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Heat treatment of wollastonite-type Y–Si–Al–O–N glasses

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Cumulative work over the last twenty years has defined the glass-forming regions in several M–Si–Al–O–N systems (M = Mg, Ca, Y, Ln) with the resulting crystalline products identified after heat treatment. Glass-forming regions in nitrogen-rich sialon glasses have been recently reported and heat treatment of some of these glasses in the Y–Si–Al–O–N system has been performed. The crystallization of yttrium-containing glasses is particularly sensitive to small variations in composition and heat treatment temperature and in the current work the results of three series are discussed: (1) a single composition, $Y_{15.2}Si_{14.6}Al_{8.7}O_{54.6}N_{6.9}$ (16 e/oN), treated at 30 °C intervals between 875–1410 °C; (2) compositions of a constant Y : Si : Al ratio of 3 : 3 : 2 and up to 32 e/oN and (3) selected compositions lying on the 28 e/o N plane. Two different sets of crystalline products are found to form above and below 1200 °C.

1. Introduction

The glass-forming regions in several M–Si–Al–O–N systems (M = Mg, Ca, Y, Ln) [1–5] have been investigated as a function of heat treatment sequences and the resulting crystalline products in these systems have been identified. In most cases the heat treated products are multiphase, although some glass ceramics have been reported [6–9]. Glass-forming regions in nitrogen-rich Y, Nd and La sialon glasses have been recently investigated [10] and the regions of maximum nitrogen content were identified. The glass-forming regions of the Y–Si–Al–O–N system thus defined at 1700 °C are shown in Fig. 1, with the maximum nitrogen content at the composition $Y_3Si_3Al_2O_9N_3$ (33.3 e/o N).

Fig. 2 shows the well-established crystalline phases in the Y–Si–Al–O–N system. It can be seen that there are no ternary Y_2O_3–Al_2O_3–SiO_2 compounds, nor any quaternary Y–Al–O–N phases. Those that do occur lie either along the Y_2O_3–Al_2O_3 join or are formed in the Y–Si–O–N system, with the associated ranges of solid solution into the five-component system formed by Si, Al and O, N substitution. In this figure the only 5-component phase is the B-phase, which has a range of composition extending along the line $YSiO_2N$–$YAlO_3$ from ∼44–62 m/o $YAlO_3$, but is usually referred to by the mid-point composition Y_2SiAlO_5N. However, recent investigations have established the existence of several other Y–Si–Al–O–N phases which are discussed in detail elsewhere [9]. These include the U-phase, $Y_3Si_3Al_3O_{12}N_2$ [7, 11]: the I_w-phase, $Y_{18-x}Si_{12}Al_6O_{42+3x}N_{12-3x}$ ($x = 2, 3$) [4, 5, 9]; the Q-phase, $YSi_2Al_2O_{6.8}N_{1.13}$ [9] and the D-phase, $YSi_2AlO_4N_2$ [9, 13].

In the course of heat treatment investigations in the Y–Si–Al–O–N system one of the most commonly observed low temperature devitrification products is the B-phase. This was thought originally to be a possible glass ceramic, but since it lies outside the glass-forming region it is impossible to make pure without a trace of some other crystalline product(s). However, with the addition of excess SiO_2 in the starting mixture it is possible to make a glass at 1700 °C which, on heat treatment at an appropriate temperature, will give only B-phase with some residual glass. The results of one such composition have been investigated in the present work.

The addition of SiO_2 to the B-phase composition necessarily reduces the nitrogen content in the starting mixture to around 20 e/o or less. Up to this amount the glass-forming region is relatively large, but with greater nitrogen content the glass volume reduces considerably (see Fig. 1), so that to obtain a glass, the starting composition must be very specific. As a result, very little devitrification work has been carried out in higher nitrogen containing samples. Thus, in the present work, such glasses have been prepared and heat treated at a range of temperatures.

