Materials Science Research International, Vol.6, No.4 pp.249-254 (2000)

General paper

Single Crystal Elastic Constants of ß-Silicon Nitride Determined by X-Ray Powder Diffraction

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ABSTRACT: The X-ray elastic constants of pressureless sintered β-silicon nitride (Si_3N_4), were experimentally determined for ten different diffractions by using Kα radiations of Cu, Co, Fe, Cr and V. The X-ray compliances, $(1+\nu'_X)/E'_X$ and ν'_X/E'_X (E'_X = Young's modulus, ν'_X = Poisson's ratio), change as a second power function of $\cos^2\phi$ (ϕ = angle between the diffraction plane normal and the c-axis of hexagonal crystal) . Using the simplex method, the elastic constants of single crystals of β-silicon nitride were determined from the measured values of the X-ray compliances on the basis of the average of Voigt and Reuss models and Kröner's model, combined with the self-consistent analysis of multi-phase materials. The obtained result shows a high stiffness in the c-direction of hexagonal crystals, but the degree of anisotropy is not so large as the whisker data reported by Hay et al.

Key words: *Stress measurement, X-ray method, Elastic constant, β-silicon nitride, Simplex method*

1. INTRODUCTION

The X-ray and neutron diffraction methods are very powerful non-destructive techniques to measure the residual stress in crystalline materials. In both methods, the stress is determined from the measured lattice strains. Since the lattice strain measured by diffraction methods is different from the strain measured by mechanical methods, the elastic constants for diffraction stress measurements are different from the mechanical values. They are called the diffraction elastic constants or the X-ray elastic constants, and are dependent on diffraction planes. The diffraction elastic constants for single-phase polycrystals can be derived from the single crystal elastic constants by using Kröner model [1] or the average of Voigt and Reuss models [2]. The influence of the secondary phases on the diffraction elastic constants can be predicted by the self-consistent model [3]. By following the inverse way of the above derivation, it is possible to determine the single crystal elastic constants from the diffraction elastic constants determined by X-ray powder diffraction [2, 4].

The elastic constants of single crystals of new materials are not always known, because it is sometimes difficult to obtain a large-sized crystal enough to measure the elastic constants, by the ultrasonic method for example. For β Si_3N_4, the only data reported are those by Hay et al. [5]. They obtained the elastic constants of silicon nitride whiskers by the nanoindentation method under several assumptions of the characteristics of elastic constants of hexagonal crystals. In the present paper, the X-ray elastic constants of pressureless sintered β Si_3N_4 were measured for ten different diffractions, and then used to determine the elastic constants of single crystals.

Received March 24, 2000
Accepted July 26, 2000

2. DIFFRACTION ELASTIC CONSTANTS

2.1. Micromechanics for Diffraction Elastic Constants of Single-Phase Polycrystals

2.1.1. Voigt model

In Voigt model [6], the strain in each crystal is assumed to be uniform and equal to the macrostrain. The diffraction values of Young's modulus and Poisson's ratio, E_X and ν_X, are equal to the mechanical values, E and ν. The diffraction compliances, S_1 and S_2, are given from the single-crystal elastic constants, c_{ij}, as follows:

$$\frac{S_2}{2}=\frac{1+\nu_X}{E_X}=\frac{15}{7c_{11}+2c_{33}-5c_{12}-4c_{13}+12c_{44}}, \quad (1)$$

$$S_1=-\frac{\nu_X}{E_X}=\frac{3}{(2c_{11}+c_{33}+2c_{12}+4c_{13})}\times\frac{(4c_{44}-c_{11}-c_{33}-5c_{12}-8c_{13})}{(7c_{11}+2c_{33}-5c_{12}-4c_{13}+12c_{44})}. \quad (2)$$

