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Structure Determination of α-Quartz up to 68 × 10⁸ Pa

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Abstract

High-pressure single-crystal structure determinations of α-quartz (SiO_2) have been performed up to 68×10^8 Pa using a new measuring procedure on an automatic four-circle diffractometer. The lattice constants have been determined up to 73×10^8 Pa. The *a* lattice constant decreases from 4·921 (1) (10^8 Pa) to 4·664 (2) Å (73×10^8 Pa) and the *c* lattice constant from 5·400 (4) (10^8 Pa) to 5·246 (3) Å (73×10^8 Pa). The *c/a* ratio increases from 1·097 to 1·125 (73×10^8 Pa). The volume change in this pressure range is about 13% and agrees with the elastic constants determined by ultrasonic measurements. The SiO_4 tetrahedra are very incompressible up to 68×10^8 Pa; the Si—O bond distance and the Si—O bond angle remain constant. The Si—O—Si angle decreases from 142 (10^8 Pa) to 132° (68×10^8 Pa). The cross-section of the channels in the structure parallel to the *c* axis becomes smaller up to 68×10^8 Pa.

Introduction

The phase diagram of SiO_2 has been investigated many times, but all phase boundaries which have been found for high-pressure phases terminate in the temperature range 773–873 K (Böhler & Arndt, 1974; Sato, 1976). Thus the stability region of the two high-pressure (and high-temperature) phases of SiO_2, coesite and stishovite, have not been investigated at room temperature.

The last single-crystal structure determination of α-quartz under normal conditions was performed by Le Page & Donnay (1976), but several structure determinations have been made before. The first high-pressure studies on α-quartz were done by McWhan (1967). He used X-ray powder methods and a solid pressure transmitting medium, NaCl. Up to 150×10^8 Pa he did not find any phase transformation, only a linear compression.

As a result of the recent developments in high-pressure techniques, it is now possible to measure the X-ray intensities of single crystals under high hydrostatic pressure with an automatic four-circle diffractometer. In our case the high hydrostatic pressure was produced by a diamond anvil cell (Keller & Holzapfel, 1977). However, this high-pressure cell restricts the measurable reciprocal space and causes considerable absorption effects on the intensity measurements. Therefore, we have developed a new software (Denner, Schulz & d'Amour, 1978) to improve the intensity measurements.

We find α-quartz (low-quartz) to be a convenient compound to test this software, because it has the following properties:

(1) Easy to cut in any desired form, avoiding any difficulties concerning the preparation of the high-pressure cell.

(2) Small unit cell and relatively high space-group symmetry, but not all atoms at fixed positions.

Experimental

To apply high hydrostatic pressure, a diamond anvil cell, developed by Keller & Holzapfel (1977) and adapted to an automatic four-circle diffractometer by

Denner, Dieterich, Schulz, Keller & Holzapfel (1978), was used. The gasket material used was Inconel, which was prepressed to a thickness of about 80 μm. The diameter of the gasket hole was 180 μm. The crystals of α-quartz were cut into thin sheets of about 60 μm thickness perpendicular to the c axis. The dimensions of the crystal investigated were 60 × 60 × 80 μm. A CsCl crystal of similar dimensions was also put into the gasket hole. Using Decker's equation of state (Decker, 1971) the pressure was evaluated by the changes of the lattice constants of the CsCl crystal. The pressure transmitting medium was a 4:1 mixture of methanol: ethanol (Piermarini, Block & Barnett, 1973) which gives hydrostatic pressure up to 100×10^8 Pa.

The intensity measurements and the determination of the lattice constants were made on a Philips four-circle diffractometer using Mo $K\alpha$ radiation (graphite monochromator). A new high-pressure measuring procedure developed by Denner, Schulz & d'Amour (1978) was used for the intensity measurements. The advantages and improvements of this new measuring procedure are:

(1) The overlapping of reflections of the sample and the CsCl crystal or the two diamond anvil crystals is avoided.

(2) Each reflection is measured at an optimized ψ value.

(3) Each intensity is immediately corrected for possible absorption.

(4) The available space of the reciprocal lattice which can be measured is enlarged by measuring the reflections at $\psi \neq 0$ and not in the symmetrical setting.

