

Crystallization of osumilite from modified basaltic glasses

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Osumilite-type phases, which have high temperature stability and low linear thermal expansion coefficients, were crystallized from modified basalt glass composition. To satisfy the compositional requirements of osumilite molecules, a deliberate amount of kaolin, sand, magnesite and TiO₂ should be added to the basalt. The crystallization process was investigated by DTA, X-ray diffractometry and SEM. The effect of compositional changes on bulk crystallization and growth morphology was also studied. The linear thermal expansion coefficient was measured to characterize the produced glass-ceramics.

1. Introduction

The structure of osumilite-type minerals [1] with the general formula $CB_2A_2T_2T_3Ti_2O_{30}$ is characterized by six-membered double-rings of (Si, Al)O₄ tetrahedra which are stacked along the *c*-axis. These double rings are interconnected by T2 tetrahedra and octahedra (A-site) thus forming channels along the *c*-axis which may be occupied by large alkali- or alkaline-earth cations (C-site at 0,0,1/4). The B-site is located between two octahedra parallel to the *c*-axis. The crystal chemistry and occurrence of natural double-ring silicates have recently been reviewed [2].

In the past few years some synthetic osumilite-type phases suitable for technical application as the crystalline basis in glass-ceramic materials have attracted the interest of ceramists and engineers. This is mainly due to the high-temperature stability and low linear thermal expansion coefficients of some of these phases. Mixture of osumilite-type composition can be melted easily and homogeneous glasses are obtained after quenching to room temperature [1].

MAS osumilite (Mg₂Al₄Si₁₁O₃₀) is an interesting osumilite-type phase which was first discovered [30] as a metastable accessory compound in crystallization products of glasses with compositions close to the joint cordierite-SiO₂. Addition of a small amount of BaO to an MgO–Al₂O₃–SiO₂ glass composition yields a product with MAS osumilite as the main phase [4 and 5]. Though metastable, MAS osumilite can endure temperatures up to 1150 °C for a long time. At higher temperatures it decomposes into cordierite and cristobalite. The most interesting property of this osumilite phase is its linear thermal expansion behaviour which resembles that of cordierite: while the *a*-axis expansion is low but positive, the *c*-axis shows a negative expansion with $\alpha_a = 2.6 \times 10^{-6}/K$ and $\alpha_c = -1.9 \times 10^{-6}/K$ (25 to 600 °C)

yielding an overall linear thermal expansion coefficient of $1.1 \times 10^{-6}/K$ which is nearly as low as that of cordierite.

Crystal-structure refinement data [1] are still lacking for most synthetic osumilite-type phases. Structure refinements exist only for alkali-containing roedderite-type phases. Khan et al. [6] presented data for K₂Mg₅Si₁₂O₃₀ based on single-crystal measurements. Nguyen et al. [7] did extensive work on several sodium, potassium and lithium containing roedderite-type phases using X-ray powder techniques. Those authors stated that, depending on the kind of alkali cations present, the occupation of the B- and C-sites is different: while the smaller Na⁺ favours the nine-coordinated B-site, the larger K⁺ prefers the twelve-coordinated C-site. However, they obtained MAS osumilite as a major phase besides much anorthite, β -quartz ss, cristobalite and traces of magnesium titanate phases and thus were not able to determine its exact composition.

Hence, in this paper the authors report on the crystallization behaviour of three modified basalt glass compositions based on osumilite and the linear thermal expansion of the resulting glass-ceramics.

To formulate osumilite-based glass-ceramic batch composition, a chemico-mineral molecular norm (CIPW) (8) was adopted to recalculate the chemical composition of basalt into osumilite and anorthite molecules. In this method of calculation, and to achieve the highest possible amount of osumilite from such polycomponents basalt composition, Fe²⁺ ions of basalt may be totally oxidized into Fe³⁺ ions by adding a deliberate amount of NH₄NO₃. Almost most of the oxidized basalt composition, forming components, even Ca²⁺, up to certain limits, can find place in the osumilite structure as K₂Mg₂Al₃Si₉Al₃O₃₀, Na₂Mg₂Al₃Si₉Al₃O₃₀ and CaMg₂Fe₃³⁺Si₉Al₃O₃₀. Some of the Ca²⁺ ions were allotted to the latter osumilite derivative and the rest was allotted to an anorthite phase.