2.1.2. Reuss model

Reuss model [7] assumes that the stress in each crystal is uniform and equal to the macrostress. The values of S_1 and S_2 are expressed in term of single crystal compliances, s_{ij}, as follows [8]:

$$\frac{S_2}{2}=\frac{1+\nu_X}{E_X}=\frac{1}{2}(2s_{11}-s_{12}-s_{13})$$

$$-\frac{1}{2}(5s_{11}-s_{12}-5s_{13}+s_{33}-3s_{44})\cos^2\phi$$
$$+\frac{3}{2}(s_{11}-2s_{13}+s_{33}-s_{44})\cos^4\phi\ , \qquad (3)$$

$$S_1=-\frac{\nu_X}{E_X}=\frac{1}{2}(s_{12}+s_{13})$$
$$+\frac{1}{2}(s_{11}-s_{12}-s_{13}+s_{33}-s_{44})\cos^2\phi$$
$$-\frac{1}{2}(s_{11}-2s_{13}+s_{33}-s_{44})\cos^4\phi\ , \qquad (4)$$

where ϕ is the angle between the normal of the diffraction plane (hkl) and the c-axis.

The mechanical elastic constants can be obtained by taking the average. The average of $\cos^2\phi$ is 1/3, and that of $\cos^4\phi$ is 1/5.

2.1.3. Average of Voigt and Reuss models

Hill [9] has shown that the Voigt and Reuss averages represents bounds of the elastic modulus of polycrystalline materials. The numerical means of S_1 and S_2 can be approximations for diffraction elastic compliances. For mechanical elastic constants, the mean of shear modulus and the bulk modulus will be used as an approximation. Here, this model is called Voigt-Reuss average model.

2.1.4. Kröner's model

According to Kröner's model [1], the strain tensor in a crystal in polycrystals subjected to the applied stress σ^A_{kl} is given by

$$\varepsilon_{ij}=\sum_{k=1}^{3}\sum_{l=1}^{3}\left(s_{ijkl}+t_{ijkl}\right)\sigma^A_{kl}\ , \qquad (5)$$

where s_{ijkl} is the compliances of single crystals. The value of t_{ijkl} is the additional term due to the constraint by neighboring grains, and is determined as a function of single crystal compliances with the use of Eshelby's inclusion mechanics [10, 11]. For hexagonal polycrystals of spherical grains with random orientation, the diffraction compliances, S_1 and S_2, are related to the mechanical Young's modulus and Poisson's ratio, E and ν, as follows:

$$\frac{S_2}{2}=\frac{1+\nu_X}{E_X}=\frac{1+\nu}{E}+\frac{2t_{11}-t_{12}-t_{13}}{2}$$
$$-\frac{5t_{11}-t_{12}-4t_{13}-t_{31}+t_{33}-3t_{44}}{2}\cos^2\phi$$
$$+\frac{3(t_{11}-t_{13}-t_{31}+t_{33}-t_{44})}{2}\cos^4\phi\ , \qquad (6)$$

$$S_1=-\frac{\nu_X}{E_X}=-\frac{\nu}{E}+\frac{t_{12}+t_{13}}{2}$$
$$+\frac{t_{11}-t_{12}-2t_{13}+t_{31}+t_{33}-t_{44}}{2}\cos^2\phi$$
$$-\frac{t_{11}-t_{13}-t_{31}+t_{33}-t_{44}}{2}\cos^4\phi\ , \qquad (7)$$

where t_{ij} is the matrix notation of t_{ijkl}. The mechanical elastic constants of polycrystals are also calculated from the single crystal elastic constants by using the equation derived by Kneer [12].

2.2. Micromechanics for Diffraction Elastic Constants of Multi-Phase Polycrystals

For the case of multi-phase materials, the mean stress of the diffracting phase is not equal to the macrostress. Secondary phases of sintered ceramics, such as glassy phase and pores, may influence the diffraction elastic constants. The diffraction elastic constants of multi-phase materials correlate the lattice strain of the diffracting phase to the macrostress. Among several models of elastic deformation of multi-phase materials, the self consistent model was found to give the best estimation of the diffraction elastic constants of sintered alumina [3]. According to the self-consistent model, the diffraction values of Young's modulus and Poisson's ratio of multi-phase materials, E'_X and ν'_X, are related to those of single-phase polycrystals, E_X and ν_X, as follows :

$$\frac{1+\nu'_X}{E'_X}=\frac{1+\nu_X}{E_X}B'\ , \qquad (8)$$

$$-\frac{\nu'_X}{E'_X}=\frac{1+\nu_X}{E_X}\frac{A'-B'}{3}-\frac{\nu_X}{E_X}A'\ , \qquad (9)$$

