journal

J. Am. Ceram. Soc., **81** [8] 2188–90 (1998)

A New, Low-Temperature Polymorph of O′-SiAlON

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A new phase in the Si-Al-O-N system has been identified, following syntheses based on the nitridation of silicon/clay mixtures at low temperatures (<1350°C). The structure of the new phase was determined using a combination of diffraction and high-resolution imaging techniques, and this new phase possessed the same sheet structure as O′-SiAlON ($Si_{2-x}Al_xO_{1+x}N_{2-x}$) but with a different stacking arrangement. It is considered to be a low-temperature polymorph of O′-SiAlON and transforms to conventional O′-SiAlON at temperatures greater than ~1350°C.

I. Introduction

THE Si-Al-O-N system has become the subject of widespread research since the initial discovery[1,2] that aluminum and oxygen can be substituted into the Si_3N_4 lattice. One reason for the intensity of the research effort is the many different SiAlON phases that can be prepared, each of which presents different physical properties. The Si-Al-O-N phase diagram was explored in the early history of SiAlON research, and by the time Jack performed his review in 1976,[3] all the presently known phases had been discovered. In this communication, we describe the structure of the first new SiAlON to be found since that times: a low-temperature polymorph of O′-SiAlON ($Si_{2-x}Al_xO_{1+x}N_{2-x}$).[4]

II. Experimental Procedure

Mixtures of clay (light kaolin, BDH Chemicals Pty., Ltd., Poole, U.K.), silicon (grade 4D, Permascand AB, Ljungaverk, Sweden), and silica (Superfine Quartz, Commercial Minerals Ltd., Auckland, New Zealand) were blended for 20 h in a ball mill using Si_3N_4 media and hexane solvent. Major impurities (>0.05%) in this clay are 0.75% K_2O, 0.45% Fe_2O_3, 0.35% MgO, 0.21% P_2O_5, and 0.14% Na_2O. The stoichiometry for each mixture was calculated according to the following reaction scheme, illustrated for the $x = 0.2$ O′-SiAlON composition:

$$0.1Si_2Al_2O_5(OH)_4 + 1.35Si + 0.25SiO_2 + 0.9N_2 \rightarrow Si_{1.8}Al_{0.2}O_{1.2}N_{1.8} + 0.2H_2O$$

After drying, the powder was lightly pressed (8 MPa) into disks 15 mm in diameter and heated under flowing H_2 (10%) in N_2 for 8 h at 1270°C.

X-ray diffractometry (XRD) was performed using a system (Model PW1700, Philips Research Laboratories, Eindhoven, The Netherlands) with a post-diffraction graphite monochromator and Co$K\alpha$ radiation. High-resolution electron microscopy (HREM) utilized a 200 keV instrument (Model 200CX, JEOL, Tokyo, Japan) equipped with a high-resolution (C_s = 0.41 mm) pole piece. Simulated HREM images were calculated with the EMS software system,[5] using values of 0.5 mrad for beam divergence and 100 Å for focal spread.

III. Results and Discussion

The first indications of the formation of a new phase arose when the XRD patterns of reacted mixtures could not be matched to any known compounds. The unmatched XRD peaks were particularly apparent in samples reacted at temperatures <1300°C, which is a temperature considerably lower than those normally used for solid-state syntheses of O′-SiAlON (e.g., 1800°C[6]). The ability to prepare SiAlON phases at low temperature was a consequence of the synthesis method used and, in particular, the use of clay and silicon as reactants. Adding small amounts of iron (1.5% as Fe_2O_3) improved the reaction rate, as has been observed for the nitridation of silicon to Si_3N_4.[7] The results obtained here do not show whether the iron or other impurities derived from the clay have any role in stabilizing the new phase, in a manner similar to the additional cations used to stabilize α-SiAlON. However, we do note that the level of impurities in the present material is considerably lower than that required to stabilize α-SiAlON.

The composition of the new phase approximated that of O′-SiAlON, as reacted mixtures with this composition produced the highest yields. In addition, the new phase transformed to O′-SiAlON at 1350°C without a significant weight change and without the appearance or disappearance of secondary phases. All these factors have led us to believe that the low-temperature conditions used here permitted the synthesis of a new, low-temperature polymorph of O′-SiAlON.