2. Experimental procedure

Samples were prepared by melting compositions from appropriate mixtures of the following powders: Si_3N_4 (Grade LC10 - HC Starck Berlin); Al_2O_3 (Grade A17-Alcoa Chemie GMBH); SiO_2 (Analar Grade - BDH Chemicals Ltd); Y_2O_3 (99.9%-Rare Earth Products). The powders were mixed by hand in isopropanol and uniaxially pressed into 5–20 g pellets; these were

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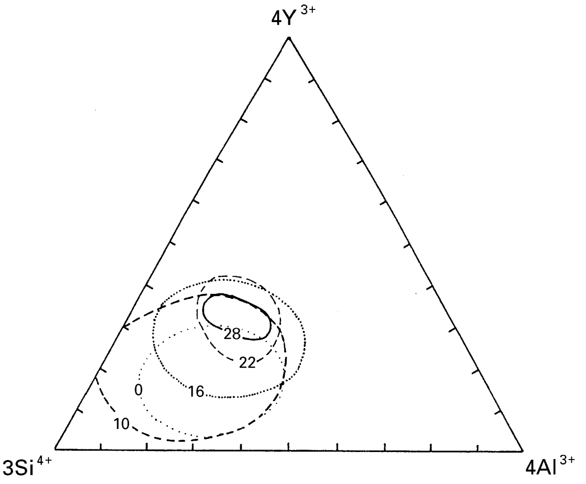

Figure 1 Glass forming regions at 1700 °C in the Y–Si–Al–O–N system.

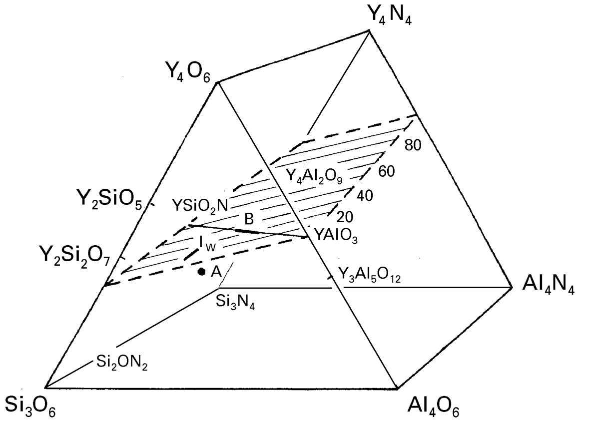

Figure 3 Representation of the $Y_n(Si, Al)_3(O, N)_9$ plane in the Jänecke prism.

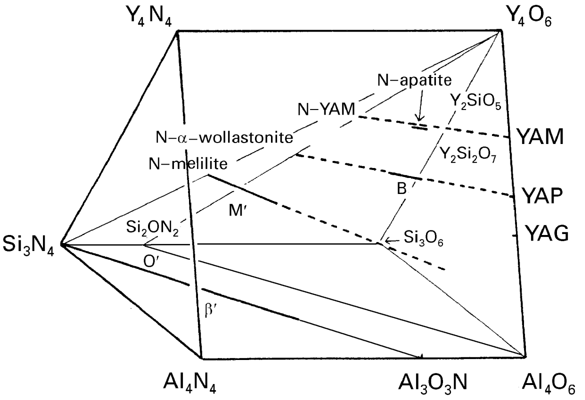

Figure 2 Crystalline phases in the Y–Si–Al–O–N system.

melted at 1650–1750 °C in N_2 in a graphite element furnace or a graphite induction furnace for 30 min using a graphite crucible lined either solely with BN or with a 50/50 BN/Si_3N_4 powder mix.

The heat treatments were performed in a molybdenum-wound vertical furnace, or a silicon carbide horizontal furnace in flowing N_2 at various temperatures in the range 850–1400 °C. The crystalline products were identified by means of a Hägg–Guinier focusing camera and CuKα_1 radiation. Subsequent microstructural studies were carried out on a Hitachi S2400 scanning electron microscope (SEM) equipped with a Link energy dispersive X-ray analysis (EDX) system.

3. Results and discussion

Fig. 3 shows a Jänecke prism representation of the Y–Si–Al–O–N system illustrating the position of the $Y_n(Si, Al)_3(O, N)_9$ plane on which lie the wollastonite phase, the B-phase and the I_w-phase [9]. Lines of constant e/o nitrogen are marked on this plane to indicate relative depth into the prism.

