

SHORT COMMUNICATIONS

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Identification of a new trace 114R SiC by HREM

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Abstract

Using electron diffraction patterns and high-resolution electron microscopy (HREM), a trace 114R SiC in commercial α -SiC powder (mainly 6H SiC according to X-ray diffraction) has been discovered. In a hexagonal unit cell its stacking sequence is [(33)₄(34)₂]₃, the periodicity along the *c* axis is 286.14 Å and *a* = *b* = 3.073 Å. 114R belongs to the structure series of (33)_{*n*}34(33)_{*m*}34 predicted theoretically by Pandey & Krishna [*Mater. Sci. Eng.* (1975), **20**, 243–249] on the basis of the faulted matrix model.

1. Introduction

It is well known that SiC crystallizes in various ordered structures, all of which have the same *a* and *b* dimensions of the hexagonal unit cell but differ along *c*. The repeat period *c* of these structures depends on the number of Si–C double layers in the unit cell. Long-period polytypes usually consist of unit cells of more common types like 6H, 15R and 4H that are periodically interrupted by stacking faults. So far more than 160 polytypes have been reported, but only about one-half of the crystal structures are known (Trigunayat, 1991; Kuo *et al.*, 1982). Despite the great number of SiC polytypes, the probability of the occurrence of long-period polytypes with larger size is very small (Fisher & Barnes, 1990).

It has been recognized that high-resolution electron microscopy (HREM) is a powerful tool for identifying the local variants in crystals. This is not possible by X-ray diffraction (XRD) owing to its averaging effect. HREM can provide the most direct and reliable evidence for the determination of the stacking sequence of polytypes, but instances of complete structural determination of SiC polytypes by HREM are very few (Rai *et al.*, 1984). The present paper reports an attempt to determine the structure of 114R SiC, which occurs in very small amounts in commercial α -SiC powder. To the best of our knowledge, 114R SiC has not been reported previously, but its stacking sequence, [(33)₄(34)₂]₃, is very similar to those of the observed structures of 96R [(33)₃(34)₂]₃ and 222R [(33)₆34(33)₄34]₃, belonging to the structure series (33)_{*n*}34(33)_{*m*}34 (where *n* and *m* are any integer) resulting from doubly faulted screw dislocation ledges in the 6H matrix, which has been predicted theoretically by Pandey & Krishna (1975). This study provides new information on SiC polytypes and shows fully the advantage of HREM in identifying trace polytypes.

2. Experimental

114R SiC was observed during a study of the effect of ball milling on the structure of α -SiC. The specimen, which was

supplied by Shenyang Reagent Works of China, consisted mainly of 6H SiC according to XRD. The specimen containing 114R was taken from a powder milled for 6 h in a WL-1 planetary ball mill under an argon atmosphere. The milled α -SiC powder with an adequate amount of Al powder as a binder was milled again for a few hours, and ball-like or fragment-like particles were obtained by cold welding. Some of them were mechanically ground to a thickness of about 40 μ m and dimpled with a Gatan model 656 dimple grinder. These samples were then ion-beam thinned to give foils suitable for HREM observations. The HREM observations were carried out using a JEOL-2000EXII electron microscope operated at 200 kV (a point-to-point resolution of 2.1 Å).

The average grain size of the original (unmilled) SiC powder is about 0.9 μ m and after milling there is no apparent change in the grain size. The results of the TEM examination shows that an absolute majority of the grains are 6H SiC. Almost every crystallite throughout the electron-transparent region in a number of specimens milled for different times has been examined. Only a few grains in the sample milled for 6 h were found to have electron diffraction patterns (EDPs) as shown in Fig. 1(a) which cannot be indexed as one of the known polytypes. Fig. 1(a) is taken along the [010] direction of the hexagonal lattice. On each closely packed spot row along *c** there are five bands containing stronger diffraction spots approximately evenly distributed in the reciprocal distance $r^* = 1/d$, where *d* is the distance between the closely packed layers (2.51 Å) and the corresponding diffraction spot is 0,0,114. Between these stronger diffraction spots there are closely arranged fine and weak spots with equal spacing of (1/38)*r**. This indicates that there is a long-period polytype based on the 6H structure. Hence it can be roughly concluded that this new polytype may be either 38H or 114R. It is noted that on the 00*l* array only reflections with *l* = 0, $\pm N$, $\pm 2N$, ... are permitted and that the other spots should be extinguished, where *N* is the number of the layers in a unit cell along the *c* axis. However, they all appear due to double diffraction, which is a frequently observed phenomenon.