where

$$A'=\frac{3(1-\nu')E_0}{(1+\nu')E_0+2(1-2\nu_0)E'}\ , \qquad (10)$$

$$B'=\frac{15(1-\nu'^2)E_0}{2(4-5\nu')(1+\nu')E_0+(7-5\nu')(1+\nu_0)E'}\ , \qquad (11)$$

and E' and ν' are the mechanical Young's modulus and Poisson's ratio of multi-phase materials, and E_0 and ν_0 are those of the diffracting phase.

2.3. Experimental Determination of Diffraction Elastic Constants

In the experiment by the X-ray method, the diffraction compliances, S'_1 and S'_2, are determined from the changes of the slope and the intercept of the linear regression lines in the $2\theta_\psi$-$\sin^2\psi$ diagram taken under the different values of the uniaxial applied stress σ_A as follows [3]:

$$\frac{S'_2}{2}=\frac{1+\nu'_X}{E'_X}=-\frac{\cot\theta_0}{2}\frac{\partial}{\partial\sigma_A}\left(\frac{\partial\, 2\theta_\psi}{\partial\sin^2\psi}\right)\ , \qquad (12)$$

$$S'_1=-\frac{\nu'_X}{E'_X}=-\frac{\cot\theta_0}{2}\frac{\partial(2\theta_{\psi=0})}{\partial\sigma_A}\ , \qquad (13)$$

where $2\theta_0$ is the diffraction angle of the stress-free materials.

For stress measurement by the $\sin^2\psi$ method, the slope of the $2\theta_\psi$-$\sin^2\psi$ diagram is multiplied by the stress constant, K (MPa/deg), defined by

$$K = -\cot\theta_0 \frac{E'_X}{2(1+\nu'_X)} \frac{\pi}{180} . \qquad (14)$$

Therefore, the value of $S'_2/2=(1+\nu'_X)/E'_X$ is particularly significant for X-ray stress measurement.

3. EXPERIMENTAL PROCEDURE

The experimental materials are pressureless sintered β Si_3N_4 (SN1) [13]. The mechanical properties are presented in Table 1. The aspect ratio of needle-like grains was 4.2 for SN1. The specimen was 10 mm in width, 4 mm in thickness and 55 mm in length. The specimen surface for X-ray measurement was finished by lapping.

The diffraction elastic constants were experimentally determined by the $\sin^2\psi$ method for ten different diffractions by Kα radiations of Cu, Co, Fe, Cr, and V characteristic X-rays. The conditions of X-ray measurement are summarized in Table 2. The X-ray equipment had a parallel beam optics and the iso-inclination mechanism (Ω-diffractometer). The value of the $\sin^2\psi$ was changed from 0 to 0.6 with an interval of 0.1 to obtain the $2\theta_\psi$-$\sin^2\psi$ diagram. The diffraction angle was determined as the center of the half breadth at the 2/5 to 4/5 height of the peak position depending on the diffraction as shown in Table 2.

The four-point bending stress was applied to the specimen. The X-ray was irradiated on the tension side of the bent specimen and the applied strain was monitored by a strain gage glued on the specimen surface. The $2\theta_\psi$-$\sin^2\psi$ diagram was obtained at five strains : 0, 400×10^{-6}, 800×10^{-6}, 1200×10^{-6}, 1600×10^{-6}. The applied stress was calculated by multiplying the strain by the mechanical Young's modulus.

4. EXPERIMENTAL RESULTS

The measured relations between $2\theta_\psi$ and $\sin^2\psi$ were all linear and did not show any systematic non-linearity [13]. The slope and the intercept of the regression line in $2\theta_\psi$-$\sin^2\psi$ diagram changed linearly with the applied stress. The diffraction elastic constants determined by using Eqs. (12) and (13) are summarized in Table 3, where the confidence limit of 68.3% is also indicated in the table. For the stress measurement with high accuracy, the 323 diffraction by Cu-Kα_1 radiation, 251 and 232 diffractions by Fe-Kα radiation, and 411 diffraction by V-Kα radiation were recommended, because the the confidence limit is narrow and the stress constant is small.