3.1. Effect of change in heat treatment temperature

As previously mentioned, early efforts to produce near single phase B-phase showed the necessity of adding excess SiO_2 to move the starting composition into the glass-forming region. The most reproducible of these samples has the composition $Y_{15.2}Si_{14.6}Al_{8.7}O_{54.6}N_{6.9}$ (15.94 e/o N) and is marked at point A in Fig. 3. During heat treatment experiments it was noted that small unscheduled fluctuations in temperature, normally assumed to be within experimental error, resulted in a remarkable variation in crystalline products. A heat treatment series was therefore carried out, in which glass samples of the same composition were annealed individually at temperature intervals of about 30° between 875–1410 °C to establish the principal crystalline phases at each temperature. In all cases a certain amount of residual glass is assumed, but has not been quantified. Table 1 shows the X-ray products and visual intensities; the intensities are represented graphically in Fig. 4. From these results it can be seen that two distinct sets of crystalline phases exist approximately above and below 1200 °C. For this particular sample, crystallization begins at about 860 °C, with the B-phase being the only phase existing with the accompanying glass. As more B-phase crystallises, the composition of the residual glass becomes more silica rich, so that the I_w-phase also forms between 1060–1200 °C. Although wollastonite is the most stable phase in this temperature range (< 1250 °C), the relatively low nitrogen content of the starting mixture allows only a small amount to form. Above ~1200 °C all these phases have decomposed to form yttrium aluminum ganet (YAG) and apatite, with δ- and β-$Y_2Si_2O_7$ also present. Table II lists the compositional ranges of all these observed phases and confirms the equilibrium of products at any temperature. Any excess nitrogen is assumed to remain in a small amount of uncrystallized glass.

A comparison can be made with the results reported by Leng–Ward and Lewis [5] who prepared glasses of composition $Y_{1.04}Si_{1.27}Al_{1.27}(O, N^{0-30})$ i.e., containing 0, 10, 20, 30 e/o N; the heat treatment was carried out at 1100 and 1250 °C. At 1100 °C the 10 and 20 e/oN samples contained Al_2O_3 and the I_w-phase while at 1250 °C β-$Y_2Si_2O_7$ and Si_2ON_2 were respectively the strongest phases, with some YAG, mullite and Al_2O_3. No B-phase or wollastonite were

TABLE I Heat treatment products from $Y_{15.2}Si_{14.6}Al_{8.7}O_{54.6}N_{6.9}$ glasses

T (°C)	h	glass	B	I_w	Woll	δ	YAG	Ap	β
1700	0.5	*	tr						
1410	18		–	–	–	–	s	m	mw
1380	24		–	–	–	–	vs	ms	mw
1350	65		–	–	–	tr	vs	ms	mw
1320	16		–	–	–	mw	s	ms	w
1290	20		–	–	–	mw	s	m	mw
1240	?		–	–	–	m	s	ms	mw
1215	24		–	?	w	m	ms	mw	–
1180	18		w	ms	mw	–	vw	?	?
1165	120		mw	s	vw	–	–	–	–
1140	16		vs	m	mw	–	?	–	–
1100	22		s	w	vw	–	–	–	–
1070	64		s	w	–	–	–	–	–
1040	21		s	–	–	–	–	–	–
990	16	*	mw	–	–	–	–	–	–
955	64	*	vvw	–	–	–	–	–	–
915	41	*	tr	–	–	–	–	–	–
875	62	*	tr	–	–	–	–	–	–

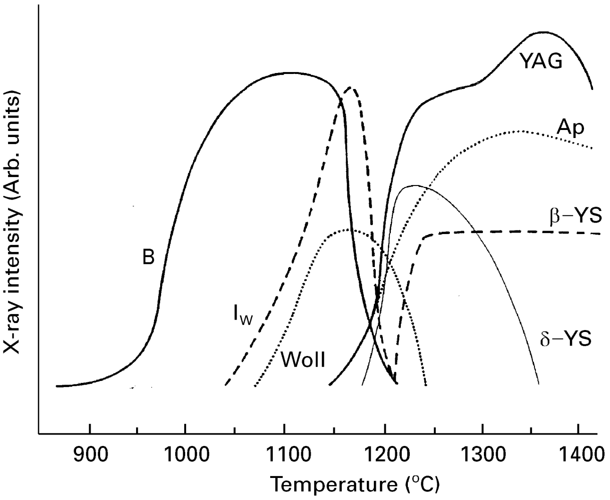

Figure 4 Heat treatment products from $Y_{15.2}Si_{14.6}Al_{8.7}O_{54.6}N_{6.9}$ glasses.