150 reflections could be measured (about 15 were unobserved) in the ω scan mode up to sin $\theta/\lambda = 0.53$ Å⁻¹. 60 of these were symmetry independent. This means, using this new software, about 40% of the whole reciprocal space up to sin $\theta/\lambda = 0.53$ Å⁻¹ can be measured. Using the standard procedure with the symmetrical setting ($\psi = 0$) for the intensity measurements, only 30% of the whole reciprocal space (sin $\theta/\lambda \leq 0.53$ Å⁻¹) can be measured. The usual Lorentz and polarization corrections were applied.

At the highest pressure value (73×10^8 Pa) only lattice constants have been determined and no structural computations have been performed, because more than 70% of the intensities collected were unobserved after application of Lorentz and polarization corrections.

The amount of twinning was estimated by the Le Page & Donnay (1976) procedure and found to be negligible within experimental error. As start parameters the atom parameters given by Le Page & Donnay (1976) and their space-group setting were used in the least-squares refinements.

The space group $P3_2 21$ was used for all least-squares refinements, because there was no evidence that the space-group symmetry had changed. For all structural computations the programs of the XRAY system (1972) were used. All reflections had unit weights. The R values ranged between 5·6% and 9·9% for all pressure sets.

In Table 1 the lattice constants for the different pressure values are given. In Fig. 1(a) the pressure dependence of the lattice constants is compared with the results of McWhan (1967), Figs. 1(b) and 1(c) show the pressure dependence of the c/a ratio and the volume change in the pressure range up to 73×10^8 Pa. The results of McWhan (1967) show a somewhat lower compressibility than our measurements. The changes of the lattice constants show that in the pressure range up to 73×10^8 Pa

$$\Delta a/a_0 \text{ (McWhan)} < \Delta a/a_0 \text{ (this work)}$$

$$\Delta c/c_0 \text{ (McWhan)} > \Delta c/c_0 \text{ (this work)}.$$

Table 1. *Lattice constants of α-quartz in the pressure range up to* 73×10^8 Pa

$p (\times 10^8$ Pa)	a (Å)	c (Å)	c/a	V (Å³)
0·001	4·921 (1)	5·400 (4)	1·097 (1)	113·2 (1)
19	4·832 (2)	5·347 (4)	1·107 (1)	108·1 (1)
37	4·765 (2)	5·296 (3)	1·112 (1)	104·2 (1)
54	4·731 (2)	5·280 (2)	1·116 (1)	102·4 (1)
60	4·704 (3)	5·261 (4)	1·118 (2)	100·8 (1)
68	4·684 (2)	5·252 (3)	1·121 (1)	99·8 (1)
73	4·664 (2)	5·246 (3)	1·125 (1)	98·8 (1)

Table 2. *Atom parameters and isotropic temperature factors of α-quartz in the pressure range up to* 68×10^8 Pa

Atom (Wyckoff notation)		$p (\times 10^8$ Pa) 0·001	19	37	54	60	68
Si (3a)*	x	0·472 (2)	0·463 (2)	0·456 (1)	0·456 (3)	0·452 (3)	0·449 (3)
	B (Å²)	0·7 (3)	0·8 (3)	0·5 (2)	1·0 (4)	1·0 (4)	0·9 (4)
O (6c)*	x	0·408 (4)	0·409 (3)	0·409 (3)	0·412 (5)	0·400 (6)	0·404 (7)
	y	0·265 (4)	0·279 (3)	0·295 (3)	0·302 (5)	0·298 (5)	0·301 (6)
	z	0·117 (2)	0·107 (2)	0·101 (2)	0·098 (3)	0·095 (2)	0·092 (3)
	B (Å²)	1·0 (5)	0·9 (4)	0·7 (4)	1·2 (6)	1·4 (7)	0·3 (6)

* The space-group setting refers to Le Page & Donnay (1976).

This gives a considerably lower change of the c/a ratio for McWhan's than for our experiments. Probable reasons for these discrepancies are:

