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Study of the devitrification behaviour of a barium magnesium aluminosilicate glass-ceramic

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Abstract

This work presents the most important aspects of the devitrification behaviour of a barium magnesium aluminosilicate (BMAS) glass-ceramic with the Ba-osumilite stoichiometry. The melt-derived BMAS glass-ceramic was first pulverised and subsequently hot pressed to produce sintered powder compacts, some of which were subjected to post-sintering heat treatments in air. The BMAS glass devitrification behaviour was studied by means of scanning electron microscopy (SEM), electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and X-ray diffraction (XRD). This study revealed that at temperatures <1000 °C, the BMAS glass crystallisation yielded several metastable crystalline phases (i.e. celsian, hexacelsian, α/β-cordierite, and β-quartz$_{ss}$) instead of the thermodynamically stable Ba-osumilite. On the other hand, annealing of the BMAS glass at temperatures ≥1000 °C caused the transformation of all metastable phases to Ba-osumilite. Understanding the crystallisation behaviour of the BMAS glass-ceramic is essential in order to use this material as matrix in fibre-reinforced composites suitable for high-temperature structural applications.

Keywords: Glass-ceramics; Sintering; Microstructure-final; Electron microscopy; Composites

1. Introduction

Glass-ceramics with the Ba-osumilite stoichiometry have long been considered as promising matrix materials for fibre-reinforced composites suitable for high-temperature structural applications. This is attributed to the low thermal expansion coefficient ($\alpha = 2.8 \times 10^{-6}\,°\text{C}^{-1}$ in the 20–500 °C range) and good high-temperature resistance of Ba-osumilite (the osumilite melting point is $T_\text{f} \approx 1370\,°\text{C}$).[1,2] For example, Ba-osumilite glass-ceramics have often been reinforced with continuous Nicalon® SiC fibres due to the small thermal expansion coefficient mismatch between the fibres ($\alpha = 3.1 \times 10^{-6}\,°\text{C}^{-1}$ at 25 °C) and the osumilite-based matrix; the resulting SiC/BMAS composites combine a flexural strength of 400–700 MPa with a fracture toughness of 3–4 MPa m$^{1/2}$, depending on the matrix microstructure and the fibre content.[1] The manufacturing of both strong and tough composites relies greatly on the understanding of the matrix crystallisation behaviour, which was limited and fragmented for the BMAS glass-ceramic.[1–3] This work tried to establish a good understanding of the BMAS glass devitrification.

2. Experimental procedure

The melt-derived barium magnesium aluminosilicate (BMAS) glass-ceramic studied in this work was manufactured by AEA Technology, Harwell, UK. The as-received glass (in cullet form) was pulverised into a fine powder (90% of the powder particles had a diameter <10 μm) using a Fritsch 05.102 planetary mill with grinding elements made of corundum (Al_2O_3). Glass powder compacts were sintered on a W 100/150-2200-50 LAX KCE hot press in vacuum, under various conditions of temperature (850–1300 °C) and pressure (0–20 MPa). Some of the sintered powder compacts were subjected to isothermal heat treatments in air, in the 860–1300 °C temperature range, and for periods as long as 1000 h. The sintering and post-sintering heat treatments helped to understand the BMAS glass devitrification behaviour, which was essential for the processing of composites with a controlled matrix microstructure.

Both as-sintered and heat treated powder compacts were characterised using XRD, SEM, EPMA, and TEM. XRD patterns were acquired using a Philips PW 1010 diffractometer equipped

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with a Cu Kα radiation source. The microstructural changes during the crystallisation of the BMAS glass were studied using (a) a Philips XL30 SEM equipped with a field emission gun (FEG), (b) a Jeol JXA 733 EPMA, and (c) a Philips CM200 FEG TEM. Quantitative elemental analysis of various microstructural features was done by EPMA, using pure standards of Si, Al, Mg, and $BaSO_4$ so as to determine the Si, Al, Mg, and Ba contents of these features, whereas their O content was calculated by difference. The preparation of TEM thin foils involved cutting, dimpling, and ion milling with Ar ions using a Gatan 600 equipment.

