

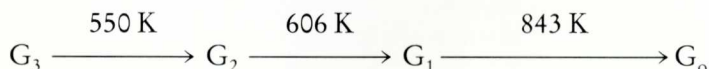
ATOMIC STRUCTURE AND TWINNING OF RbLiCrO₄ CRYSTALS

I.P. MAKAROVA

Institute of Crystallography, USSR Acad. Sci., Moscow, USSR

INTRODUCTION

RbLiCrO₄ crystals belong to the MLiAX₄ family, where M = K, Rb, Cs, NH₄-group, AX₄ = BeF₄, SO₄, CrO₄. The atomic structure of all these crystals can be regarded as a β-tridimite derivative. Phase transitions in crystals of a double rubidium and lithium chromate, RbLiCrO₄ were first reported in [1]. The data obtained using differential-thermal analysis, optical polarization and powder diffraction technique, as well as measurements of birefringence and the generation of the second optical harmonics [1, 2] enabled us to establish the following sequence of structural transformations in RbLiCrO₄ crystals upon heating:



The $G_3 \longrightarrow G_2$ transition is the first order phase transition. The G_3 and G_2 phases are polar, optically uniaxial, besides, the G_2 phase exhibits optical activity [2]. Our study was aimed at the determination and refinement of the crystal structure of RbLiCrO₄ in the G_3 and G_2 phases. We also intended to elucidate the character of twinning in this compound.

EXPERIMENTAL

The data were collected on an ENRAF-NONIUS CAD-4F autodiffractometer (graphite monochromator, MoK_α-radiation, $\theta/2\theta$ scan). We used three samples of single crystals, machined into spheres 0.0280(5) cm in diameter (sample I, T = 293 K), 0.0260(5) cm (sample II, T = 428 and

493 K), 0.0220(5) cm (sample III, $T = 523, 553$ and 583 K). The main crystal data are listed in Table 1. Reflection intensities were measured in the total sphere of reciprocal lattice at 428 K, at other temperatures – in reciprocal lattice hemisphere.

The analysis of diffraction pattern of the G_3 phase revealed systematic $hh2hl$ absences with $l \neq 2n$, which correspond to space groups $P31c, P3\bar{1}c, P6_3mc, P\bar{6}2c, P6_3/mmc$. The absence of inversion centre (a signal of the second optical harmonics was detected in phase G_3) led to a choice between three space groups: $P31c, P\bar{6}2c, P6_3mc$. The $P31c$ group was preferable for the G_3 phase after the structural models had been refined with allowance for anomalous scattering and twinning by merohedry.

The main difficulty in structure determination and finding crystal symmetry of $RbLiCrO_4$ was due to the fact that the samples were twinned by merohedry [3]. The point group $3m$ for $RbLiCrO_4$ crystals is a subgroup with the index 4 of a holohedral point group $6/mmm$. In this case there are four possible variants of twin domains and three laws of twinning by merohedry: $2 \parallel [001], m \perp [001]$ and $\bar{1}$. At equal total volumes of twin domains of two orientations the symmetry of the diffraction pattern is raised up to groups $6mm, \bar{6}2m$ or $\bar{3}m$, respectively. If there are twin domains of four orientations simultaneously, the symmetry is raised up to the group $6/mmm$. In case of twinning by the two-fold axis or plane m the Laue class is $6/mmm$. These two cases can be distinguished according to the diffraction pattern only provided there is significant anomalous scattering. In the case

Table 1. $RbLiCrO_4$. Crystal data obtained for specimen I at 293 K, II – at 428 K, 493 K, III – at 523 K, 553 K, 583 K.

parameter	temperature (specimen)					
	293 K (I)	428 K (II)	493 K (II)	523 K (III)	553 K (III)	583 K (III)
space group	$P31c$	$P31c$	$P31c$	$P31c$	$P6_3$	$P6_3$
z	2	2	2	2	2	2
$a, \text{\AA}$	5.4021(9)	5.423(1)	5.438(1)	5.453(1)	5.463(1)	5.471(1)
$c, \text{\AA}$	9.175(1)	9.161(1)	9.160(2)	9.151(1)	9.147(2)	9.140(4)
$V, \text{\AA}^3$	231.89	233.32	234.64	235.68	236.39	236.95
$(\sin\Theta/\lambda)_{\max}, \text{\AA}^{-1}$	1.00	1.00	1.00	0.77	0.72	0.74
$N_i (I \geq \sigma_1)$	2870	4680	1988	1641	1560	1511
$N_{i \text{ unique}} (I \geq 3\sigma_1)$	911	823	632	440	379	379
$R_{av}, \%$	3.0	4.4	6.2	5.5	8.0	13.6
$V_1 : V_2$	3.4 : 1	8.3 : 1	8.3 : 1	1.2 : 1	1.6 : 1	1.6 : 1
$R_w, \%$	2.87	2.12	2.69	3.50	3.42	4.64
$R, \%$	3.20	2.63	3.32	3.65	3.46	4.29

of inversion twinning the Friedel's pairs of reflections are equal even if there is anomalous scattering.