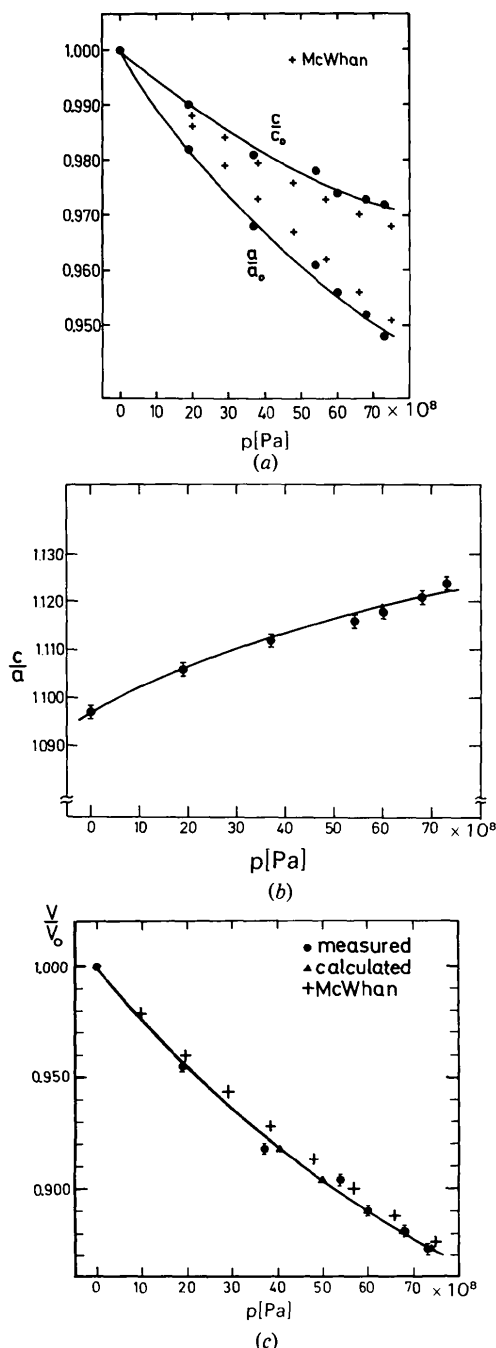(1) No exact hydrostatic pressure for McWhan's experiments, because NaCl was the pressure transmitting medium.

(2) Only eight reflections were used to determine the lattice constants.

In Table 2 the refined atomic parameters for all pressure points are given; as can be seen the isotropic thermal parameters show no uniform tendency.*

Results and discussion

α-Quartz is built of SiO_4 tetrahedra linked together so that every oxygen atom is common to two tetrahedra (common corner). The SiO_4 tetrahedra are linked to helical chains parallel to the c axis forming large open channels.

Bond distances and angles are tabulated in Table 3. Fig. 2 shows the behaviour of the Si—O distances and O—Si—O angles within the SiO_4 tetrahedron as well as the variation of the Si—O—Si angle in the pressure range up to 68×10^8 Pa. For comparison, the values for β-quartz are also given in the diagram. The mean value of the Si—O bond distance remains constant within the pressure range. The difference between the maximum and minimum values of these distances is not increased. Within the error limits, the SiO_4 tetrahedron seems to be unchanged and (very) incompressible. A similar effect has been reported by Hazen (1976) for forsterite.

From these facts it follows that the distances between the oxygen atoms of each tetrahedron remain unchanged (these contacts represent the edges of a SiO_4

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34070 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
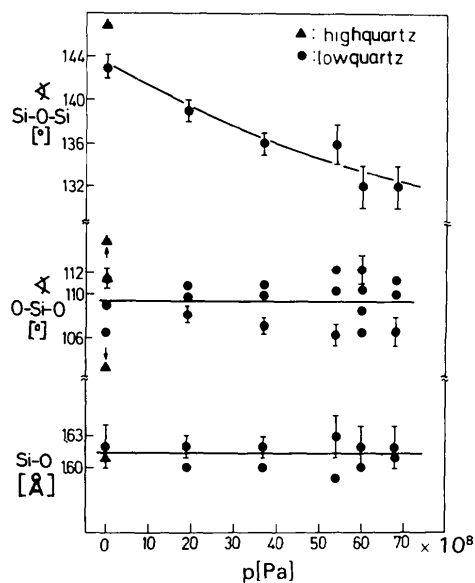

Fig. 1. (a) Relative change of the a and c lattice constants of α-quartz compared with McWhan's (1967) results, (b) pressure dependence of the c/a ratio of α-quartz, (c) pressure–volume relationship of α-quartz. The solid line corresponds to a least-squares fit of the measured data by a Birch equation of state.

Fig. 2. Variation of Si—O distances, O—Si—O bond angles and Si—O—Si bond angle with pressure.