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Table 1. Chemical compositions in wt% of the parent glass BO*

oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂
wt%	53.54	19.32	10.55	4.69	4.21	2.14	0.62	4.93

* 2 and 4 % of MgO were added to this composition to yield BOM₁ and BOM₂ respectively.

To satisfy the compositional requirements of osumilite molecules, the norm calculations reveal that ≈16 kaolin, ≈0.89 sand, 3.1 magnesite and 5.77 TiO₂ (in wt%) should be added to the basalt. This base composition may yield 80.97 wt% osumilite. In order to facilitate the melting of the base composition and to catalyze the formation of osumilite glass-ceramic, a deliberate amount of TiO₂ and F⁻, such as MgF₂, was added. The fluorine was added with the view that it may replace one atom of oxygen in CaMg₂Fe₃³⁺Si₉Al₃O₃₀ molecule to give CaMg₂Fe₃³⁺Si₉Al₃O₂₉F₂.

Consequently, three glasses were prepared and denoted by BO, BOM₁ and BOM₂, where the letters BO indicate the basalt-osumilite composition, and M₁ and M₂ indicate the addition of MgF₂ in different quantities.

2. Experimental

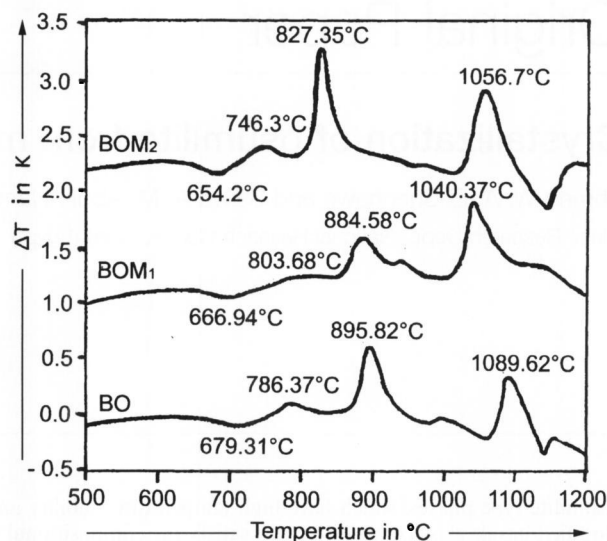
The starting glass composition (table 1) was prepared from (in wt%) ≈74 % basalt rock as a main reagent and 16 % kaolin, 0.9 % sand, 3.1 % magnesite, and 5.77 % TiO₂ as modifying agent. 3 g NH₄NO₃ as oxidizing agent was added. MgF₂ was added by 2 or 4 wt% as nucleating agent to the batch. This composition corresponds to a mixture of ≈80 % osumilite and the rest were anorthite, β-quartz ss and titanium bearing phase. The composition was melted at 1500°C for 4 h in a platinum crucible. The melt was then cast into hot steel moulds in the form of discs (1 cm thick) and rods (1x1x10) cm³ which were transferred to a muffle furnace at 650°C for annealing.

It is worth mentioning that lower viscosities and good working traits were noticed especially in compositions containing a high content of MgF₂ from which a longer glass fibre could be drawn over relatively longer durations according to the adopted qualitative viscosity test [8].

Differential thermal analyses of the prepared glass were carried out under N₂ atmosphere in a Perkin-Elmer 7-series DTA system. The analyses were carried out using ≈70 mg of the powdered samples (90 to 250 μm), the heating rate was maintained at 10 K and constant flow rate of N₂ was kept at 50 cm³/min. Corundum was used as a reference material.

