with the β''-alumina framework and not with the mobile cations. In some cases, partial hydration of the divalent β''-aluminas is quite difficult to avoid and can have dramatic effects on the structural, electrical, and optical properties of the compounds. In addition to these measurements on the aluminas, we have also synthesized several β''-ferrites for the first time. A comparison of the hydration reactions of Ba(II)-β''-ferrite and Ba(II)-β''-alumina suggests that the β''-ferrite lattice is less hygroscopic than the β''-alumina lattice.

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Supplementary Material Available: A listing of interatomic distances, atomic positions, and structure factor amplitudes (32 pages). Ordering information given on any current masthead page.

Topological and Geometrical Characterization of Sites in Silicon Carbide Polytypes

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Sites in SiC polytypes are classified by the numbers of neighbors they have. It is shown that classification by numbers of geometrical neighbors and by numbers of topological neighbors leads to identical results, with the topological description leading to a convenient label for the type of site. The type of site in a layer depends only on the type (h or c) of neighboring layers and not on the type of the layer itself. Ideal coordinates and identification of sites are given for a number of simpler polytypes. A possible application to Si NMR is indicated.

Introduction

Considerable interest is attached to the phenomenon of polytypism in compounds. The SiC polytypes in particular have been intensively investigated because of their valuable physical properties. The question of why particular polytypes occur is a subject of intensive study,[1] but that topic is not addressed here. However, recent applications[2,3] of MASS NMR have focused attention on identifying the different types of site in these crystals. The problem is also of interest to ESR studies[4] and presumably to other spectroscopies also. This paper takes a predominantly topological approach to this problem and presents a new classification of types of site in polytypes with structures based on the principle of closest-sphere packings. Definitions and terminology relevant to the naming of polytypes are to be found in the monograph by Verma and Krishna[5] and in a recent International Union of Crystallography report.[6]

It should be emphasized that the purpose of this paper is to propose a concise and exact notation for different kinds of site; something which, to my knowledge, has not been done fully before. Reference to physical measurements, in particular NMR spectroscopy, is solely in the context of comparison with other systems of identifying different kinds of site, although it is believed that the system of classifying sites presented here will ultimately prove useful in this and other spectroscopic contexts.

In the closest packing of spheres,[5] the structure can always be described in terms of a hexagonal cell. The atoms lie on 3^6 layers centered over one of $0,0,z$, $^1/_3,^2/_3,z$, or $^2/_3,^1/_3,z$. These three positions are conventionally labeled A, B, and C. Stacking of layers in close packing is customarily denoted by a sequence of symbols c and h. An h layer is one that has the same symbol (A, B, or C) for the layers above and below; a c layer has different symbols for the layers above and below. The two simplest examples are cubic close packing (c = ABCABC...) and hexagonal close packing (h = ABAB...). As is well-known, as far as first and second neighbors are concerned, the h and c packings have the same numbers of neighbors although their arrangement in space is different. They differ however in numbers of further neighbors. Thus h has 2 and 18 neighbors at distances of $\sqrt{8/3}$ and $\sqrt{3}$ times the nearest-neighbor distance, whereas the corresponding numbers for c are 0 and 24.

In more complex polytypes of closest packing there will be a number of distinct types of site according to whether an atom in the layer and its neighboring layers is c or h. To take an example, the sphere packing ABCACB... can be symbolized hcc. The A layers are h, and the B and C layers (which are related by symmetry) are c. There are thus two distinct types of site. If one examines the *numbers* and *distances* of neighbors of an atom in the h layer,

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it will be found that for the first 134 neighbors these are the same as in cubic close packing. Thus if one characterizes a site by numbers and distances of neighbors, it is not the symbol (h or c) of the layer that is important but the symbols of the neighboring layers. Indeed it is shown below for sphere packings that if one limits oneself to neighbors in a sphere of radius less than $\sqrt{6}$ times the nearest neighbor distance, three types of layer can be distinguished according to whether the neighboring layers are both h, both c, or one h and one c.