Table 3. Si—O, O—O *distances and* Si, O *angles of* α-*quartz in the pressure range up to* 68 × 10⁸ Pa

The first four O—O distances are edges of the Si—O₄ tetrahedron, the fifth is the shortest O—O distance, which is no edge (n.e.) of the SiO₄ tetrahedron.

	p (× 10⁸ Pa)					
	0·001	19	37	54	60	68
Si—O	1·62 (2) Å	1·60 (2) Å	1·62 (2) Å	1·63 (3) Å	1·63 (4) Å	1·60 (3) Å
Si—O'	1·62 (2)	1·62 (1)	1·60 (1)	1·59 (2)	1·62 (3)	1·62 (2)
O—Si—O'	106·5 (11)°	110·0 (7)°	110·0 (7)°	110·8 (12)°	108·7 (17)°	110·1 (15)°
O—Si—O''	111·7 (6)	111·2 (4)	111·2 (4)	110·3 (6)	112·2 (9)	111·6 (8)
O—Si—O'''	109·2 (8)	108·3 (5)	107·1 (5)	106·4 (8)	106·6 (1·1)	106·7 (9)
O'—Si—O''	109·2 (7)	108·3 (5)	107·1 (4)	106·4 (7)	106·6 (1·0)	106·7 (7)
O'—Si—O'''	111·7 (7)	111·0 (5)	111·2 (4)	110·3 (7)	112·2 (1·0)	111·6 (9)
O''—Si—O'''	108·7 (11)	109·8 (9)	110·4 (7)	112·6 (13)	110·6 (18)	110·3 (15)
Si—O—Si	142 (2)	138·9 (11)	135·7 (10)	134 (2)	131 (2)	132 (2)
O—O'	2·59 (3) (Å)	2·60 (2) (Å)	2·66 (1) (Å)	2·68 (3) (Å)	2·65 (4) (Å)	2·63 (3) (Å)
O—O''	2·67 (2)	2·66 (2)	2·66 (2)	2·64 (3)	2·69 (5)	2·67 (3)
O—O'''	2·64 (2)	2·61 (2)	2·59 (2)	2·58 (3)	2·60 (5)	2·59 (4)
O''—O'''	2·63 (2)	2·65 (2)	2·63 (1)	2·65 (2)	2·66 (4)	2·66 (3)
O—O (n.e.)	3·30 (2)	3·12 (2)	2·99 (1)	2·93 (2)	2·85 (4)	2·84 (3)

tetrahedron). This is shown in Table 3 and Fig. 3, where the values for β-quartz are also given. The only changes in the α-quartz structure under high hydrostatic pressure concern the arrangement of the SiO₄ tetrahedra. These are indicated by the considerable changes in the Si—O—Si bond angle and the O—O distances between the different tetrahedra, see Fig. 2 and Table 3. The torsion of the tetrahedra against each other is increased. There were no indications of an approximation of a more symmetrical arrangement of the tetrahedra as in β-quartz.

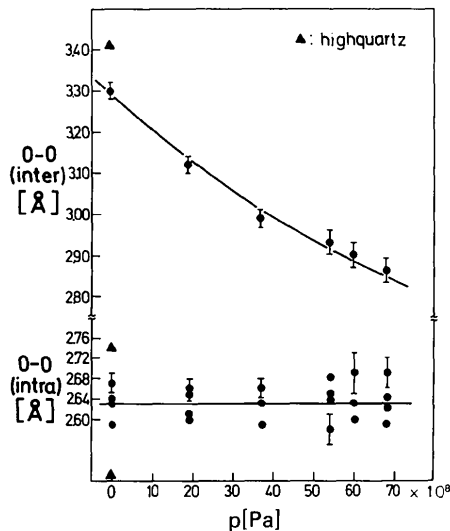The connection between the SiO₄ tetrahedra is similar for both the α-quartz and the β-quartz structures. The main difference between the two structures is the higher space-group symmetry $P6_322$ for β-quartz. The cross-section of the channels parallel to the c axis is a perfect hexagon in β-quartz, considering only the Si atoms. In α-quartz it is slightly distorted. This difference can be demonstrated by the Si—O—Si angle. Fig. 2 shows the pressure dependence of this angle. With increasing pressure the difference between the Si—O—Si angles of the two quartz structures increases. Also the torsion [given by the tilt angle φ (Megaw, 1973)] of the SiO₄ tetrahedra about the a axis becomes larger. This is shown in Fig. 4 by the pressure and temperature dependence of this tilt angle φ. Generally, we can say that the structural difference between α-quartz and β-quartz becomes more evident with increasing pressure.