TABLE II Compositional ranges of crystalline products

Phase	Composition	e/o N
B-phase	$Y_2Si_{0.8}Al_{1.2}O_{5.2}N_{0.8}$	18.75
	Y_2SiAlO_5N	23.08
	$Y_2Si_{1.2}Al_{0.8}O_{4.8}N_{1.2}$	27.27
I_w-phase	$Y_{15}Si_{12}Al_6O_{51}N_3$	8.11
	$Y_{16}Si_{12}Al_6O_{48}N_6$	15.79
Wollastonite	$YSiO_2N$	42.86
Apatite	$Y_5Si_3O_{12}N$	11.11
Silicate	$Y_2Si_2O_7$	0
YAG	$Y_3Al_5O_{12}$	0

observed, due to the relative deficiency of yttrium in this sample compared with that in the present work; hence the heat treated products from yttrium sialon glasses depend not only on temperature, but also on the Y : Si : Al ratio of the starting glass.

3.2. Effect of change in nitrogen content

In order to investigate the effect of any change in the nitrogen content on the devitrification products, a series of glasses was prepared with the constant Y : Si : Al cation ratios of 3 : 3 : 2 at which the highest nitrogen content in the yttrium sialon system has been observed. These were heat treated at temperatures of 1050, 1150 and 1350 °C for 64–68 h and the results are listed in Table III. It can be seen that, as before, the products forming at 1050 and 1150 °C i.e., B-phase, I_w-phase and wollastonite decompose to give YAG, a mixture of yttrium silicates and some other oxynitride phase at 1350 °C. The B-phase is stable in all samples only below 1100 °C, while at 1150 °C the I_w-phase predominates in samples of up to 20 e/oN, as does wollastonite where the nitrogen content is greater than 20 e/o. At this temperature there is also observed about 10% of the new Q-phase [9], believed to have the composition $YSi_2Al_2O_{6.8}N_{1.13}$ although the nitrogen content may be greater than 20 e/o; the proportion of this phase increased to ∼20% when the heat treatment time was increased to 1000 h. At 1350 °C the yttrium silicates observed also seem to form two groups, i.e. up to 20 e/oN δ- and β-$Y_2Si_2O_7$ are found while the complementing oxynitride is apatite. In samples of higher nitrogen X_2–Y_2SiO_5 is the predominant phase with a second phase thought to be α-$Y_2Si_2O_7$. In addition are Si_2ON_2 and β-Si_3N_4 which are non-yttrium containing due to the higher Y content of the X_2-silicate.

3.3. Effect of change in aluminium content

Four compositions of equal Y : Si ratio and containing 28 e/o N were prepared and the relative Al content varied; results are shown in Table IV. Samples labelled "⋯-x" reached the required 1350 °C but this temperature was not held; the presence of wollastonite for a short time only shows, therefore, that 1350 °C is the upper limit of the stability range of this phase, which then decomposes to yttrium silicates and β-silicon nitride after a longer time. At 1150 °C, however, the products are less consistent due to the presence of a significant amount of U-phase in two samples. This phase was first observed [11] in the course of sialon