Although the crystallites prepared were too small for single-crystal analysis, the structure was solved by using a combination of HREM and selected-area electron diffraction. Electron diffraction patterns taken from different zone axes suggested an orthorhombic unit cell, and preliminary structural coordinates were proposed on the basis of the HREM images. Simulation of these images and the XRD pattern confirmed the proposed structure, which was subsequently refined from the observed XRD data using the Rietveld technique. Some small discrepancies between the observed and calculated XRD patterns remained after the refinement; these discrepancies were ascribed to the presence of planar defects in the specimen (this point will be discussed later in the paper). However, the overall agreement (Bragg factor (R) of 5.37%, goodness of fit is 10.3) was sufficient to give us considerable confidence in the validity of the model. Structural coordinates that resulted from these refinements are given in Table I, and tabulated XRD pattern data are provided in Table II.

The structure is best described by comparing it with O′-SiAlON,[6] and projections of both structures are shown in Fig. 1. For simplicity, we will consider the $x = 0$ composition (Si_2N_2O), although the actual specimen that was examined contained 10 mol% of aluminum and oxygen, substituted on

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T. Ekström—contributing editor

Manuscript No. 190375. Received February 16, 1998; approved April 27, 1998.

Table I. Positional Coordinates from Rietveld Refinement[†]

Atom	Position *x*	Position *y*	Position *z*
Si (Al)	0.3226 (4)	0.0865 (9)	0.1275 (15)
N (O)	0.2847 (9)	0.3857 (19)	0
O	0	0.5	0.085 (4)

[†] Space group is *Bba*2; cell parameters are $a = 8.8488(13)$ Å, $b = 5.3752(6)$ Å, and $c = 4.8355(5)$ Å. There is 10 mol% substitution of Al on the Si sites and of O on the N sites.

Table II. XRD Pattern Data[†]

hkl	d_{calc}	d_{obs}	Intensity ratio, I/I_0
200	4.424	4.433	86.5
210	3.416	3.418	38.1
111	3.331	3.337	100.0
020	2.688	2.690	20.5
002	2.418	2.419	42.7
311	2.280	2.282	15.3
121	2.270	2.274	16.4
400	2.212	2.210	2.3
202	2.122	2.124	3.5
410	2.046	2.047	8.1
212	1.9735	1.9747	4.5
022	1.7975	1.7982	6.9
230	1.6607	1.6607	7.1
511	1.5878	1.5879	4.3
412	1.5617	1.5608	2.6
113	1.5209	1.5220	5.3
600	1.4748	1.4749	4.5
521	1.4135	1.4133	2.4
430	1.3923	1.3919	6.7
313	1.3679	1.3678	11.4
123	1.3657		

[†] Co$K\alpha_1$ radiation, wavelength of 1.78896 Å.