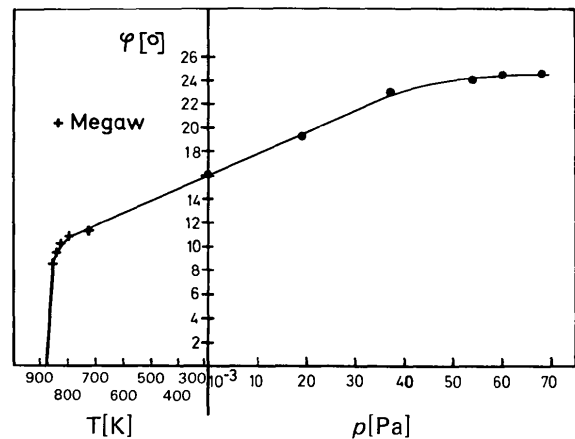This agrees with Hazen (1977) who found an 'inverse relationship' between thermal expansion and

Fig. 3. O—O distances in α-quartz. The word 'intra' means edges of the SiO₄ tetrahedron and 'inter' no edge of a tetrahedron.

Fig. 4. Pressure and temperature dependence of the tilt angle φ of the SiO₄ tetrahedra about the a axis.

compression. A first indication of this effect was given by the change of the c/a ratio which increases in the pressure range up to 73 × 10⁸ Pa, while at increasing temperature the c/a ratio decreases to reach the value for β- or high-quartz at 846 K (Smith, 1963).

Fig. 5 shows a view along the trigonal axis with the arrangement of the tetrahedra and the cross-sections through the channels which are parallel to the c axis. The dotted lines show how the cross-section of the channels changes under increased pressure; it becomes smaller. This explains why under pressure the c/a ratio increases and the a lattice constant decreases much more than the c lattice constant. Perpendicular to the c axis the structure responds to increased pressure by
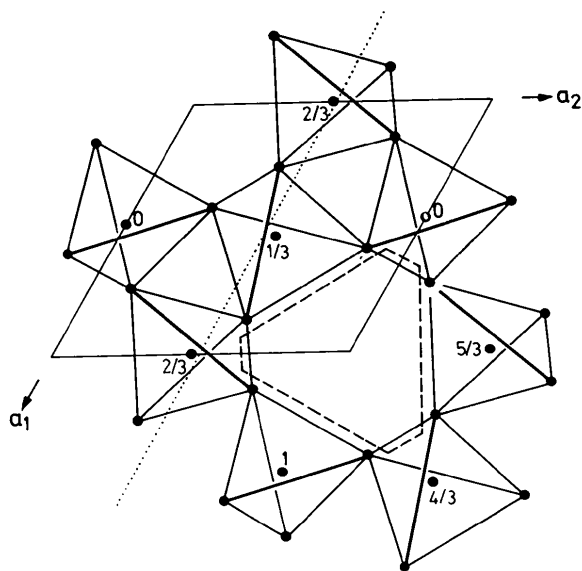

Fig. 5. View along the c axis, which shows a cross-section through the channels (parallel to the c axis). The broken line represents the change of the channel cross-section with increased pressure.
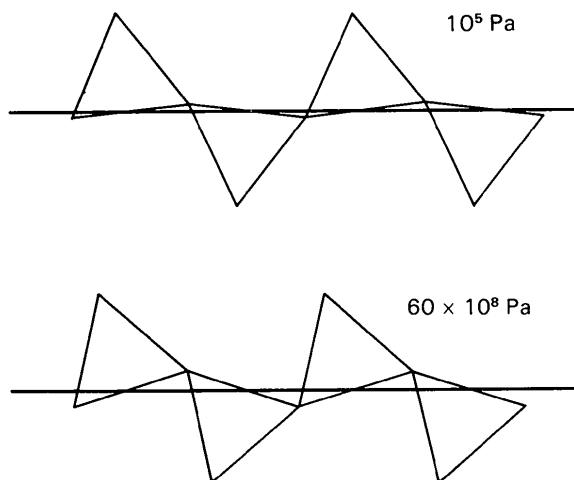

Fig. 6. Schematic drawing of a line (given in Fig. 5 by a dotted line) of linked tetrahedra which is parallel to the a axis and its change with increased pressure.

narrowing the channels. The compression of the so-called 'helices' of the SiO₄ tetrahedra parallel to the c axis appears to be more difficult.

Fig. 6 shows the deviation of a line of linked tetrahedra from a straight line parallel to the a axis. The deviation of the tetrahedra from this line increases with pressure.

The pressure–volume relation can be represented by a Birch equation of state (Birch, 1947).

$$p(x) = \tfrac{3}{2}B_0[x^{7/3} - x^{5/3}][1 - \tfrac{3}{4}(4 - B_0')(x^{2/3} - 1)]$$

$x = V_0/V$; B_0, B_0' isothermal bulk modulus and its pressure derivative at normal pressure.