According to Voigt-Reuss average and Kröner's models, the X-ray compliances, S'_1 and S'_2, change as a second power function of $\cos^2\phi$ (ϕ= angle between the diffraction plane normal and the c-axis of hexagonal crystal) as shown Eqs. (1) to (7). The X-ray compliances are plotted against $\cos^2\phi$ in Fig. 1. The variations of the

Table 1. Mechanical properties of silicon nitride.

Material	Bulk density ρ, Mg/m^3	Young's modulus E, GPa	Poisson's ratio ν	Bending strength σ_B, MPa	Fracture toughness K_{IC}, MPa$\sqrt{m}$
SN1	3.22	294	0.281	659	6.4

Table 2. Measurement conditions.

Characteristic X-ray	Diffraction	Diffraction angle $2\theta_0$, deg	Scanning range, deg	$\sin^2\psi$ (0.1 step)	Breadth method	$\cos^2\phi$
Cu-Kα_1	323	141.260	138~145	0~0.6	4/5	0.708
Co-Kα_1	203	148.091	145~152	0~0.6	4/5	0.920
Fe-Kα	251	155.332	152~158	0~0.6	2/5	0.116
	610	149.299	146~152	0~0.6	2/5	0
	142	142.553	139~145	0~0.6	1/2	0.494
	232	135.059	130.5~137.5	0~0.6	1/2	0.519
Cr-Kα	212	131.649	129~134	0~0.6	1/2	0.745
	330	129.479	127~131	0~0.6	1/2	0
	411	125.668	123~128	0~0.6	1/2	0.196
V-Kα	411	152.682	149~155	0~0.6	1/2	0.196

compliances are not large and close to the mechanical values drawn with the dot-dash line in the figures. The regression relations for $S_2'/2$ (10^{-3}/GPa) and for $-S_1'$ (10^{-4}/GPa) are by the second order polynomial of $\cos^2\phi$ are

$$\frac{S_2'}{2}=\frac{1+\nu_x'}{E_x'}=3.90+2.12\cos^2\phi-2.50\cos^4\phi\ , \tag{15}$$

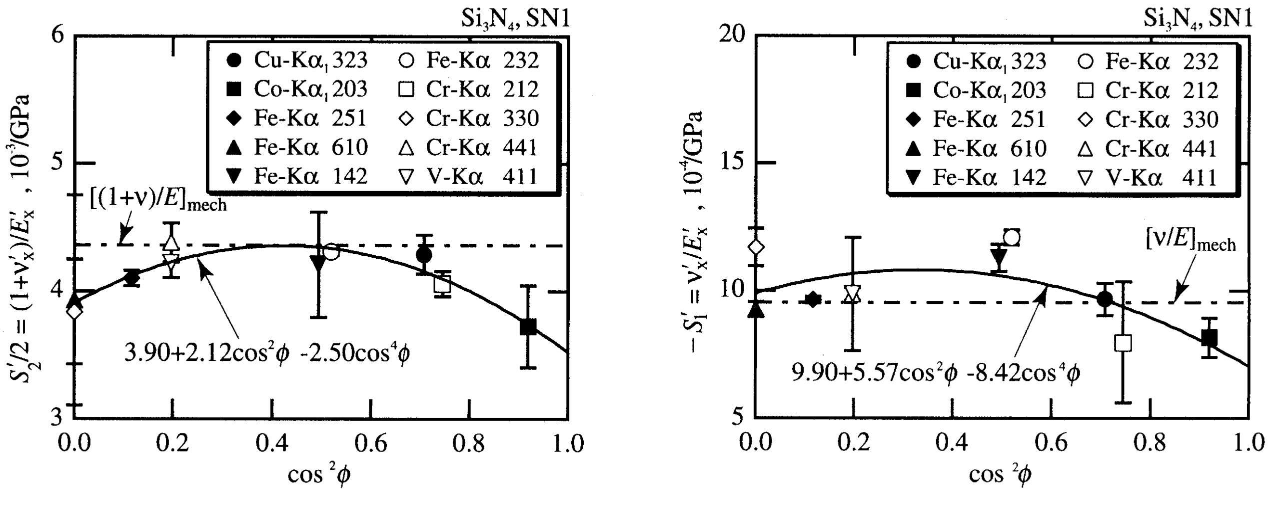
$$-S_1'=\frac{\nu_x'}{E_x'}=9.90+5.57\cos^2\phi-8.42\cos^4\phi\ . \tag{16}$$