3. Results and discussion

The nominal stoichiometry of the Harwell BMAS glass-ceramic was that of Ba-osumilite, i.e. $BaO\cdot 2MgO\cdot 3Al_2O_3\cdot 9SiO_2$ ($BaO\cdot 2MgO\cdot 3Al_2O_3\cdot 9SiO_2 = BM_2A_3S_9$: 2.08 Ba, 4.17 Mg, 12.50 Al, 18.75 Si, 62.50 O, all in at.%). However, quantitative elemental analysis by EPMA revealed that the Harwell BMAS glass-ceramic was, on the average, enriched in Ba with respect to the $BM_2A_3S_9$ stoichiometry. The determined by EPMA compositional fluctuation of the Harwell BMAS glass-ceramic was as follows: 2.16 ± 0.21 Ba, 4.02 ± 0.41 Mg, 12.36 ± 1.01 Al, 18.40 ± 1.34 Si, 63.06 ± 8.12 O, all in at.%. Knowing the fluctuation in the composition of the as-received glass is important, since the BMAS glass devitrification behaviour proved to depend strongly on the local glass composition.

The devitrification of the BMAS glass below 1000 °C produced mainly a series of metastable phases instead of the thermodynamically stable Ba-osumilite ($BaO\cdot 2MgO\cdot 3Al_2O_3\cdot 9SiO_2 = BM_2A_3S_9$, hexagonal). The detected metastable phases were: (1) celsian ($BaO\cdot Al_2O_3\cdot 2SiO_2 = BAS_2$, monoclinic), (2) α/β-hexacelsian (BAS_2, orthorhombic/hexagonal), (3) β-quartz$_{ss}$ ($2MgO\cdot 2Al_2O_3\cdot \eta SiO_2 = M_2A_2S_\eta$ with variable η; in this study, it is believed that $\eta \approx 7$), and (4) α/β-cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2 = M_2A_2S_5$, hexagonal/orthorhombic); apart from forming as single crystals, celsian and β-cordierite produced a metastable eutectic structure as well. The precipitation of metastable phases, which will be addressed in this article, is attributed to that fact that the free energy barrier for the nucleation of Ba-osumilite seems to be very large at temperatures <1000 °C, inhibiting its formation. On the other hand, the crystallisation of the BMAS glass yielded progressively more Ba-osumilite above 1000 °C, resulting in osumilite-based ceramics at temperatures ≥1200 °C.

The BMAS glass crystallisation started typically after about 1 h at ∼975 °C with the formation of crystalline phases with the $BaO\cdot Al_2O_3\cdot 2SiO_2$ (BAS_2) stoichiometry (Fig. 1). The formation of Ba-rich primary phases is explained based on the fact that the Harwell glass was, on the average, richer in Ba than the $BM_2A_3S_9$ composition. Two types of Ba-rich primary phases were detected: non-faceted celsian dendrites (Fig. 1a and b), and faceted hexagonal discs of hexacelsian (Fig. 1c). This study showed that the nucleation of celsian (BAS_2, monoclinic) was fast in the 900–950 °C range, while its growth rate was highest in the 1050–1070 °C range. The last observation was in agreement with the work of Winter et al.[1], who found that celsian crystals grew fastest at ∼1050 °C. In the work of Winter et al.[1] as well as in this study, the amount of celsian decreased substantially above 1200 °C in favour of Ba-osumilite. With respect to the hexacelsian phase (BAS_2, hexagonal), this work validated the existing hypothesis[1] that the effective nucleation range for hexacelsian lies below 900 °C, by producing hexacelsian-rich materials that were isothermally annealed first at 850 °C for 30 min −23 h ('nucleation' step) and subsequently at 1070 °C for 30 min ('growth' step). Almost invariably, small amounts of hexacelsian persisted in the devitrified glass up to 1300 °C despite the fact that hexacelsian is thermodynamically stable between 1590 and 1760 °C (i.e. the melting point T_f of composition BAS_2) while celsian is stable between 1590 °C and room temperature; the perseverance of hexacelsian is attributed to the sluggishness of the hexacelsian-to-celsian transformation.