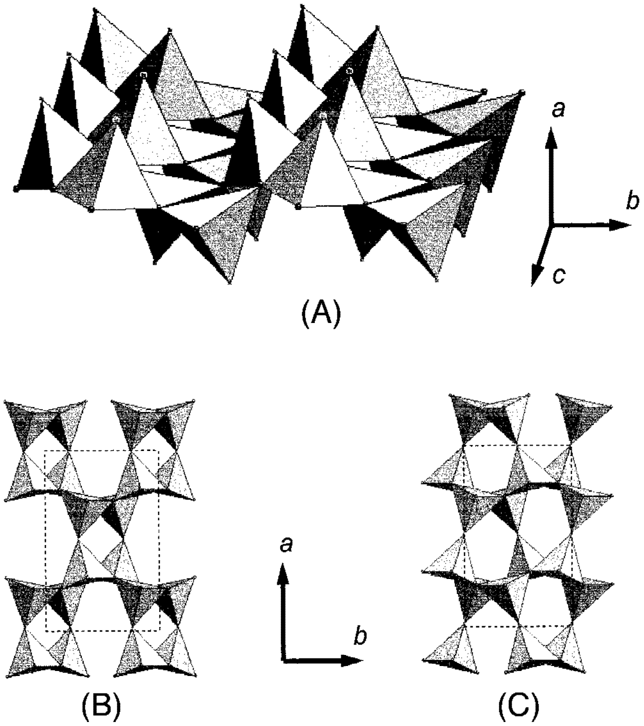

Fig. 1. Polyhedral representations of (A) a single sheet of O′-SiAlON, (B) a projection of O′-SiAlON on the (001), and (C) an equivalent projection of the new compound. Each silicon atom is tetrahedrally coordinated to one oxygen atom (at $x = 0, 0.5$) and three nitrogen atoms.

the Si and N sites, respectively. Conventional Si_2N_2O is composed of layers of SiN_3O tetrahedra, parallel to (100), that are linked through a corner sharing of their nitrogen atoms (Fig. 1(A)). Tetrahedra that are adjacent in the ***b***-direction have the oxygen atoms at their apices alternately directed upward and downward in a regular sequence. Tetrahedra that are similarly oriented (i.e., either upward or downward) form zig-zag chains that are oriented parallel to the ***c***-axis. Each upward-pointing chain in one layer meets a downward-pointing chain in the layer above it to complete the three-dimensional arrangement (Fig. 1(B)). This arrangement leads to two different distances between the apical oxygen atoms in a single layer: a shorter distance between oxygen atoms within a chain, and a longer distance between those in neighboring chains. The projection shown in Fig. 1(B) shows that the tetrahedra are tilted slightly so that their apices are not oriented exactly along the ***a***-axis. This skewed orientation has the effect of adjusting the Si−O−Si bond angles so that they are not in an unfavorable 180° configuration.

The new structure (Fig. 1(C)) is composed of similar layers of SiN_3O tetrahedra; however, this structure has a more pronounced tilting of the tetrahedra around the central axis of the zig-zag chains. The effect of this greater tilting is to make the O−O distances within and between the zig-zag chains in each layer equivalent. This arrangement, in turn, allows the layers to be stacked in a new configuration so that each chain in one layer bridges two chains in the adjoining layer, rather than being directly above and below the adjoining layers, as in the original structure. The bond angles and lengths of the two structures are comparable, although the smaller unit cell of the new material increases its density from 2.80 g/cm^3 to 2.90 g/cm^3, which is consistent with the general rule that low-temperature polymorphs have higher-density structures.

Although the layer structure of the new material facilitates a new stacking arrangement, it does not preclude the arrangement found in conventional Si_2N_2O. HREM images revealed several planar faults parallel to (100) that we believe to be isolated occurrences of just such behavior. An example is shown in Fig. 2, which includes a simulation of the image expected from a single planar fault. Above the fault, the simulation is best compared with the experimental image immediately to the right (Fig. 2(B)); however, below the fault, the area to the left (Fig. 2(A)) provides the best match. The simulation reproduces the main features of the observed image correctly, including the overall appearance of the planar fault as well as the relative displacement along the ***b***-direction of the structure above and below the fault. Stacking faults have also been observed by HREM in X-phase SiAlON,[8] although, given the scarcity of structural data concerning X-phase, it is unclear how they relate to the present observations. It seems likely that the planar faults in the new compound have an important role in its transformation to O′-SiAlON, because they represent local regions of the conventional O′-SiAlON structure. The faults may be either the initial stages of a transformation already underway or intrinsic defects that act as nucleation sites for subsequent transformation at a higher temperature. Such transformations, which involve shear along a crystallographic plane, have been shown to occur between the polymorphs of Mg_2SiO_4 spinel.[9]

The discovery of this new phase is of interest to SiAlON research, not simply because it is a new material but also for its polymorphic relationship to O′-SiAlON. The polymorphism of other phases in the Si-Al-O-N system, notably Si_3N_4, has been shown to offer many practical benefits. For example, when fabricating ceramic bodies from Si_3N_4, it is advantageous to begin with α-Si_3N_4 powder, because, although it transforms to the β-phase modification when hot-pressed, the final body exhibits superior mechanical properties than if it were fabri-