5. ELASTIC CONSTANTS OF SINGLE CRYSTAL OF SILICON NITRIDE

The elastic constants of single crystals can be determined from the measured values of the diffraction elastic constants by the simplex method [14]. Figure 2 shows the flowchart for the determination of the single crystal elastic constants. Voigt-Reuss average model and Kröner's model are used for the calculation of the X-ray elastic constants and the polycrystalline elastic constants. The isotropic mechanical elastic constants shown in Table 1 were used as the initial values of the single crystal elastic constants for the simplex method. The initial values of the X-ray elastic constants, E_x' and ν_x' are the same as the mechanical values. The sum of the square of the difference between the calculated and experimental values of

Table 3. X-ray elastic constants and stress constant for SN1.

Characteristic X-ray	Diffraction	X-ray compliances		X-ray elastic constants			Stress constant K, MPa/deg
		$(1+\nu_x')/E_x'$, 10^{-3}/GPa	ν_x'/E_x', 10^{-4}/GPa	$E_x'/(1+\nu_x')$, GPa	E_x', GPa	ν_x'	
Mechanical	——	4.36	9.56	230	294	0.281	——
Cu-Kα_1	323	4.29±0.15	9.68±0.63	233	301	0.292	-719
Co-Kα_1	203	3.73±0.32	8.18±0.76	268	343	0.281	-677
Fe-Kα	251	4.10±0.06	9.65±0.13	244	319	0.308	-470
	610	3.93±0.82	9.29±0.28	254	333	0.309	-612
	142	4.21±0.41	11.3±0.53	237	325	0.368	-706
	232	4.31±0.03	12.1±0.29	232	322	0.388	-841
Cr-Kα	212	4.06±0.10	7.98±2.37	246	306	0.244	-966
	330	3.84±0.41	11.7±0.74	261	375	0.438	-1079
	411	4.38±0.15	9.88±2.21	228	295	0.292	-1025
V-Kα	411	4.22±0.11	9.88±0.25	237	309	0.306	-507



(a) $(1+\nu_x')/E_x'$ vs. $\cos^2\phi$ (b) ν_x'/E_x' vs. $\cos^2\phi$

Fig. 1. Relation between X-ray compliances and $\cos^2\phi$ (Experiment).

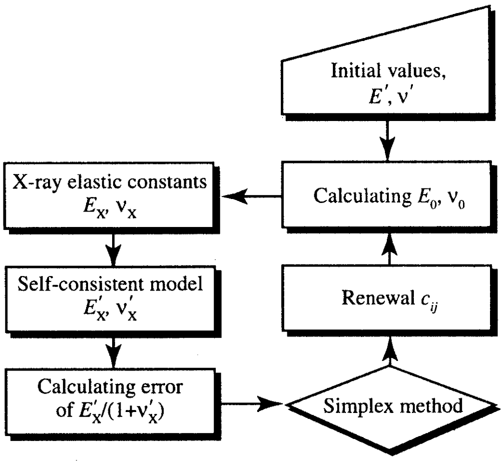


Fig. 2. Procedure for determining elastic constants of single crystal silicon nitride.

$S_2'/2=(1+\nu_X')/E_X'$ for all the measured diffractions is used as the error function. The accuracy of the experimental data for S_2' is larger than that for S_1', so the only the S_2' value is adopted in the error function. The simplex method is used to reduce the error function. New values of the single crystal elastic constants are obtained, and then the second approximations of the mechanical elastic constants of polycrystals are obtained by Voigt-Reuss average or Kneer's equation. From the second approximations, the X-ray elastic constants, E_X and ν_X, were determined by Eqs. (1) to (7). Then, the X-ray elastic constants of E_X' and ν_X' are calculated by Eqs. (8) and (9). The simplex method is again adopted to reduce the error function. The third approximations of the single crystal elastic constants are obtained. This calculation loop is repeated until to get the minimum value of the error function.