It can be seen from Fig. 1(a) that the intensity distribution of the spots on the $\bar{1}0l$ and $10l$ arrays has no twofold symmetry about the 00*l* array (or *c** axis), so the possibility of 38H with sixfold symmetry about *c** can be excluded. Let us consider another possibility, that of 114R SiC based on the 6H structure. A structure series of (33)_{*n*}34(33)_{*m*}34 exists on the 6H structure and 114R is in accordance with this formula when *n* = 4, *m* = 0. Table 1 lists the calculated relative moduli of the structure factors of the $\bar{1}0l$ diffraction spots, $|F_{\bar{1}0l}|_R$, for 114R SiC with a [(33)₄(34)₂]₃ stacking sequence, which semi-quantitatively corresponds to the intensities of the electron diffraction spots. It can be seen that except for $\bar{1},0,38$ there are four regions

containing several stronger spots on the $\bar{1}0\ell$ row in a reciprocal distance r^* , of which the centers are at $\bar{1},0,20, \bar{1},0,56, \bar{1},0,74$ and $\bar{1},0,95$. The calculated intensity distribution agrees well with the experimental result; in particular, both the calculated and experimental results reveal that more spots with stronger

Table 1. Relative values of the calculated $|F_{\bar{1}0\ell}|_R$ for 114R with a $[(33)_4(34)_2]_3$ stacking sequence

Only $|F_{\bar{1}0\ell}|_R$ with $\ell = 2 + 3n$ (n is any integer) are not equal to zero due to extinction. Values are scaled to $|F_{0,0,114}| = 100$ and are given in intervals of 5.

ℓ	$ F_{\bar{1}0\ell} _R$	ℓ	$ F_{\bar{1}0\ell} _R$	ℓ	$ F_{\bar{1}0\ell} _R$
2-14	<5	56	50	83	10
17	10	59	20	86	10
20	30	62-65	<5	89	10
23	10	68	10	92	10
26-35	<5	71	20	95	20
38	50	74	35	98	10
41-50	<5	77	30	101	10
53	10	80	10	104-113	<5

intensity appear between $\bar{1},0,74$ and $\bar{1},0,95$. In addition, except $\bar{1},0,38$ and $\bar{1},0,95$, the other intensity centers deviate slightly from the positions of the diffraction spots of 6H SiC, which should be at $\bar{1},0,19, \bar{1},0,57$ and $\bar{1},0,76$. Hence it is very reasonable to consider that this new polytype is 114R based on the 6H structure.

In order to prove further the proposed structure of this polytype, HREM images were taken. Fig. 1(b) is a one-dimensional lattice fringe image formed by symmetrically selecting several low-order 00ℓ reflections in which after every four narrow dark fringes there are two wide dark fringes. The spacing of the narrow fringes is 15.1 Å, corresponding to six stacking layers, and that of the wide fringes is 17.6 Å, corresponding to seven stacking layers. Unfortunately, one-dimensional lattice fringes can not provide much more information.

Fig. 2 is a two-dimensional lattice image formed by symmetrically selecting several low-order reflections on the $00\ell, 10\ell$ and $\bar{1}0\ell$ arrays, and it can be seen clearly that six stacking layers correspond to the (33) stacking sequence while seven stacking layers correspond to the (34) stacking sequence. A unit of 38 layers exists with a stacking $(33)_4(34)_2$. This is a subunit, and three such units form a complete unit cell of 114R SiC, i.e. $[(33)_4(34)_2]_3$; the corresponding parameter c of the hexagonal unit cell is 286.14 Å. The EDP, one-dimensional fringe image and two-dimensional lattice image are in good agreement and it can be seen that the two-dimensional lattice image provides the most direct and reliable evidence.

Comparing Fig. 1(b) with Fig. 2 suggests that the change in the fringe contrast just corresponds to the reversal of the stacking sequence.

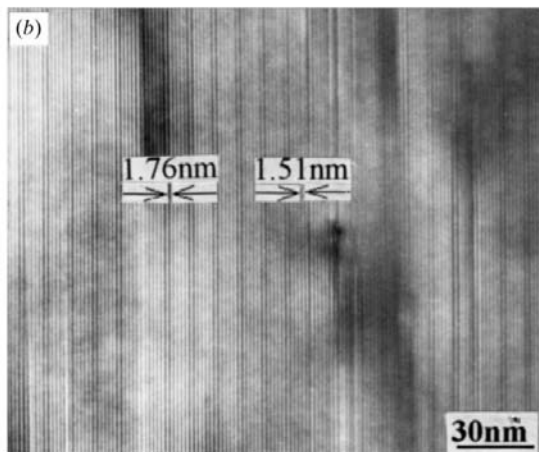
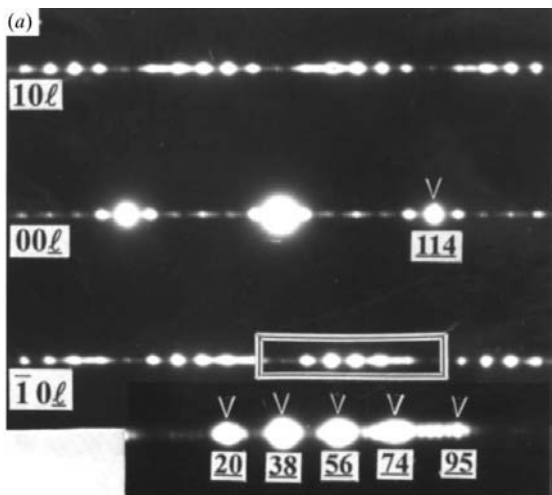