Analysis of SiC Polytypes

The polytypes of SiC and similar materials[5,7] may be (and often are) described in terms of close packing of Si, with C in half of the tetrahedral sites (either all those "pointing up" the axis normal to the layers or all those "pointing down"). One still uses h and c to symbolize the nature of the Si packing, but there is an important distinction now from simple sphere packings; in the hcc polytype the two c Si layers are different, and to know which is which, one needs to know which tetrahedral sites are filled. In this paper the sequence of layers from left to right is along the direction defined by the Si to C vector of a Si–C bond normal to the layers. Thus if Greek letters are used for the carbon positions hcc becomes $B\beta A\alpha C\gamma B\beta C\gamma A\alpha$... with this convention, as opposed to $A\beta B\alpha A\gamma C\beta B\gamma C\alpha A\beta$... for filling of other set of sites.

It is convenient to consider these structures as infinite graphs. In the language of graph theory[8] the atoms are *vertices* and the bonds are *edges*. A *circuit* is a sequence of edges that begins and ends at the same vertex and contains no edge more than once. A *chain* is a sequence of adjacent edges from a vertex to another distinct vertex that again contains no edge more than once. The length of a circuit or chain is the number of edges it contains. In discussions of four-connected infinite graphs (or *nets*) it is common[9] to characterize the vertices by the lengths of the shortest circuits that begin and end on a node, although as discussed below, that procedure is not useful in the case of the graphs of the silicon carbide polytypes.

The silicon carbide polytypes are often labeled NX, where N is a number that denotes the number of layers in the repeat unit and X is a letter that denotes[6] the kind of Bravais lattice: C for (face-centered) cubic, H for hexagonal, R for rhombohedral, and T for trigonal. The simplest polytypes of SiC are 3C (c) and 2H (h). These structures are a coloring of the diamond and lonsdaleite nets, respectively, and topologically all vertices of the net are equivalent in each case. By a *coloring* is meant that if we consider all vertices to be the same (gray) initially, the net can be colored by making some of the vertices black (e.g., silicon) and the rest white (e.g., carbon). In conventional group theory[10] an operation that converts black to white or vice versa is known as an antisymmetry operation.

It is difficult to distinguish these SiC structures and their polytypes topologically on the basis of circuits, as in all of them each pair of edges (bonds) is contained on two six-circuits that are the shortest in the structure. Accordingly the vertices are distinguished by the number of their kth neighbors.[11] A kth neighbor in this topological sense is defined as one for which the shortest chain (or path) to the reference node consists of k bonds. In terms of the familiar ball and stick models, a kth neighbor is one that is connected to the reference ball by a minimum of k sticks.

Of all the polytypes the diamond structure has the smallest and the lonsdaleite net the largest number of kth neighbors. For these two structures empirical expressions for the number of kth neighbors, n_k, have been derived. For diamond

$$n_k = [5k^2/2] + 2 \quad (1)$$

and for lonsdaleite

$$n_k = [21k^2/8] + 2 \quad (2)$$

In these expressions the brackets indicate rounding *down* to an integer. The equations have been found by inspection and checked for $k \leq 100$ (about 10^6 vertices).

As diamond has the smallest value of n_k, it is convenient to characterize nodes of nets by d_k, the amount that n_k for a node is greater than n_k for the diamond net. For all nets $d_1 = d_2 = 0$ and in practice it is most useful to go out only to fifth neighbors and identify nodes by three integers $d_3d_4d_5$. Thus the nodes in diamond are 000 and in lonsdaleite they are 123. d_i refers to C neighbors of Si when i is odd and to Si neighbors when i is even.

All polytypes of SiC have symmetry $P3m1$, $R3m$, or $P6_3mc$ except for the sphalerite form, which is cubic ($F\bar{4}3m$). For a Si–C bond length of r and regular tetrahedral bonds, the hexagonal unit cell parameters are $a = \sqrt{(8/3)}r$ and $c = 4Nr/3$ where N is the number of layers in the unit cell and specified in the name of the polytype. The number of crystallographically distinct Si (and C) atoms is N for T polytypes, $N/2$ for H polytypes, and $N/3$ for R and C polytypes. In these structures there are anticenters (or centers of antisymmetry[10]) that interchange Si and C, and in describing the structures, the origin of z is taken at such an anticenter so that the coordinates of C are $1 - x_{Si}$, $1 - y_{Si}$, $1 - z_{Si}$. The coordinates of the vertices of the monatomic nets (C or Si polytypes) are the same as those for silicon carbide but now in the centric space groups $Fd\bar{3}m$, $P\bar{3}m1$, $R\bar{3}m$, and $P6_3/mmc$. Because of the anticenter, Si and C can be interchanged in all the structural parts of the paper (the C and Si neighbors of C correspond to the Si and C neighbors of Si, etc.). Regardless of the space group, the site symmetry at all vertices (atom sites) in all SiC polytypes and in the parent monatomic structures (except of course 3C) is $3m$ (C_{3v}).