TABLE III Heat treatment products from $Y_3Si_3Al_2(O, N)$ samples

T °C	Sample	Composition	e/o N	Woll (4/2)*	B	I_w	YAG	YS	other
1050	819-3	$Y_3Si_3Al_2O_{12.15}N_{0.90}$	10	–	mw	vs	–	–	–
	820-3	$Y_3Si_3Al_2O_{11.34}N_{1.44}$	16	–	vs	–	tr	–	–
	817-3	$Y_3Si_3Al_2O_{10.80}N_{1.80}$	20	–/mw	vs	–	–	–	–
	818-3	$Y_3Si_3Al_2O_{10.26}N_{2.16}$	24	s/-	m/m	–	–	–	–
	807-3	$Y_3Si_3Al_2O_{9.72}N_{2.52}$	28	vs/s	–	–	–	–	–
	821-3	$Y_3Si_3Al_2O_{9.45}N_{2.70}$	30	-/s	s	–	–	–	–
	816-3	$Y_3Si_3Al_2O_{9.18}N_{2.88}$	32	vs/vs	vw	–	–	–	–
1150	819-1	$Y_3Si_3Al_2O_{12.15}N_{0.90}$	10	–	–	vs	tr	–	Q(vw)
	820-1	$Y_3Si_3Al_2O_{11.34}N_{1.44}$	16	w/-	w	vs	tr	–	–
	817-1	$Y_3Si_3Al_2O_{10.80}N_{1.80}$	20	s/-	–	vs	vw	–	–
	818-1	$Y_3Si_3Al_2O_{10.26}N_{2.16}$	24	s/-	–	ms	vvw	–	–
	807-1	$Y_3Si_3Al_2O_{9.72}N_{2.52}$	28	vs/-	–	w	–	–	–
	821-1	$Y_3Si_3Al_2O_{9.45}N_{2.70}$	30	vs/-	tr?	–	tr	–	–
	816-1	$Y_3Si_3Al_2O_{9.18}N_{2.88}$	32	vs/-	tr?	–	tr?	–	–
1350	819-2	$Y_3Si_3Al_2O_{12.15}N_{0.90}$	10	–	–	–	s	β(m), δ(tr)	–
	820-2	$Y_3Si_3Al_2O_{11.34}N_{1.44}$	16	–	–	–	s	δ(w), β(tr)	ap(m)
	817-2	$Y_3Si_3Al_2O_{10.80}N_{1.80}$	20	-/vw?	–	–	s	δ(w)	ap(m)
	818-2	$Y_3Si_3Al_2O_{10.26}N_{2.16}$	24	–	–	–	s	X_2(mw), α?(vw)	ox(vw)
	807-2	$Y_3Si_3Al_2O_{9.72}N_{2.52}$	28	–	–	–	s	X_2(mw), α?(w)	βSN(w)
	821-2	$Y_3Si_3Al_2O_{9.45}N_{2.70}$	30	m/-	–	–	s	X_2(mw), α?(w)	–

* indicates relative proportions of 4-layer and 2-layer $YSiO_2N$

TABLE IV Heat treatment products from 28 e/o N samples

T °C	Sample	Composition	e/o N	Woll (4/2)*	B	I_w	YAG	YS	other
1050	806-3	$Y_3Si_3Al_{1.5}O_{9.18}N_{2.38}$	28	vs/mw	–	w	–	–	–
	807-3	$Y_3Si_3Al_{2.0}O_{9.72}N_{2.52}$	28	vs/s	–	–	–	–	–
	815-3	$Y_3Si_3Al_{2.5}O_{10.26}N_{2.66}$	28	–/m	vs	–	–	–	–
	805-3	$Y_3Si_3Al_{3.0}O_{10.80}N_{2.80}$	28	-/w	vs	–	–	–	?(tr)
1150	806-1	$Y_3Si_3Al_{1.5}O_{9.18}N_{2.38}$	28	vs/-	–	mw	–	–	–
	807-1	$Y_3Si_3Al_{2.0}O_{9.72}N_{2.52}$	28	vs/-	–	w	–	–	–
	815-1	$Y_3Si_3Al_{2.5}O_{10.26}N_{2.66}$	28	s/-	w	–	vw	–	U(s)
	805-1	$Y_3Si_3Al_{3.0}O_{10.80}N_{2.80}$	28	-/w	vs	–	–	–	U(m)
1350	807-x	$Y_3Si_3Al_{2.0}O_{9.72}N_{2.52}$	28	ms/-	–	–	s	–	ox(vw)
	815-x	$Y_3Si_3Al_{2.5}O_{10.26}N_{2.66}$	28	ms/-	–	–	s	–	ox(vw)
1350	806-2	$Y_3Si_3Al_{1.5}O_{9.18}N_{2.38}$	28	–	–	–	s	X_2(mw), δ(w) α?(w)	βSN(w)
	807-2	$Y_3Si_3Al_{2.0}O_{9.72}N_{2.52}$	28	–	–	–	s	X_2(mw), α?(w)	βSN(w)
	815-2	$Y_3Si_3Al_{2.5}O_{10.26}N_{2.66}$	28	–	–	–	s	X_2(mw), α?(w)	βSN(w)
	805-2	$Y_3Si_3Al_{3.0}O_{10.80}N_{2.80}$	28	–	–	–	s	X_2(mw), α?(w)	βSN(w)