The solid line in Fig. 1(c) corresponds to a least-squares fit of the Birch equation (Syassen & Holzapfel, 1978). The results

$$B_0 = 365\ (9) \times 10^8\ \text{Pa} \qquad B_0' = 5\cdot9\ (4)$$

are in good agreement with the values given by McSkimmin, Andreatch & Thurston (1965), $B_0 = 374 \times 10^8$ Pa, $B_0' = 6\cdot3$ from their ultrasonic measurements.

Conclusions

Single-crystal structure investigations on α-quartz under high hydrostatic pressure up to 73 × 10⁸ Pa showed no phase transformation, only a continuous compression. The volume decreases in this pressure range by about 13%. The c/a ratio increases from 1·097 to 1·125; this means there is no tendency to reach the theoretical value of 1·0981 for tetrahedra with exact $\bar{4}$ symmetry. The Si—O bond angles and distances of the tetrahedron itself remain constant, i.e. the Si—O tetrahedron is very incompressible. Only the torsion of the tetrahedra against each other is increased. So the Si—O—Si angle decreases from 142 (atmospheric pressure) to 132° (68 × 10⁸ Pa). Obviously, the large open channels parallel to the c axis, which are typical of the quartz structure, respond to the pressure much better by decreasing their cross-section than do the helices of the SiO₄ tetrahedra along the c axis.

The calculated values for the bulk modulus B_0 and its pressure derivative B_0' are in good agreement with the results from ultrasonic measurements.

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Détermination de la Structure Cristalline de EuGa₂S₄

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Abstract

$EuGa_2S_4$, $M_r = 419.5$, is orthorhombic, space group *Fddd* with $a = 20.727$ (7), $b = 20.454$ (6), $c = 12.197$ (2) Å, $Z = 32$, $D_m = 4.2$, $D_x = 4.3$ Mg m^{-3}, $V = 5171$ Å^3. The structure was solved by direct methods with *MULTAN* 76 and refined by full-matrix least-squares calculations to $R = 0.076$ for 966 observed reflexions. The Eu atoms have an eightfold coordination, and the Ga a fourfold coordination.

Introduction

Les chalcogénures ternaires de formule générale AB_2X_4 où A, B sont des cations et X représente S, Se ou Te, forment un nouveau groupe de composés de structures cristallines diverses dont les propriétés physiques dépendent de la nature des cations. Nitsche (1975), dans un article de synthèse sur les composés ternaires, donne un aperçu des propriétés possibles de cette famille de minéraux. Le ternaire de formule $EuGa_2S_4$ a été synthétisé pour la première fois par Eholié, Gorochov, Guittard, Mazurier & Flahaut (1971).

Ces auteurs proposent comme groupe spatial *Bbmm* et obtiennent à partir de réflexions indexées sur un diagramme de poudre les paramètres cristallins suivants: $a = 10,21$, $b = 10,36$ et $c = 6,094$ Å.

Peters & Baglio (1972) donnent le diagramme de poudre aux rayons X d'une série de produits photoluminescents dopés à l'europium et confirment l'existence du ternaire $EuGa_2S_4$ cristallisant dans le système orthorhombique. Ils attribuent un nouveau groupe spatial *Fddd* ainsi que de nouveaux paramètres cristallins: $a = 20,716$, $b = 20,404$, $c = 12,200$ Å.

Donohue & Hanlon (1974) préparent une série de ternaires de formule AB_2X_4 dont le composé qui nous intéresse et indiquent certaines de ses propriétés physiques: point de fusion, ordre de grandeur de la résistivité électrique, *etc.* Ils proposent à nouveau les paramètres cristallins donnés par Eholié *et al.* (1971).

Aliev, Kurbanov, Rustamov, Alidzhanov & Salmanov (1976) publient les courbes de variation thermique de la conductivité, du pouvoir thermoélectrique et du coefficient d'effet Hall des composés EuB_2X_4 avec $B = $ Ga ou Al, et $X = $ S, Se ou Te. Ces auteurs donnent également les paramètres cristallins de Eholié *et al.* (1971).

Le diagramme de phase quasi-binaire $EuS–Ga_2S_3$ décrit par Barnier & Guittard (1976) met en évidence des phases vitreuses pour des compositions voisines de $EuS + Ga_2S_3$.