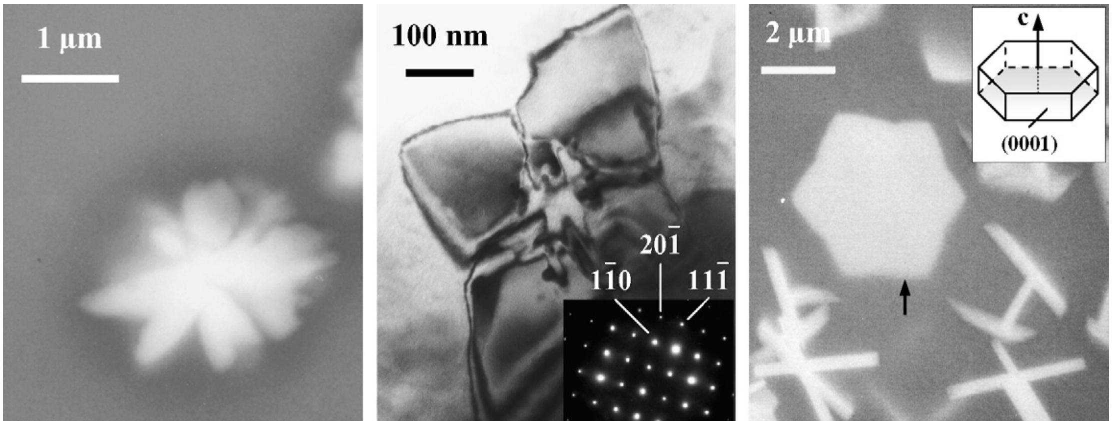

Fig. 1. (a) Backscattered electron (BSE) image of a primary celsian dendrite formed in a material sintered at 975 °C for 2 h. (b) Bright field (BF) image of a celsian dendrite that formed after 4 h at 975 °C. The selected area diffraction pattern (SADP) shows the [1 1 2] zone axis of celsian. (c) BSE image of hexagonal discs of hexacelsian, the basal plane of which is thought to be the (0 0 0 1) plane of hexacelsian, as shown in the small inset drawing (the arrow shows a cross section parallel to the basal plane).

The precipitation of BAS_2 primary crystals was followed by the pile-up of vitreous matter with composition $2MgO{\cdot}2Al_2O_3{\cdot}7SiO_2$ ($M_2A_2S_7$) at the crystal growth front, based on mass conservation principles as shown in reaction (1):

$$BM_2A_3S_9\ \text{glass} \rightarrow BAS_2\ \text{crystals} + M_2A_2S_7\ \text{glass} \qquad (1)$$

The devitrification of the Mg-enriched $M_2A_2S_7$ glass around the primary BAS_2 crystals produced one of the following phases: (1) β-quartz solid solution ($M_2A_2S_\eta$ with variable η, hexagonal), and (2) α/β-cordierite ($M_2A_2S_5$, hexagonal/orthorhombic). β-Quartz solid solution (β-quartz$_{ss}$) is also addressed in literature as μ-cordierite, but since the structure of μ-cordierite differs a lot from that of α/β-cordierite, μ-cordierite does not really qualify as member of the 'cordierite family'; therefore, only the name β-quartz$_{ss}$ will be used in this study to address the phase with composition $M_2A_2S_\eta$. In agreement with prior studies on cordierite-based glasses, this work showed that the devitrification of the $M_2A_2S_7$ glass started with the formation of β-quartz$_{ss}$, which transformed subsequently into α/β-cordierite; in fact, β-quartz$_{ss}$ was detected only in samples annealed below 1025 °C (Fig. 2), while samples exposed to higher temperatures contained α- and/or β-cordierite. This finding agreed with the observations of Winter et al.[1] and Jais et al.,[2] who reported that the crystallisation of their BMAS glasses begun at 900–950 °C with the formation of metastable β-quartz$_{ss}$ that was replaced completely by α/β-cordierite above 1050 °C. The β-quartz$_{ss}$ → α/β-cordierite phase transformation was accompanied by the rejection of a silica-based glass (with traces of Ba, Mg, Al, and Si), according to reaction (2); the devitrification of this silica-rich glass proved to be very sluggish.

$$M_2A_2S_7\ \text{crystal} \rightarrow M_2A_2S_5\ \text{crystal} + 2\ \text{mol of vitreous}\ SiO_2 \qquad (2)$$