* indicates relative proportions of 4-layer and 2-layer $YSiO_2N$.

densification experiments using Y_2O_3 as an additive. Heat treatment below 1200 °C gave only 10–15% U-phase and has not since been observed with any certainty. Yttrium U-phase cannot be prepared by devitrifying the glass of the same composition $\sim Y_3Si_3Al_3O_{12}N_2$, although the rare earth analogues of La–Dy form readily, particularly at the La end of the series. Nevertheless, in this work the higher nitrogen content in the starting mixtures causes the U-phase to form apparently at the expense of the I_w-phase, so that in sample 815-1 the amount observed may be as much as $\sim 50\%$.

In addition to this result it can be seen that the I_w-phase is strongest when the Si : Al ratio is 2 : 1 i.e., the ratio of the proposed composition of the I_w-phase itself [9]. This is most apparent in Table V, where results can be compared with similar samples containing 20 e/oN instead of 28 e/o. The phase labelled δ is one whose diffraction pattern is similar to δ-$Y_2Si_2O_7$ but with small variations in line positions and intensities.

Fig. 5 shows a graph of hexagonal unit cell dimensions for the range of composition along the $YSiO_2$–$YAlO_3$ line, assuming values of a and c for the $YSiO_2N$ from the corresponding monoclinic data, and for $YAlO_3$ from the ICDD card 16-219. The unit cell dimensions for the B-phase are compared with the graph, and the range of measurements is consistent with the marked B-phase range, with a translated to a line below the original $YSiO_2N$–$YAlO_3$ line so that a and c correspond to the same Si : Al ratio measured by EDX. This line extrapolates to $a \approx 0.401$ nm at the

TABLE V Heat treatment products from 20 e/oN samples

T °C	Sample	Composition	e/o N	Woll (4/2)*	B	I_w	YAG	YS	other
1050	790-4	$Y_3Si_3Al_{1.5}O_{10.2}N_{1.7}$	20	s/-	–	vs	–	–	–
	817-3	$Y_3Si_3Al_{2.0}O_{10.8}N_{1.8}$	20	-/mw	vs	–	–	–	–
	771-4	$Y_3Si_3Al_{3.0}O_{12.0}N_{2.0}$	20	–	s	–	vw	–	?(tr)
1150	790-1	$Y_3Si_3Al_{1.5}O_{10.2}N_{1.7}$	20	s/-	–	vs	–	–	–
	817-1	$Y_3Si_3Al_{2.0}O_{10.8}N_{1.8}$	20	s/-	–	vs	vw	–	–
	771-1	$Y_3Si_3Al_{3.0}O_{12.0}N_{2.0}$	20	m/-	s	mw	–	–	Q(vw), U(vvw)
1200	790-2	$Y_3Si_3Al_{1.5}O_{10.2}N_{1.7}$	20	m/-	–	vs	w	–	–
	771-2	$Y_3Si_3Al_{3.0}O_{12.0}N_{2.0}$	20	w/-	–	–	s	δ(mw)	?(w)
1350	790-3	$Y_3Si_3Al_{1.5}O_{10.2}N_{1.7}$	20	–	–	–	ms	–	ap(ms), ?(w)
	817-2	$Y_3Si_3Al_{2.0}O_{10.8}N_{1.8}$	20	vw?/-	–	–	s	δ(w)	ap(m)
	771-3	$Y_3Si_3Al_{3.0}O_{12.0}N_{2.0}$	20	–	–	–	s	δ(mw)	–

* indicates relative proportions of 4-layer and 2-layer $YSiO_2N$.

