optimum level leads to comparatively inferior properties. A high speed of extrusion was not possible at the binder level of 42% or more, because of the resultant snake-like extrusion. This cannot be classified as an extrudate irregularity because it is caused by the excessive binder in the mix.

Fincle [4] reports an increase in viscosity of the green mix at a shear rate of about $100 \sec^{-1}$. There are two possible reasons for such an increase. One is due to the extrusion near the end of the batch of carbon when the speed of extrusion gradually becomes slower. In order to maintain the speed, the pressure of extrusion must be increased which results in an increased viscosity of the mix. The second reason may be the removal of binder from the green mix at such high pressures. This would leave a mix with comparatively less binder which would give rise to increased viscosity.

Tordella [8] reports the appearance of irregularities in the polymers extruded above a critical flow rate. Since carbon mixes behave as a viscoelastic material, the possibility of extrudate irregularities occurring in this case cannot be ruled out. However, from the results of the present study, it is concluded that extrudate irregularities do not occur at least up to shear rates of $650 \sec^{-1}$. The possibility of extrudate irregularities occurring at shear rates higher than this cannot be eliminated.

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New polytypes in the Be–Si–O–N system

Huseby *et al.* [1] have recently shown the existence of a series of crystallographically similar phases at Be_3N_2-rich compositions in the Si_3N_4–Be_3N_2–BeO–SiO_2 system. These phases occur with ranges of homogeneity elongated along lines of constant metal: non-metal atom ratio $M_{m+1}X_m$ where m has values 4, 5, 6, 7 and 9. The minimum value, $m = 2$, gives beryllium nitride (Be_3N_2), the crystallography of which is well known [2, 3]. The maximum value, $m = \infty$, gives a range of compositions extending from beryllium–silicon nitride ($BeSiN_2$) to beryllium oxide (BeO). In the present communication, the unidentified powder diffraction patterns reported for the new phases [1] are indexed and interpreted in terms of wurtzite-type polymorphs containing excess metal atoms, the structures of which are directly related to their compositions and also to recently discovered M_mX_{m+1} polytypes in the Si–Al–O–N system.

The indexed diffraction patterns for compounds with $m \leqslant 6$ are given in Table I. In every case the unit cell is hexagonal with $\mathbf{a} \sim 2.8$ Å and with $\mathbf{c}$ large and varying from compound to compound in a manner characteristic of a polytypic series [4]. The cell dimensions of all the unidentified phases reported by Huseby *et al.* [1] are given in Table II together with the appropriate polytype designations.

The crystal structures of both beryllia and beryllium–silicon nitride are of the wurtzite type with a hexagonal close-packing of non-metal atoms and with the metal-atoms occupying all of the upward-pointing tetrahedra. The crystal structure of β-beryllium nitride, although originally thought to consist of alternate layers of upward

TABLE I Indexed diffraction data for unidentified phases reported by Huseby *et al.* [1]

Be_4SiN_4			$Be_9Si_3N_{10}$			$Be_6O_3N_2$			$Be_5Si_2N_6$		
hkl	d_{calc}	d_{obs}	*hkl*	d_{calc}	d_{obs}	*hkl*	d_{calc}	d_{obs}	*hkl*	d_{calc}	d_{obs}
0 06	3.20	3.20	0012	3.026	3.02	0012	2.882	2.88	0010	2.913	2.92
1 00	2.479	2.475	10 1	2.468	2.473	10 1	2.393	2.394	10 0	2.477	2.469
1 01	2.458	2.461	0015	2.421	2.420	10 4	2.312	2.308	10 1	2.468	
102, 008	2.400	2.406	01 5	2.342	2.342	0015	2.305		10 2	2.442	2.430
1 03	2.311	2.308	10 7	2.233	2.232	01 5	2.266	2.267	0012	2.425	
1 04	2.202	2.203	1010	2.045	2.044	10 7	2.158	2.159	10 4	2.345	2.343
1 06	1.959	1.961	0018	2.018	2.012	01 8	2.098	2.098	10 5	2.279	2.278
0 010	1.920	1.922	0111	1.980	1.977	0018	1.921	1.922	10 6	2.206	2.204
1 07	1.839	1.837	0114	1.790	1.789	0114	1.721	1.719	0014	2.079	2.080
1 08	1.724	1.724	1016	1.673	1.670	1016	1.606	1.607	10 8	2.047	2.042
1 09	1.617	1.616	0117	1.617	1.617	0117	1.551	1.551	1010	1.886	1.885
1 10	1.431	1.431	11 0	1.428	1.431	11 0	1.385	1.385	1011	1.808	1.807
1 012	1.344	1.345	1022	1.373	1.373	1022	1.315	1.315	1012	1.733	1.734
1 013	1.268	1.269	0123	1.331	1.331	0123	1.274	1.274	1013	1.661	1.661
2 00	1.239	1.237	1112	1.292	1.293	1025	1.199	1.198	1014	1.592	1.594
2 01	1.237		02 1	1.236	1.237	02 1	1.198		11 0	1.430	1.430
118, 202	1.229	1.229	1115	1.230	1.230		–	1.195*	1018	1.354	1.355
2 04	1.200	1.201	0126	1.216	1.216	02 4	1.188	1,187	1110	1.283	1.284
1014, 0016						1115	1.187		1020	1.255	1.255
									20 0	1.238	1.237
									20 1	1.237	
									1112	1.232	1.231