The effect of heat treatment on crystallization was studied in glass samples isothermally cured at temperatures ranging from 950 to 1200°C at ≈50 K intervals for 3 h. Some samples were heated for 24 and 30 h to study the thermal stability of the developed crystalline phases.

X-ray powder diffraction analyses of the heat-treated glass were carried out using a Philips PW/390 X-ray diffractometer with nickel-filtered CuK_α radiation. The instru-

Figure 1. DTA traces of BO, BOM₁ and BOM₂.

ment settings were maintained for all the analyses by using an external standard silicon disc.

The mineralogical composition and microstructure of the glass-ceramic were examined by scanning electron microscope, Jeol JSM-T20, on fresh-fractured surfaces of some samples.

Linear thermal expansion coefficients of some samples were measured using Linseis L74/1250 dilatometer.

3. Results

The DTA traces (figure 1) exhibit an endothermic peak in the 654 to 679°C temperature range and three exothermic peaks in the 746 to 803°C, 827 to 895°C and 1040 to 1089°C temperature ranges, which correspond to crystallization of β-quartz ss, anorthite and cristobalite, and osumilite, respectively. As was mentioned in a previous paper [9], the endothermic reaction marks the glass transition (T_g) and softening (T_s) temperatures are believed to have been caused by an increase in heat capacity due to transformation of glass structure [10]. The exothermic reaction of crystallization effects, which is accompanied by releasing heat due to its lower free energy and reaches its maximum rate near the sharpness of the exothermic peak, the higher the propensity, velocity and bulk crystallization is.

Generally the behaviour of DTA curves shows shift to lower temperature by adding MgF₂ from 2 to 4 % to the batch composition.

X-ray diffraction patterns of base composition (BO) (figure 2) heat-treated at 950°C/3 h show the crystallization of β-quartz ss as major phase besides pyroxene. Anorthite was developed and distinguished when the samples were heat-treated at 1050°C/3 h. Indefinite osumilite composition and minor cristobalite appeared on samples heat-treated at 1050°C/30 h. All phases were stable when heat-treated till 1100°C/24 h (figure 2).

Adding 2 % MgF₂ (BOM₁) to the batch composition led to the formation of metastable (MgTiO₃) geikielite phase at an early stage by heating the sample to 950°C/3 h (figure 3).