Fig. 1. Electron diffraction pattern of 114R SiC along [010]: (a) an inset magnifying the spot row in the block and (b) a one-dimensional lattice fringe image showing the periodic stacking sequence of the lattice planes along the c direction.

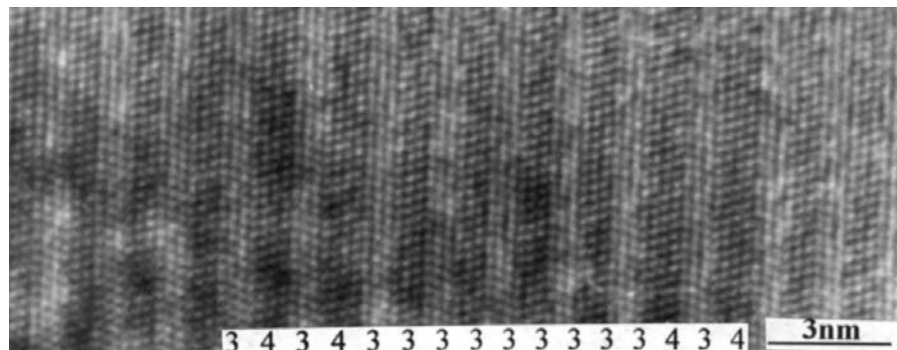


Fig. 2. Two-dimensional lattice image viewed along [010] showing clearly the $(33)_4(34)_2$ stacking sequence.

The new polytype 114R belongs to the structure series (33)*n*34(33)*m*34 with the following hexagonal unit-cell parameters:

$$114R\text{-}[(33)_4(34)_2]_3; a = b = 3.073, c = 286.14 \text{ \AA}.$$

Although 114R SiC was observed in an α -SiC specimen milled for 6 h, it is not certain that ball milling induces the formation of 114R SiC. On the one hand, on increasing the ball-milling time, no increase in the amount of 114R grains is observed. On the other hand, an increase of the ball-milling time only induces the partial transformation of the (33) sequence into the (42) and (51) sequences, which distribute randomly in the long-range (33) stacking of the 6H structure, and finally 3C(β)-SiC with more stacking faults forms (Yang *et al.*, 1999). Therefore, based on the results above, it is reason-

able to suggest that 114R SiC exists in the original α -SiC powder.

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References

- Fisher, G. R. & Barnes, P. (1990). *Philos. Mag. B*, **61**, 217–236.
 Kuo, C. L., Zhou, J., Ye, H. Q. & Kuo, K. H. (1982). *J. Appl. Cryst.* **15**, 199–205.
 Pandey, D. & Krishna, P. (1975). *Mater. Sci. Eng.* **20**, 243–249.
 Rai, R. S., Korgul, P. & Singh, G. (1984). *Acta Cryst.* **B40**, 132–138.
 Trigunayat, G. C. (1991). *Solid State Ion.* **48**, 3–70.
 Yang, X. Y., Shi, G. Y., Huang, H. L. & Wu, Y. K. (1999). *Sci. China Ser. E*. In the press.

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Energetic study of the disordered solvent in the crystal structure of an isoxazole derivative. Erratum

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Abstract

An error in printing is reported. In the paper by Pani *et al.* [*Acta Cryst.* (1998), **B54**, 872–876] the value of $\Delta\rho_{\max}$ is given incorrectly in the last sentence on page 874. The sentence

should read 'In the last difference Fourier map, the highest $\Delta\rho$ values were found near the Cl atoms ($\Delta\rho_{\max} +0.32 \text{ e \AA}^{-3}$); the final reliability indexes were $R_1 = 0.072$ over 1762 $F_o > 4\sigma(F_o)$ and $wR_2 = 0.228$ on 4029 F_o^2 for 245 refined parameters, with a goodness-of-fit of 0.96.'