*Uncertain reflection; see Table 2, in [1].

and downward-pointing tetrahedra with additional beryllium atoms inserted in the nitrogen layers at the joins of tetrahedron apices [2], was subsequently shown by Hall *et al.* [3] to be of the wurtzite type with additional downward-pointing nitrogen-tetrahedra occupied by metal atoms in every alternate layer to give an overall M_3X_2 composition. In the simplest case the layer sequence is MX-M_2X-MX-M_2X-... but there is probably an equilibrium between complete occupation of upward-pointing tetrahedra with half-occupation of downward-pointing tetrahedra, and *vice versa*. In an analogous way, the occurrence of a series of polytypes between the M_3X_2 composition of β-Be_3N_2 and the MX compositions of $BeSiN_2$ and BeO can be understood as the insertion at regular intervals of an M_2X layer into the MX layer-arrangement of the wurtzite structure, the intervals between these M_2X layers being determined by the overall composition. For this kind of structural sequence it can be predicted that along any line of compositions between Be_3N_2 ($M/X = 3/2$; $m = 2$) and a point on the $BeSiN_2$–BeO join ($M/X = 1/1$; $m = \infty$), there should be a linear or at least a smooth variation of unit-cell dimensions with composition. Fig. 1 shows that the linear relationship holds fairly well for compounds occurring along the Be_2N_2–BeO join. However, for compositions along the Be_3N_2-$BeSiN_2$ join, the *c*/*n* values given in the last column of Table II show no linear cell-dimension variation between the two end members. In fact, all these polytypes have approximately the same *c*/*n* value as beryllium nitride. Clearly, some other structural feature must be present.

The non-metal-atom stacking in β-beryllium nitride (M_3X_2) consists of a close-packed layer sequence (Zhdanow symbol, (22); Ramsdell symbol, 4H):

M M M M M M M M
A B C B A B C B ...
M M M M

with alternate M_2X and MX layers. If M_2X occurs every third layer instead of every second, the overall composition becomes M_4X_3 with a stacking

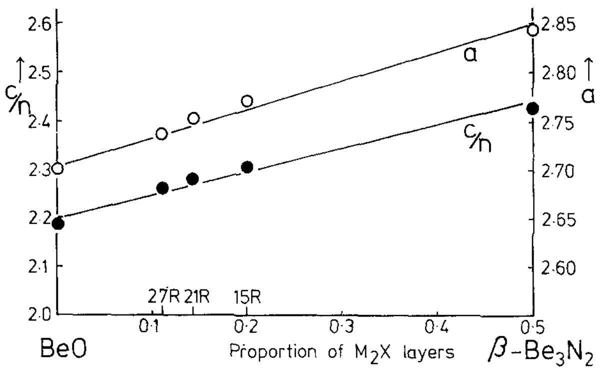

Figure 1.

TABLE II Unit-cell dimensions and polytype designation for unidentified phases reported by Huseby *et al.* [1].

Compound	Polytype	a	c	c/*n*
β-Be_3N_2	4H	2.841	9.693	2.423
$Be_6O_3N_2$	15R	2.770	34.58	2.305
$Be_8O_5N_2$	21R	2.752	47.87	2.280
$Be_9O_6N_2$*	27R(?)	2.738	61.05	2.261
$Be_8SiO_4N_4$*	27R(?)	2.816	62.91	2.330
BeO	(2H)	2.698	4.375	2.187
β-Be_3N_2	4H	2.841	9.693	2.423
Be_4SiN_4	8H	2.862	19.22	2.403
$Be_9Si_3N_{10}$	15R	2.857	36.32	2.421
$Be_5Si_2N_6$	12H	2.860	29.10	2.425
$Be_{11}Si_5N_{14}$	21R	2.860	50.98	2.428
$Be_6Si_3N_8$*	27R(?)	2.862	65.11	2.411
$BeSiN_2$	(2H)	2.880	4.687	2.343