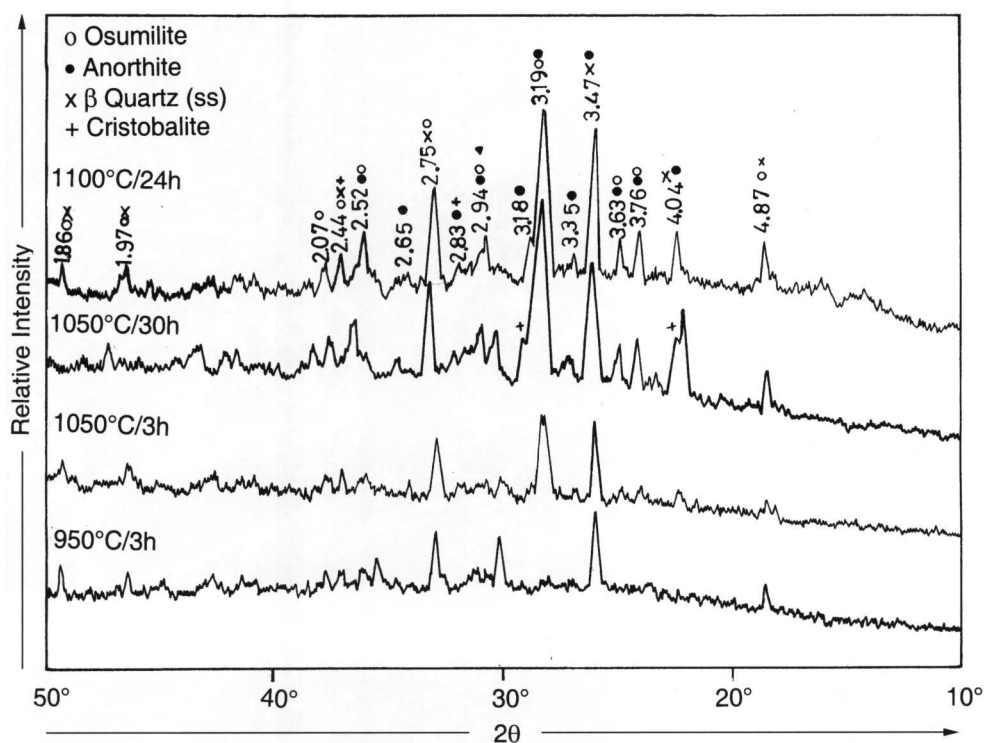


Figure 2. X-ray diffraction patterns of BO glass heat-treated at 950°C/3 h, 1050°C/3 h, 1050°C/30 h and 1100°C/24 h (d -values are given in Å).

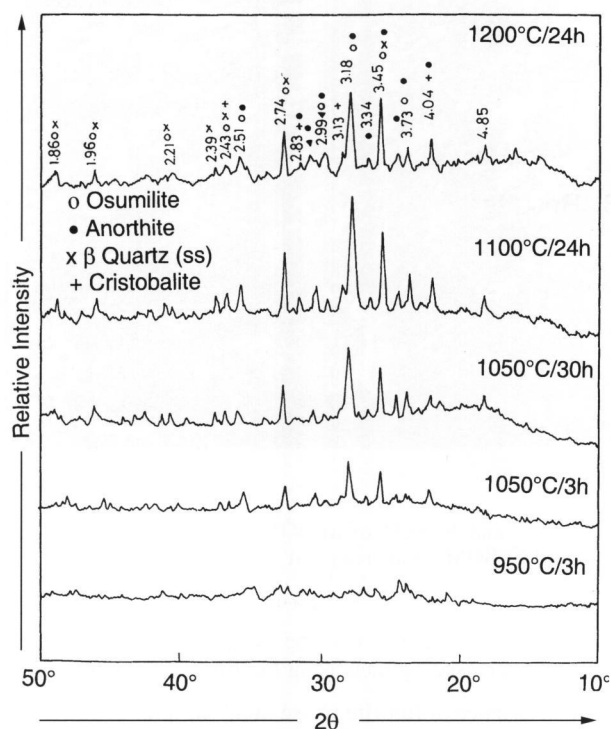


Figure 3. X-ray diffraction patterns of BOM₁ glass heat-treated at 950°C/3 h, 1050°C/3 h, 1050°C/30 h, 1100°C/24 h and 1200°C/24 h. The MgTiO₂ reflections are at $d = 3.79, 3.69$ and 3.58 Å.

This phase disappeared completely by heating the sample to 1050°C/3 h where anorthite β -quartz ss and minor pyroxene were crystallized. Increasing the time to 30 h at the same temperature led to appearance of osumilite. Cristobalite was separated and distinguished on a sample heat-treated at 1100°C/24 h. The intensity of all peaks increased and be-

came sharper and more distinguished by increasing temperature and time. All phases were still stable till 1200°C/24 h.

It was noticed that the amount of anorthite crystallized in BOM₁ was larger than that in BO with respect to crystallization of β -quartz ss.

Increasing the amount of MgF₂ added to 4% in BOM₂ glass composition did not much affect the crystallization behaviour compared to that of BOM₁, only more separation of X-ray peaks occurred which revealed more development of the crystallized phases (figure 4). MgTiO₃ did not crystallize here.

The microstructure of the resultant crystalline product is dependent on the fluorine content in the original glass. The increase of fluorine content led to the formation of volume, homogeneous and fine- to ultrafine-grained microstructures (figures 5a and b).

Thermal expansion was measured for glass-ceramic samples heat-treated at 1050°C/30 h over different temperature intervals (table 2).

It was generally observed that the linear thermal expansion of all glass-ceramic compositions increased slowly till 500°C, then began to decrease.