Neighbors (topological and geometrical) have been counted for atoms in different sites in a number of polytypes identified in Table I. These are all that have five or fewer distinct sites in the unit cell and also 21R, the next most complex well-characterized polymorph of SiC. They include all 32 possible combinations for the symbols (h or c) of the two preceding layers, the layer being studied and the two subsequent layers. In the table, the node in question corresponds to the first symbol (c or h) and the letters following specify the repeat sequence.

The following observations were made. The type of site (in the topological sense above) does not depend on whether the layer is h or c. d_3 depends only on the symbol of the preceding layer, being 0 if this is c and 1 if this is h; d_4 is then determined by the symbol following that of the layer. In all only four possibilities for d_3d_4, six possibilities for $d_3d_4d_5$, and nine possibilities for $d_3d_4d_5d_6$ are found and identified with sequences of symbols (h or c)

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Table I. Sequence of Si Layers in SiC Along the Direction of the Si to C Vector Normal to the Layers[a]

type	node	$d_3d_4d_5$	d_6	pos	z_{Si}
3C	**c**	000	0		
2H	**h**	123	4	b	1/16
4H	**c**h	123	4	a	13/32
	h**c**	002	4	b	5/32
6H	**c**ch	112	4	b	17/48
	chc	013	4	b	1/48
	h**c**c	000	0	a	3/16
9R	**c**hh	123	4	a	13/24
	h**c**h	112	4	a	13/72
	hh**c**	013	4	a	53/72
$8H_1$	**c**cch	112	2	b	21/64
	cchc	002	4	a	29/64
	chcc	011	2	b	5/64
	h**c**cc	000	0	b	45/64
$8H_2$	**c**hhh	123	4	a	29/64
	hhh**c**	013	4	b	5/64
	hh**c**h	123	4	a	13/64
	h**c**hh	112	4	b	21/64
12R	**c**chh	112	4	a	73/96
	chhc	013	4	a	17/96
	hh**c**c	011	2	a	19/32
	h**c**ch	112	2	a	11/32
5T	**c**cchh	112	2	c	9/40
	cchhc	002	4	a	7/40
	chhcc	011	2	b	5/8
	hh**c**cc	011	2	c	33/40
	h**c**cch	112	2	b	1/40
$10H_1$	**c**ccch	112	2	a	5/16
	ccchc	002	2	b	33/80
	cchcc	000	2	b	1/80
	chccc	011	2	a	9/80
	h**c**ccc	000	0	b	57/80
$10H_2$	**c**chhh	112	4	b	33/80
	chhhc	013	4	b	1/80
	hh**c**cc	011	2	a	9/80
	hh**c**ch	123	4	b	17/80
	h**c**chh	112	2	a	5/16
$10H_3$	**c**hchh	123	4	b	49/80
	chhhc	002	4	a	17/80
	chhch	123	4	b	13/16
	hh**c**hc	013	4	b	33/80
	h**c**hch	112	4	b	1/80
$15R_1$	**c**chch	112	4	a	73/120
	chchc	013	4	a	41/120
	chcc	000	2	a	3/40
	chcch	123	4	a	19/40
	h**c**chc	002	2	a	7/8
$15R_2$	**c**hhhh	123	4	a	39/40
	hhhh**c**	013	4	a	17/24
	hhh**c**h	123	4	a	13/120
	hh**c**hh	123	4	a	101/120
	h**c**hhh	112	4	a	29/120
21R	**c**cchcch	112	2	a	15/56
	cchcchc	002	4	a	55/56
	chcchcc	011	2	a	39/56
	h**c**chccc	000	0	a	23/56
	cchccch	112	4	a	19/24
	chcccchc	013	4	a	29/168
	h**c**cchcc	000	0	a	31/56

[a] The site is the first letter (bold) of the repeat sequence. Except for 5T the positions of Si are a or b of $P6_3mc$ or $R3m$ (hexagonal cell). For 5T the space group is $P3m1$. d_i is the difference in the numbers of ith neighbors from that in diamond. "pos" refers to the Wyckoff position of the space group and z_{Si} is the silicon z coordinate.

of neighboring layers as listed in Table II.