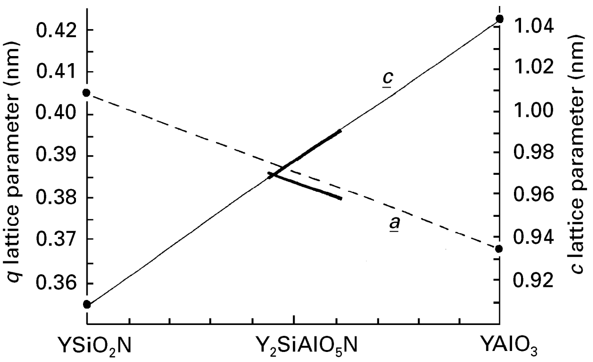

Figure 5 Unit cell dimensions for wollastonites in the range $YSiO_2N$–$YAlO_3$.

$YSiO_2N$ end, while the original intercept is at $a = 0.405$ nm. In Tables III–V the column labelled wollastonite shows two values of intensities indicating the presence of two wollastonite-type phases, one of which is the 4-layer monoclinic phase usually observed in the Y–Si–O–N system, and another which appears to index only on a hexagonal 2-layer unit cell. Previous observations during the crystallization of wollastonite glasses [6] implied that the two-layer $YSiO_2N$ phase does not exist, and that the 2-layer Nd- and Ce- analogues are merely greatly faulted versions of the corresponding well-crystallized 6-layer structures, due to the relatively low heat treatment temperature. In the present work, unit cell dimensions have been measured for all the hexagonal diffraction patterns of wollastonite using the 002, 004 and 110 reflexions, and these measurements fall into two groups. The first, with diffuse lines (probably the faulted 4-layer structure), corresponds to a and c values 0.4055–0.4046 nm and 0.912–0.916 nm respectively, and the second, quite distinct from this range with $a = 0.4030$–4.013 nm and $c = 0.923$–0.928 nm; this latter phase has a sharp hexagonal pattern and is most prominent in samples heat treated at 1050 °C. Both ranges of dimensions indicate a limited incorporation of about 4 a/o Al into the $YSiO_2N$ structure. From these results it appears that a hexagonal 2-layer $YSiO_2N$ structure forms at the lower temperature, with unit cell dimensions consistent with other 2-layer wollastonites, while the 4-layer monoclinic structure, forming above this temperature, cannot be represented precisely on the same graph.

With reference to the composition of the I_w-phase [9], although this has a unit cell 9 times its hexagonal sub-cell ($a = 0.3781$, $c = 1.006$ nm), the sub-cell dimensions can be plotted on the same graph and correspond to a composition with Si : Al = 3 : 7. Liddell *et al.* have proposed [9] that the true ratio is probably 2 : 1 and that the composition does not actually lie on the $YSiO_2N$–$YAlO_3$ line but on the $Y_n(Si, Al)_3(O, N)_9$ plane (Fig. 3), on which (Si, Al) : (O, N) is 1 : 3, a condition required by all known wollastonite-type structures. It is therefore possible that the B-phase also does not lie directly on this line, but has some other range of composition on the same plane.

4. Conclusions

Heat treatment of glasses containing more than 20 e/oN shows that wollastonite-type phases B, I_w and N-α-wollastonite are stable at temperatures up to 1200 °C, while above this temperature YAG and yttrium silicates predominate. With a regular increase in the nitrogen content the I_w-phase forms readily up to 20 e/oN, while at higher nitrogen levels wollastonite is preferentially formed. The 2-layer hexagonal $YSiO_2N$, hitherto unreported, forms only up to 1050 °C, while above this temperature the monoclinic 4-layer structure is the form commonly observed. The B-phase is stable usually only below 1100 °C, but with occasional exceptions due to changes in thermodynamic equilibrium.

Sialon wollastonite structures have been reported since the late 1970s and it has been accepted for most of the 20 years since then that the compositions of related structures all lie on or close to the $YSiO_2N$–$YAlO_3$ line. However, with the recent investigation into the I_w-phase and observations made in the present work, it can now be concluded that sialon wollastonites do not merely have compositions lying on this line, but are more widely distributed on the $Y_n(Si, Al)_3(O, N)_9$ plane. The subject is clearly much more extensive than previously anticipated.

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