHAKRABORTY, S. K. DAS, S. K. NIYOGI and R. L. THAKUR, in "Proceedings of the 10th International Congress on Glass", Kyoto, Japan, 9 July 1974, Vol. 14 (*Ceram. Soc.* Japan, Kyoto, 1974) p. 75.
12. N. P. BANSAL and M. J. HYATT, *J. Mater. Res.* **4** (1989) 1257.
13. M. C. GUILLEM VILLAR and C. GUILLEM MONZONÌS, *Talanta* **31** (1984) 550.
14. S. M. OHLBERG and D. W. STRICKLER, *J. Am. Ceram. Soc.* **45** (1962) 170.
15. H. S. KIM, R. D. RAWLINGS and P. S. ROGERS, *J. Br. Ceram. Trans.* **88** (1989) 21.
16. B. N. ROY, *J. Am. Ceram. Soc.* **73** (1990) 846.
17. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 4th Edn (Wiley, London, 1986) p. 474.
18. L. BARBIERI, C. L. BIANCHI, S. BRUNI. F. CARIATI, C. LEONELLI, T. MANFREDINI, M. PAGANELLI, G. C. PELLACANI and U. RUSSO, *J. Non-Cryst. Solids* **155** (1993) 231.

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