Adding MgF₂ to the glass composition led to a slight increase of the thermal expansion and this increase was directly proportional to the amount of MgF₂ added.

4. Discussion

Borukhove et al. [11] determined the linear thermal expansion coefficient, α , of basaltic rocks in the glassy state as

$$\alpha_{25 \text{ to } 500} = 15.94 \times 10^{-6}/\text{K} \text{ to } \alpha_{750 \text{ to } 800} = 75 \times 10^{-6}/\text{K}.$$

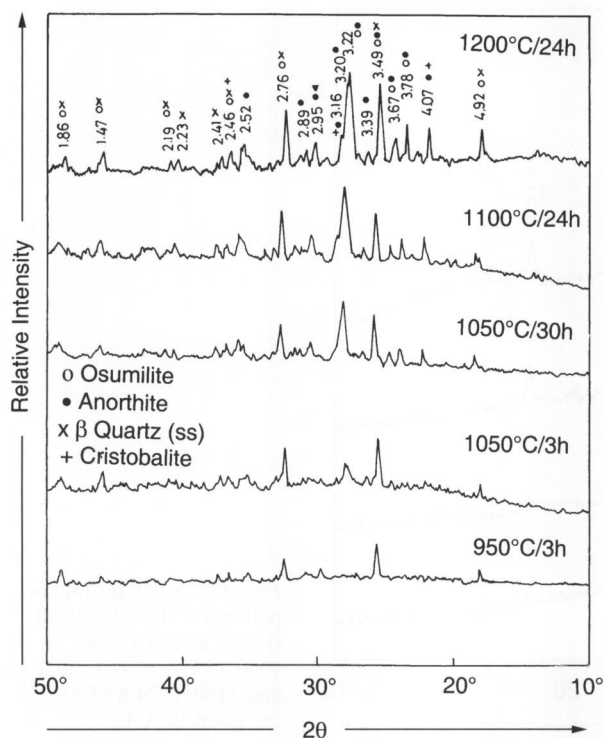


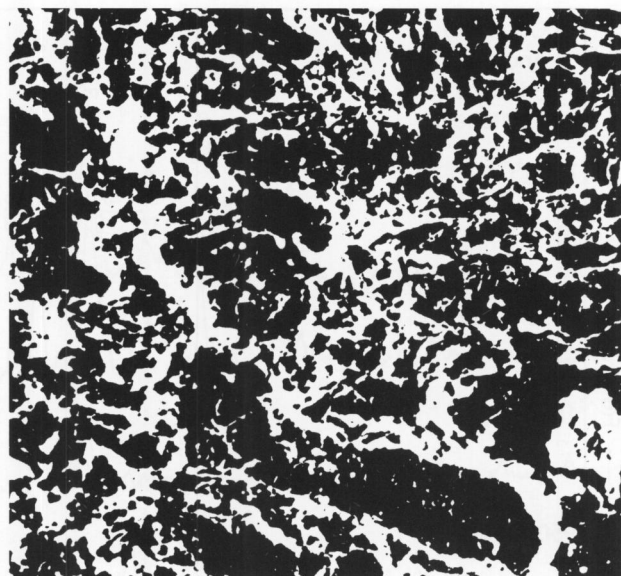
Figure 4. X-ray diffraction patterns of BOM₂ glass heat-treated at 950°C/3 h, 1050°C/3 h, 1050°C/30 h, 1100°C/24 h and 1200°C/24 h.

Table 2. Linear thermal expansion coefficient (α in 10^{-6} K^{-1}) of BO, BOM₁ and BOM₂ heat-treated at 1050°C/30 h