*If these phases are 27R polytypes the compositions are probably $M_{10}X_9$ and not M_9X_8.

sequence (Zhdanow, $(21)_3$; Ramsdell, 9R):

M M M M M M A M
A B C B C A C A B ....
M M M

The next member of the series, M_5X_4, might be expected to have the structure (Zhdanow, $(211)_2$; Ramsdell, 8H):

M M M M M M M M
A B C B C B A B ....
M M

Both end members of the series with compositions MX, i.e. BeO and $BeSiN_2$, have hexagonal close-packed layer stacking and this is apparently also favoured throughout the series. The regular faulting to give a localized cubic close-packing occurs whenever there is simultaneous occupation by metal atoms of both upward and downward-pointing tetrahedra in one layer (i.e. M_2X). The occurrence of the ccp fault avoids base-sharing by adjacent filled tetrahedra which would bring metal atoms to within impossibly close distances of one another. It can be shown that any *n*H or *n*R (Ramsdell notation) member of this polytype series can be represented by the Zhdanow symbol

$$\{2(1)^{(n/p)-2}\}_p$$

where *p* is 3 and 2 respectively for rhombohedral and hexagonal polytypes. The expected polytypes are therefore

$4H(Be_3N_2)$, 9R, 8H, 15R, 12H, 21R, 16H, 27R...

which is in good agreement with observation except that 9R and 16H are missing. It can also be seen that the M/X ratio is implicit in the polytype designation.

The difference in behaviour between the Be_3N_2–BeO and Be_3N_2–$BeSiN_2$ series is also apparent in that the region of homogeneity of each phase is not continuous along the whole of the appropriate M/X line. If the structures in both series were identical, continuous solid solution might be expected. Further confirmation of the structural differences between the Be–Si–N and Be–O–N polytypes is provided by calculating the intensities of X-ray reflections expected on the basis of the structure models proposed above. Good agreement is found for the beryllium oxynitrides (see Table III) but less satisfactory agreement is obtained for the beryllium–silicon nitrides irrespective of whatever metal-atom ordering scheme is assumed. Such observations are not

TABLE III Calculated and observed intensities for $Be_8O_5N_2$

$hk\ l$	$mF^2_{hkl}\cdot Lp$	I_{obs}	$hk\ l$	$mF^2_{hkl}\cdot Lp$	I_{obs}
0018	1	2	0120	9	3
10 1	73	100	1022	15	14
01 2	27		0123	4	7
10 4	5	–	1025	2	–
0021	76	41	0126	2	–
10 5	7		1028	2	–
10 7	4	–	11 0	58	48
01 8	9	10	0129	2	–
1010	68	51	1031	29	7
0111	45	33	0132	20	9
1013	2	5	02 1	5	5
0024	1		20 2	2	
0114	0	–	0135	0?	5
1016	0	–	1121	26	15
0117	0	–			
1019	0	–			

m = multiplicity
Lp = Lorentz and polarization correction

unequivocal because beryllium has a very small X-ray scattering factor and the good agreement in the case of the Be–O–N series merely confirms the correctness of the non-metal arrangement. For the Be–Si–N series, the scattering by silicon dominates the X-ray intensities and the poor agreement between observed and calculated values shows that the proposed siting of metal atoms may be in error. Further work is in progress to resolve these anomalies.

Similar new polytypes in which the structures are directly related to their M/X atoms-ratios have recently been found at AlN-rich compositions in the Si–Al–O–N, Mg–Si–Al–O–N and Li–Si–Al–O–N systems and have been briefly reported [5, 6]. In the "sialons", polytypes with Ramsdell symbols 8H, 15R, 12H, 21R and 27R have two symmetry-related blocks per hexagonal cell or three such blocks in each rhombohedral cell. M/X ratios are less than 1/1 and in the above five polytypes the number (m) of MX layers per block is 4, 5, 6, 7 and 9 respectively, but one layer in each block has an additional non-metal atom MX_2 giving overall compositions M_mX_{m+1}. A random distribution of MX_2 planes occurs at metal:non-metal atom ratios greater than about 9:10. Such polytypes have structures similar to those now proposed for the $M_{m+1}X_m$ polytypes observed in the Be–Si–O–N system except that the roles of the metal and non-metal atoms are reversed.

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