As mentioned in the beginning of Section 3, the BMAS glass devitrification behaviour is determined by the local glass composition. Therefore, when the glass was locally enriched in Mg, primary Mg-rich phases formed instead of the usual Ba-rich ones. For example, Fig. 3a shows the growth of a primary α-cordierite ($M_2A_2S_5$, hexagonal) crystal within a matrix of glass. However, cordierite formed more often as a secondary rather than as a primary phase: typically, β-cordierite ($M_2A_2S_5$, orthorhombic) crystals formed as a consequence of the growth of celsian crystals. This study may report two such cases: (a) the nucleation of secondary β-cordierite crystals in the Mg-enriched area surrounding primary celsian dendrites, and (b) the formation of β-cordierite crystals in the space between celsian lamellae, the growth of which is thought to be responsible for the formation of a metastable celsian-cordierite eutectic structure (Fig. 3b and c). Before commenting on the eutectic structure, it may be concluded that the nucleation of α/β-cordierite and celsian was fastest in the same temperature range (i.e. 900–950 °C), since cordierite formed in principle after celsian. The growth range of α/β-cordierite extended up to 1120 °C in agreement with Winter et al.,[1] who detected cordierite and celsian at tem-

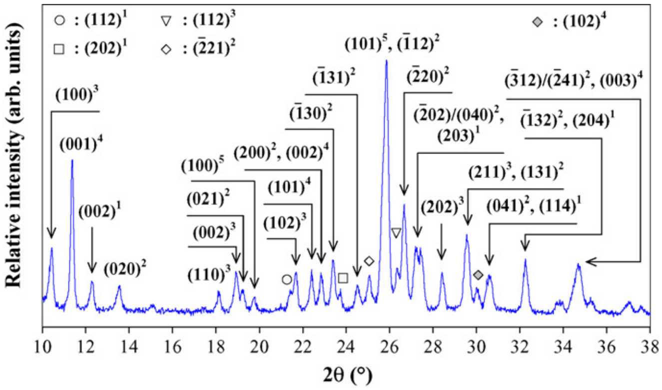

Fig. 2. XRD pattern of a material sintered at 925 °C for 7.7 h, where β-quartz$_{ss}$ is one of the main crystallisation products. The superscript numbers refer to phases: 1 = Ba-osumilite, 2 = celsian, 3 = α-cordierite, 4 = β-hexacelsian, and 5 = β-quartz$_{ss}$. It must be noted that XRD alone is insufficient to distinguish between α- and β-hexacelsian, due to the structural similarity of the two polymorphs, which leads to a nearly perfect peak overlap of their XRD patterns; the same holds for α- and β-cordierite.

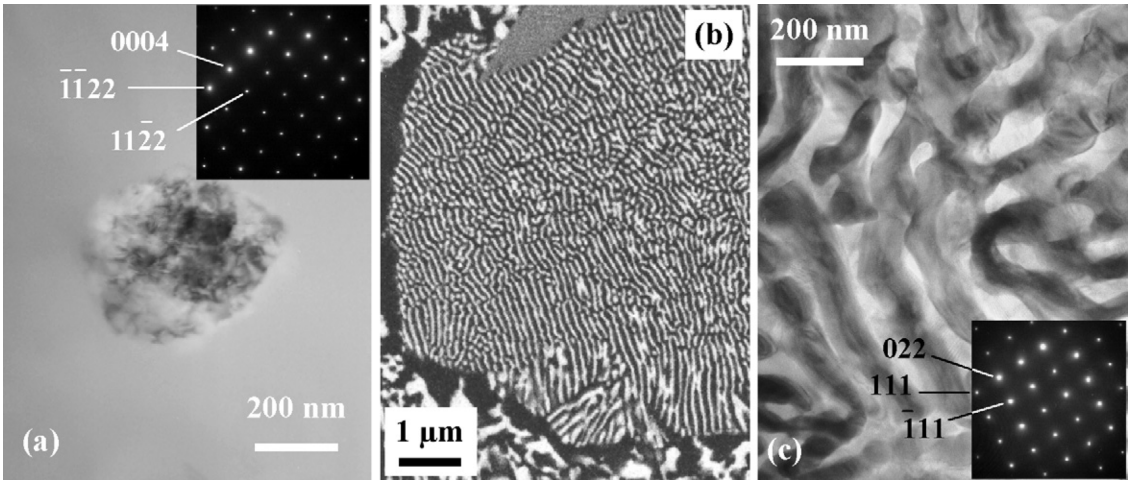

Fig. 3. (a) BF image of a primary α-cordierite crystal formed after 2 h at 975 °C. The SADP shows the [1 1̄ 0 0] zone axis of α-cordierite. (b) BSE image of the lamellar celsian-cordierite eutectic structure; the eutectic spacing is λ ≈ 0.14 μm. (c) BF image of the lamellar celsian-cordierite eutectic structure; the eutectic spacing is λ ≈ 200 nm. The SADP shows the [0 1 1̄] zone axis of β-cordierite, since the eutectic structure consists of alternating β-cordierite and celsian lamellae.