The results of single crystal elastic constants obtained by the simplex method are shown in Table 4, together with the data reported by Hay et al [5]. The polycrystalline elastic constants calculated by Voigt-Reuss average or Kneer's equation are also shown in the last two columns. The c_{33} value is larger than the the c_{11} value. The ratio of c_{33}/c_{11} is slightly smaller for the case of Kröner's model. The calculated values by Voigt-Reuss average and Kröner's model are different from the data reported by Hay et al [5]. Especially, the ratio of c_{33}/c_{11} is smaller for the present material. The elastic constants of single crystals may be dependent on the doping agents.

Using the estimated values of single-crystal elastic constants, the S_1' and S_2' values were calculated on the basis of Voigt-Reuss and Kröner's models combined with the self-consistent model. The changes of S_1' and S_2' with $\cos^2\phi$ are shown in Fig. 3. Similar results obtained using the data by Hay et al. are shown in Fig. 4. In the figures, the symbols of data are the same as Fig. 1. As seen in Fig. 4, the results calculated by Hay's data are different from the measured values. Hay's data is not applicable to the present material. For S_1' value, the difference between model predictions is very small. In Fig. 3, the calculated line for S_2' by two models are identical, and nicely approximates the measured values. For S_1' value, the line calculated based on Kröner's model gives the best approximation to the measured data. The variation of the measured values of S_1' is larger than the measured values of S_2'. More precise measurements are necessary for S_1' values.

Kröner's model assumes the grain shape is spherical. On the other hand, real grain shapes of β Si_3N_4 are needle-like with the mean aspect ratio of 4.2. In the future study, the effect of the aspect ratio on the elastic constants should be taken into account in Kröner's model, and also the accuracy of the measurements of X-ray elastic constants need to be improved. Still, the method presented in the present study will be useful for measuring single crystal elastic constants of the other new materials such as nanocrystals, where single crystal samples are not be available.