It is noteworthy that for structures with regular tetrahedra the six different topological indexes $d_3d_4d_5$ also completely determine the number of geometrical neighbors for up to 20 coordination shells ($d < 4r$, i.e., up to 7.7 Å in SiC). This means that the distinction of nodes by topological neighbors is equivalent to distinction by numbers of geometrical neighbors. The number of neighbors in each coordination shell for each type of node is indicated in Table III. d_6 (given in Table I) is also necessary to determine neighbors at further distances. It may be seen that for coordination of Si by Si (this corresponds to closest-sphere packing as discussed in the Introduction) there are three cases according to whether the layer in question has c layers on both sides (000 or 002), h layers on both sides (123), or h and c neighboring layers (011, 013, and 112).

Table II. Dependence of Numbers of Topological Neighbors on Symbols of Neighboring Layers[a]

d_3		d_3d_4		$_{d3}d_4d_5$		$d_3d_4d_5d_6$	
0	.c|..	00	.c|c.	000	cc|c.	0000	cc|cc
						0002	cc|ch
				002	hc|c.	0022	hc|cc
						0024	hc|ch
		01	.c|h.	011	cc|h.	0112	cc|h.
				013	hc|h.	0134	hc|h.
1	.h|..	11	.h|c.	112	.h|c.	1122	.h|cc
						1124	.h|ch
		12	.h|h.	123	.h|h.	1234	.h|h.

[a] The vertical line represents the layer in question which may be h or c and the stacking of layers from left to right is along the direction of a Si to C bond vector. A dot indicates that the layer may be c or h.

Table III. Numbers of Neighbors of Si of Different Topological Types (000 etc.) at Distance $d = \sqrt{pr}/3$ for $d/r < 4.0$[a]

	p	d/r	000	002	011	013	112	123
C	9	1.00	4	4	4	4	4	4
	25	1.67	0	0	0	0	1	1
	33	1.91	12	12	12	12	9	9
	49	2.33	0	0	0	0	6	6
	57	2.52	12	12	12	12	9	9
	81	3.00	16	15	16	15	9	9
	89	3.14	0	3	0	3	3	3
	97	3.28	0	0	0	0	6	6
	105	3.42	24	18	24	18	18	18
	113	3.54	0	3	0	3	3	3
	121	3.67	0	0	1	1	6	7
	129	3.79	12	12	9	9	6	3
Si	24	1.63	12	12	12	12	12	12
	48	2.32	6	6	6	6	6	6
	64	2.67	0	0	1	1	1	2
	72	2.83	24	24	21	21	21	18
	88	3.13	0	0	6	6	6	12
	96	3.27	12	12	9	9	9	6
	120	3.65	24	24	18	18	18	12
	136	3.89	0	0	6	6	6	12

[a] p is an integer (odd for Si···C distances and even for Si···Si distances), and r is the Si–C bond length.

As an attempt to characterize the long-range interactions, the Madelung potential constant was calculated for all the nodes of the idealized structures of Table I. This is α defined by the expression for the potential at a site in a crystal of point charges $\pm q$, $\phi = -\alpha q/4\pi\epsilon_0 r$. α was found to be almost entirely determined by d_3. The values are for d_3d_4 00 1.6380_6, for 01 1.6380_1, for 11 1.6413_6, and for 13 1.6413_2 variations of ±1 in the last digit (shown as a subscript) from node to node.

Comparison with Other Work

As far as I am aware, classification of sites has so far arisen only in the context of NMR observations, and these are briefly discussed here insofar as they are relevant to the problem at hand.