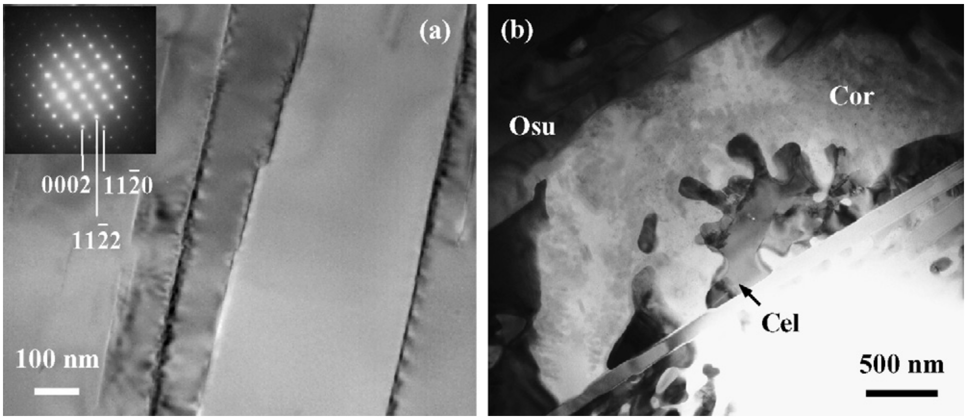

Fig. 4. (a) BF image of Ba-osumilite lamellae with numerous dislocations at the grain boundaries. The SADP shows the [$\bar{1}$ 1 0 0] zone axis of Ba-osumilite. (b) BF image showing the epitaxial formation of a cordierite (Cor) dendrite on Ba-osumilite (Osu) laths; the growth of the cordierite dendrite is followed by the formation of interdendritic celsian (Cel).

peratures >1020 °C and >970 °C, respectively, in slowly-heated BMAS glasses. It is believed that cordierite tends to form after celsian, due to the fact that the driving force for the nucleation of cordierite is smaller than the respective driving force for celsian, because the cordierite undercooling is smaller than the celsian undercooling at all temperatures (the melting point of cordierite is smaller than that of celsian, i.e. T_f (cordierite) = 1465 °C < T_f (celsian) = 1760 °C).

The prolonged annealing (3–12 h) of the BMAS glass in air, between 860 and 1000 °C resulted in the formation of a lamellar celsian-cordierite eutectic structure as shown in Fig. 3b and c. The eutectic structure, which usually nucleated on primary celsian crystals, lead to the formation of spherulite-like nodular 'colonies'. The growth of each eutectic 'colony' relied on the growth of celsian lamellae that rejected $M_2A_2S_7$ glass in the interlamellar space; the devitrification of the $M_2A_2S_7$ interlamellar glass yielded cordierite and a silica-rich glass, according to reaction (3)

$$\text{BMAS glass} \rightarrow \{\text{celsian-cordierite eutectic}\} + \text{residual silica}$$

$$\text{BM}_2\text{A}_3\text{S}_9\ \text{glass} \rightarrow \{\text{BAS}_2\ \text{crystals} + \text{M}_2\text{A}_2\text{S}_5\ \text{crystals}\} + 2\text{SiO}_2\ \text{glass} \qquad (3)$$

The metastable eutectic structure nucleated in the same temperature range as celsian and cordierite, while its growth was facilitated by the long annealing of the BMAS glass in the 860–925 °C range. This study indicated that the eutectic temperature T_E should lie somewhere in the 975–998 °C range.

Annealing of the BMAS glass-ceramic at temperatures ≥998 °C caused the transformation of the celsian-cordierite eutectic structure to the thermodynamically stable Ba-osumilite. Once nucleated, Ba-osumilite formed stacks of faceted lamellae (Fig. 4a), which 'consumed' all the metastable phases that had formed below 1000 °C due to the high free energy barrier related to the osumilite nucleation. This work showed that the range of fast Ba-osumilite nucleation lied between 1050 and 1075 °C, while its growth rate was fastest at temperatures ≥1200 °C, in accordance with a previous study.[1] However, the isothermal annealing of the BMAS glass in the 1200–1300 °C range was unable to produce a single-phase osumilite ceramic as reported elsewhere,[1,2] due to the fact that the composition of the Harwell glass deviated from that of stoichiometric Ba-osumilite.