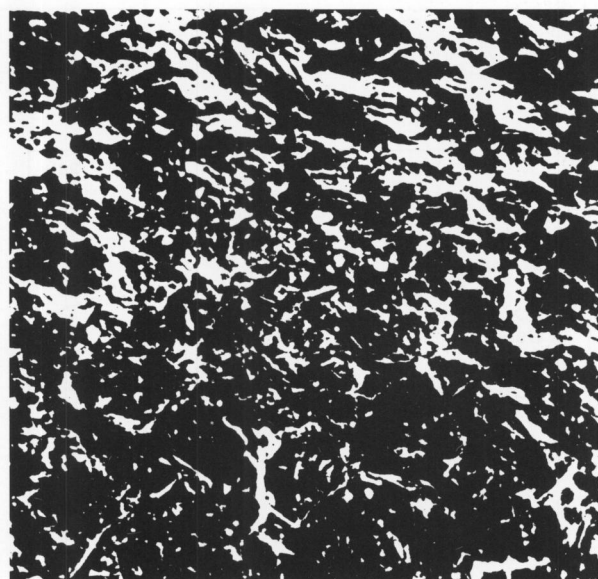
sample	$\alpha_{20 \text{ to } 300}$	$\alpha_{20 \text{ to } 400}$	$\alpha_{20 \text{ to } 500}$	$\alpha_{20 \text{ to } 600}$	$\alpha_{20 \text{ to } 700}$
BO	5.3	5.6	5.8	6.0	5.9
BOM ₁	6.4	6.4	6.4	6.1	5.9
BOM ₂	6.6	6.7	6.6	6.6	6.3

The fluorine ion, with a radius of 0.136 nm, is very close in size to the oxygen ion (radius 0.14 nm, so that a fluorine ion could replace an oxygen ion in the glass network without causing a great disturbance in the arrangement of other ions. Since the fluorine ion is monovalent, however, the overall replacement within the glass must be two fluorine ions for each oxygen ion in order to ensure electrical neutrality. A general effect of the fluorine would be the replacement of the strong =Si–O–Si= linkages by pairs of the weaker ≡Si–F linkages with the result that the glass network structure would be weakened [12].

In other words fluorine substitution for bridging oxygen ions leads to weakening the glass network due to the formation of $[\text{SiO}_3\text{F}]^{3-}$ groups with a general formula $[\text{SiO}_{(4-x)}\text{F}_x]^{4-x}$ which may increase as the fluorine content increases [13]. Due to the weakening of the glass structure, fluorine also modifies the kinetic barriers for nucleation and growth of crystals, which can take place at lower temperatures. Vogel and Höland [14] found that what took place in a fluorine-free MgO–Al₂O₃–SiO₂ glass at temperature as high as 1130°C could be achieved at 960°C by the addition of fluorine. This effect is reflected in decreasing T_g , T_s and T_c , in the tendency for the linear thermal expansion coefficient of



a) | 10 μm



b) | 10 μm

Figures 5a and b. SEM of a) BOM₁ heat-treated at 1050°C/30 h and b) BOM₂ heat-treated at 1050°C/30 h.

the glass to be increased in the sample containing MgF₂, and it is increased by increasing the fluorine content.

The absence of fluorite phase in all samples heat-treated at different temperatures indicates that the F⁻ ion in the glassy phase may replace one atom of oxygen in CaMg₂Fe³⁺Si₉Al₃O₃₀ to give CaMg₂Fe₃³⁺Si₉Al₃O₂₉F₂.

The relatively low viscosity and high volume crystallizability exhibited by the present titania- and fluoride-containing glasses may be also related to the weakening effect of either titanium or fluorine ions on the network structure of the glass [15 to 19]. According to those authors, Ti⁴⁺ ions can act as network former and exit in silicon equivalent fourfold coordinated sites. However, Ti⁴⁺ has a field strength of 1.04 considerably above that of the fourfold-coordinated Al³⁺ (0.96), which is known to enter the net-

work structure, but below that of the major glass network-forming Si^{4+} (1.56). Therefore, introducing weaker Ti–O bonds will weaken the network structure, which, in turn, is reflected in lowering the viscosity of melts or glasses and consequently leads to more mobilization of the glass-forming elements, i.e., to crystallization.

It was observed that TiO_2 can segregate forming small crystallines of MgTiO_3 , which act as heterogeneous nucleation sites for the crystallization of the glass matrix in compositions containing MgF_2 .

5. References

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