In their analyses of NMR data for the 3C, 6H, and 15R polytypes of SiC, Guth and Petusky (GP)[2] and Hartman et al. (HRSW)[3] independently concluded that four types of sites should be considered, three of which occurred in the polytypes studies. Their classification (Roman nu-

Table IV. Identification of Sites in Some Polytypes of SiC[a]

polytype		sequence	OK	GP	HRSW
2H	Si	hhhhh	123	IV	D
3C	Si	ccccc	000	I	A
6H	Si(1)	cchcc	000	III	B
	Si(2)	chcch	112	II	C
	Si(3)	hcchc	013	I	A
15R	Si(1)	hchcc	002	III	B
	Si(2)	chcch	112	II	C
	Si(3)	hcchc	013	I	A
	Si(4)	cchch	000	III	B
	Si(5)	chchc	123	II	C

[a] The numbering of silicon atoms is that used by Guth and Petusky (GP).[1] OK refers to the present work, and HRSW refers to Hartman et al.[2]. "Sequence" shows the two layers above and below the layer in question (bold).

merals for GP and letters for HRSW) in the "hc" notation is according to the symbol of the layer (boldface) and that preceding it. They are as follows:

cc I A hc II C ch III B hh IV D

This classification neatly explains the observation of three equal peaks in 6H and three peaks at approximately the same positions but in an intensity ratio 1:2:2 in 15R.

It is not planned to enter a discussion of the factors entering into NMR shifts at this point. However, it is pointed out that sites of types I and III (A and B) have exactly the same number of geometrical and topological neighbors as each other, as do sites of types II and IV (C and D). In Table IV the sites in the polytypes under discussion (and 2H) are identified, and the different classifications given. If the distribution of carbon neighbors should prove to be an important factor in NMR shifts, then a division into three groups, (000 and 011), (002 and 013), and (112 and 123), is proposed from examination of the data in Table III. This classification would equally explain the data, but the identification of correspondences between different polytypes is different. To resolve such questions, NMR data on more polytypes will be required. As can be seen from Table IV, data for 2H would be particularly interesting.

Discussion

The analysis presented here is readily extended to further neighbors if required for very complex polytypes should that prove necessary at some time in the future.

Changing a layer from h to c or vice versa does not, as has been seen, change the numbers of neighbors of an atom in that layer; it merely rotates those "above" the plane by 180° with respect to those "below". Should such an effect prove important, as proposed[2,3] for NMR, the sites identified in the present paper will all split into two twin-related sets, but the present analysis will still stand. One simply has to replace, e.g., 123 by 123h and 123c according to whether the layer in question is h or c. On the other hand, effects such as subtle changes of interlayer spacings with "hexagonality"[12] have not been considered and may well be important in some instances.

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Sol-Gel Route to Niobium Pentoxide

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Niobium pentoxide powders were synthesized via the sol-gel route. Monolithic gels can be reproducibly obtained when the hydrolysis of niobium alkoxides $Nb(OR)_5$ is performed in the presence of acetic acid. This carboxylic acid reacts with the alkoxide and leads to the formation of new $Nb(OR)_{5-x}(OAc)_x$ ($0 < x < 1$) precursors. Therefore the whole hydrolysis-condensation process is modified. The different steps of the synthesis, from the molecular precursor $Nb(OPent^n)_5$ ($Pent^n$ is a normal pentyl group) to the crystalline oxide were characterized by ^1H NMR, ^{13}C CP MAS NMR, and infrared spectroscopies, thermal analysis, and X-ray diffraction. Xerogels are obtained after drying the gel at 80 °C. They are made of an oxo-polymer network in which some alkoxy groups and acetate ligands remain bonded to niobium. These organic groups are removed upon heating in air leading to the crystallization of T-Nb_2O_5 at around 550 °C.

Introduction

Sol-gel processing is a very promising approach for the synthesis of glasses or ceramics.[1,2] One of the main reasons for this interest arises from the rheological properties of sols and gels that allow the easy fabrication of fibers[3] or coatings[4] by such techniques as spin drawing or dip coating. Sol-gel chemistry is based on inorganic polymerization reactions.[5] Molecular precursors, mainly metal alkoxides, are generally used as starting materials. A macromolecular network is then obtained via hydrolysis and condensation. Transition-metal alkoxides with a d^0 electronic configuration (Ti(IV), Zr(IV), Ta(V), Nb(V), etc.)

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