The present study confirmed that Ba-osumilite lies in the primary field of mullite ($3Al_2O_3 \cdot 2SiO_2 = A_3S_2$, orthorhombic), since mullite cuboids formed in the matrix of SiC/BMAS composites processed at ∼1350 °C (Fig. 5). Winter et al.[1] also reported that Ba-osumilite melts incongruently at 1370 ± 20 °C, producing mullite and a liquid phase. The findings of the present study are summarised in Fig. 5, which shows the nucleation and growth ranges of the major phases produced during the devitrification of the Harwell BMAS glass. It should be emphasised that the nucleation and growth curves are qualitative and must not be regarded as the outcome of accurate measurements of the nucleation density, or the growth rate of each one of the crystallisation products.

One final observation of the present work is that the BMAS glass 'catalysed' its own devitrification, in such a way that the

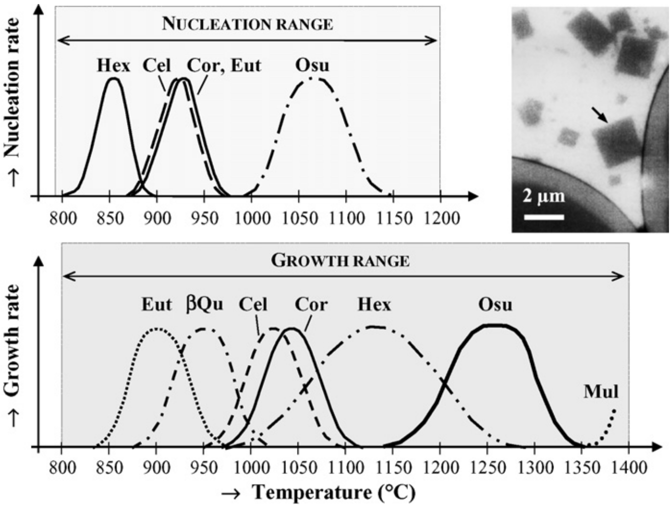

Fig. 5. Nucleation and growth rate curves for the major products of the BMAS glass devitrification. The abbreviations mean—Hex: hexacelsian, Cel: celsian, Cor: cordierite, Eut: eutectic, Osu: Ba-osumilite, βQu: β-quartz$_{ss}$, and Mul: mullite. The BSE micrograph in the upper right corner shows mullite cuboids (arrow) in the matrix of a SiC/BMAS composite hot pressed at ∼1350 °C for 30 min.

formation of one crystalline phase in the glass 'triggered' the formation of other phases until almost all glass transformed into a multiphase ceramic. This phenomenon, which may be called "self-catalysing devitrification", is attributed to the fact that the glass preferred to reach the equilibrium crystalline state via a sequence of intermediate steps involving the production of easy-to-form metastable phases rather than in a single step. An example of this phenomenon was the epitaxial nucleation of cordierite on Ba-osumilite (Fig. 4b), which has been previously reported during the devitrification of BaO-containing $M_2A_2S_{11}$ glasses[4] and BMAS glasses.[2] These previous studies suggested that the (0 0 1) and (4 2 0) planes of cordierite were parallel to the respective planes of osumilite, and that the epitaxial nucleation of cordierite on osumilite was caused by their similar lattice parameters: a is 9.770 Å in α-cordierite and 10.160 Å in Ba-osumilite.

4. Conclusions

This study focused on the crystallisation behaviour of a glass-ceramic with the Ba-osumilite nominal stoichiometry. It was found that the devitrification of this BMAS glass-ceramic below 1000 °C produced several metastable crystalline phases with various growth morphologies (i.e. celsian dendrites, hexagonal discs of hexacelsian, lamellar celsian-cordierite eutectic, α/β-cordierite and β-quartz$_{ss}$ in various shapes). On the other hand, annealing of the BMAS glass at temperatures $\geq$1000 °C transformed all metastable phases to lamellae of the thermodynamically stable phase Ba-osumilite.

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