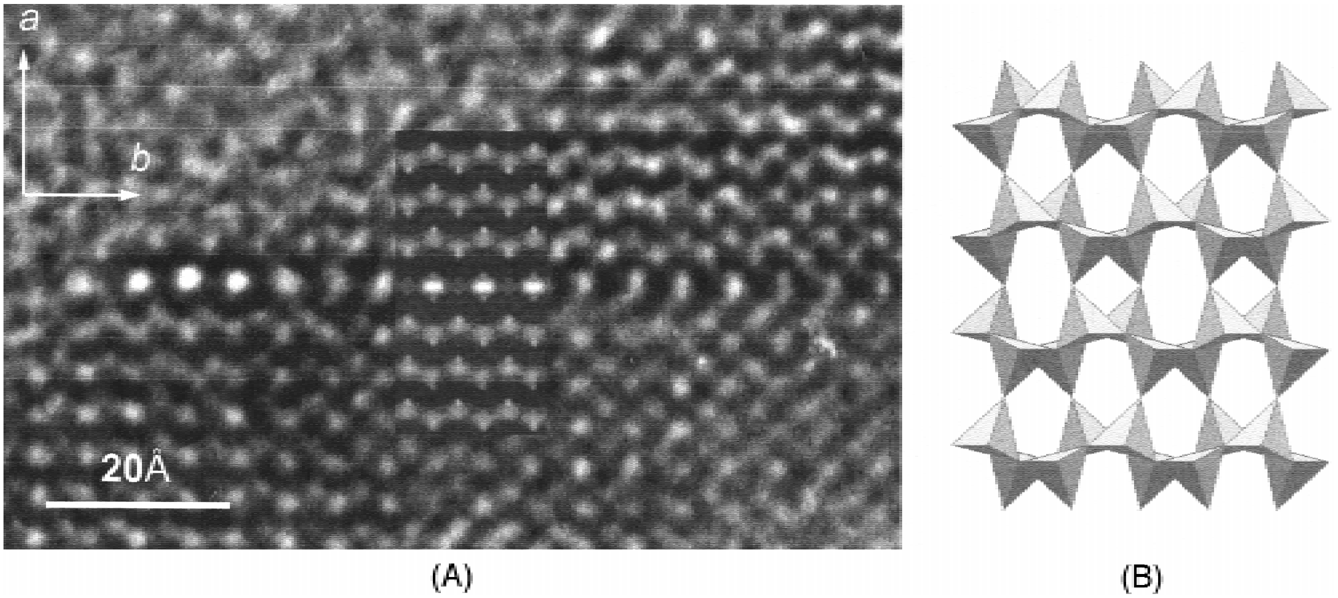

Fig. 2. (A) HREM image of a planar defect within the new material; a simulated image (thickness of 58 Å, defocus of −475 Å) is shown in the inset. (B) Structural model used for the simulation.

cated directly from β-Si_3N_4 powder.[10] In addition, the substituted analogs of Si_3N_4—α′- and β′-SiAlON—each possess different physical properties and, thereby, lend themselves to different applications: α′-SiAlON is intrinsically a harder material, whereas β′-SiAlON forms an acicular microstructure more readily, which imparts a higher fracture toughness.[11] Whether similar behavior can be found in the relationship between the present material and O′-SiAlON remains to be determined.

IV. Summary

By using a synthesis route based on the nitridation of mixtures of silicon and clay, a low-temperature polymorph of O′-SiAlON has been prepared. This new polymorph contains the same structural elements as conventional O′-SiAlON, with sheets of corner-shared $(Si,Al)(O,N)_3O$ tetrahedra linked through their apical oxygen atoms. The positioning of one sheet above another is different in the new material, which has a smaller unit cell and, consequently, a higher density. Stacking faults observed via high-resolution electron microscopy have been identified as being individual sheets of conventional O′-SiAlON, which leads to the possibility of a solid-state shear transformation between the two polymorphs.

Acknowledgment: The authors wish to acknowledge the assistance of Profs. K. H. Jack and D. P. Thompson in the preparation of this manuscript.

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