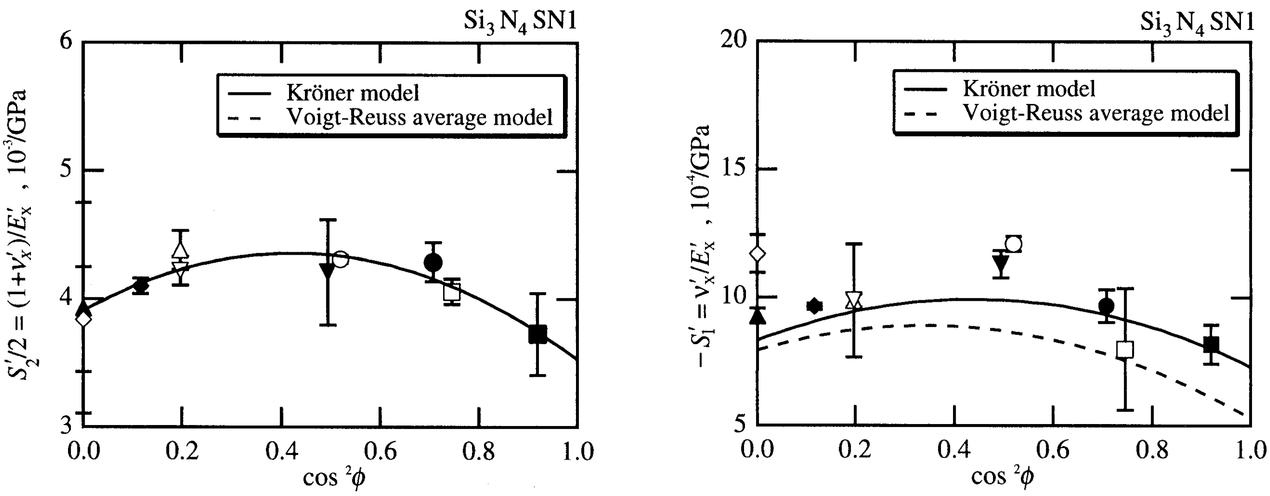
6. CONCLUSIONS

(1) The X-ray elastic constants of pressureless sintered β Si_3N_4 (SN1) were experimentally determined with the $\sin^2\psi$ method for ten different diffractions by using Kα radiation of Cu, Co, Fe, Cr and V. The X-ray compliances, $(1+\nu_X')/E_X'$ and ν_X'/E_X' (E_X' = Young's modulus, ν_X' = Poisson's ratio), change as a second power function of $\cos^2\phi$ (ϕ = angle between the diffraction plane normal and the c-axis of hexagonal crystal).
(2) Using the simplex method, the elastic constants of

Table 4. Elastic constants of β Si_3N_4 (SN1).

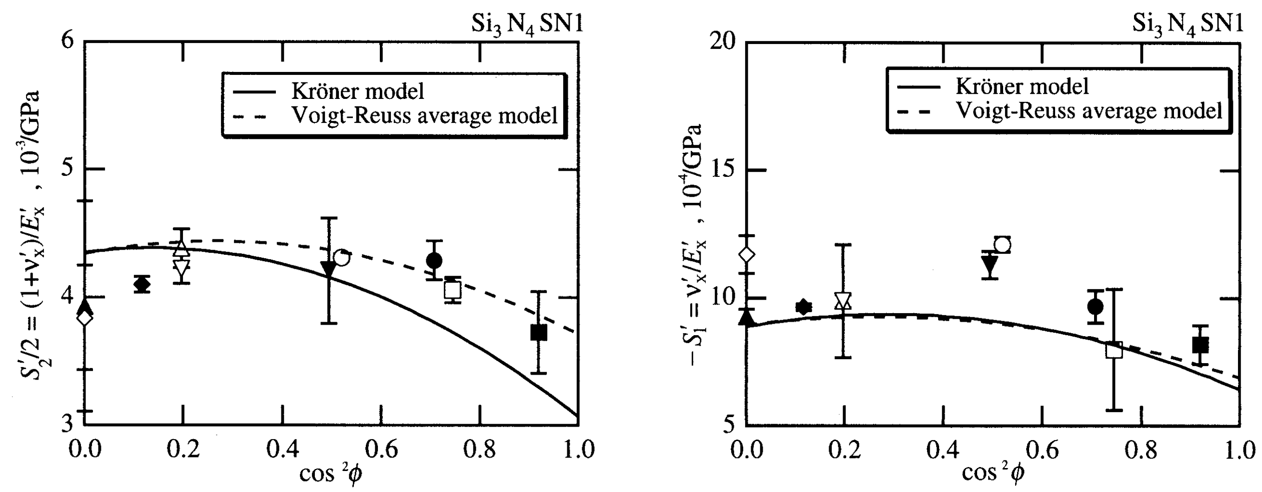
Model	Single crystal elastic constant, GPa					Polycrystal	
	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	E_0 , GPa	ν_0
Voigt-Reuss average	413	173	60	553	122	350	0.245
Kröner model	439	166	142	494	106	330	0.282
Hay et al. [5]	343	136	120	600	124	319* 318**	0.259* 0.259**

* Calculated by Voigt-Reuss average model
** Calculated by Kröner's model (Kneer's equation)



(a) $(1+\nu'_X)/E'_X$ vs. $\cos^2\phi$ (b) ν'_X/E'_X vs. $\cos^2\phi$

Fig. 3. Relation between X-ray compliances and $\cos^2\phi$ (Prediction).



(a) $(1+\nu'_X)/E'_X$ vs. $\cos^2\phi$ (b) ν'_X/E'_X vs. $\cos^2\phi$

Fig. 4. Relation between X-ray compliances and $\cos^2\phi$ (Prediction based on Hay's data).

single crystals were determined from the measured values of the diffraction elastic constants on the basis of Voigt-Reuss average model and Kröner's model, combined with the self-consistent analysis of the effect of the secondary phases. The estimated results of β Si_3N_4 showed a high stiffness in the c-direction of hexagonal crystals, but the degree of anisotropy is not so larger as the whisker's data reported by Hay et al.

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