Comparison of R_{av} of intensities in the G_3 phase for groups $31m$, $6mm$, $\bar{6}2m$, $\bar{3}1m$ and $6/mmm$ (upon averaging in groups $31m$, $6mm$, $\bar{6}2m$, the Friedel's pairs were not averaged) made the group $31m$ (sp. gr P31c) preferable. Besides, anomalous dispersion, in fact, influenced remarkably the scattering, that excluded the centre of inversion $\bar{1}$ as a twinning symmetry element for all the three samples. A comparison of R_{av} for the groups $\bar{6}2m$ and $6mm$ showed that the plane m is the most probable twinning element for sample I. No unambiguous symmetry group was chosen for sample II. The two-fold axis was a most probable twinning element for sample III.

In the diffraction pattern of the phase G_2 of $RbLiCrO_4$ crystals the only type of systematic absences among reflections $000l$ with $l = 2n$ corresponds to three space groups: $P6_3$, $P6_3/m$, $P6_322$. Taking into account the absence of the centre of inversion (the second optical harmonics is observed) and optical activity of the crystals in this particular phase, we arrived at the only space group $P6_3$. During refinement of the structural model of these crystals one should take into account a possible twinning by merohedry. The point group 6 of the phase G_2 of $RbLiCrO_4$ crystals is a subgroup with the index 4 of a holohedral space group $6/mmm$, that leads to four possible variants of twin domains and three laws of twinning by merohedry: $m \parallel [001]$, $2 \perp [001]$, $\bar{1}$. Accordingly, in case of equal total volumes of two twin partners the symmetry of the diffraction pattern will be raised up to groups $6mm$, 622 or $6/m$. If the sample under study contains simultaneously twin domains of four orientations the group will be raised up to $6/mmm$. Groups $6mm$ and 622 can be distinguished according to the diffraction pattern only provided there is remarkable anomalous scattering. Optical, pyroelectrical and X-ray topography data were used to analyze twinning in the phase with the symmetry $P6_3$ of $KLiSO_4$ crystals in [4].

Comparison of R_{av} for sample III at 553 and 583 K in groups 6 , $6mm$, 622 , $6/m$, $6/mmm$ (upon averaging in groups 6 , $6mm$, 622 the Friedel's pairs of reflections were not averaged) showed that R_{av} for group $6mm$ is lower, the symmetry plane $m \parallel [001]$ is more probable as a twinning element in sample III.

The observed reflection intensities were converted to moduli of structure amplitudes for all the temperatures with allowance for kinematic, polarization and absorption factors. All the calculations, including refinement of structural models using LSM with allowance for observed weighting factors were made according to the PROMETHEUS program system [5]. Atomic scattering curves and dispersion corrections for them $\Delta f'$ and $\Delta f''$ were taken from [6]. Correction for extinction in isotropic approximation was made following the Becker-Coppens formalism [7].

CRYSTAL STRUCTURE OF RbLiCrO_4

The atomic coordinates of the KLiSO_4 structure at 298 K [8] were taken as the starting model for refinement of the structure of RbLiCrO_4 at 293 K. For other temperatures we chose structural parameters obtained at a lower temperature. The differences between structural models corresponding to space groups $P31c$ in the phase G_3 and $P6_3$ in the phase G_2 are mainly in dissimilar mutual orientation of the layers built up of six-membered rings formed by alternating $[\text{CrO}_4]$ and $[\text{LiO}_4]$ tetrahedra, figure 1. In fact, this is a rotation of the triangular bases of the tetrahedra formed by O(2) atoms about the three-fold axis in one of the two layers. The $[\text{CrO}_4]$ tetrahedra from one layer are joined with $[\text{LiO}_4]$ tetrahedra from the second layer by common vertices which are O(1) atoms. Rb atoms occupy sites on the main symmetry axes in channels formed by six-membered rings.

After the structural parameters were refined in the phase G_3 , sp. gr. $P31c$, the analysis of difference electron density maps revealed residual density peaks, which formed a triangle about the three-fold axis. This triangle was equal in size to a triangle made up of O(2) atoms and rotated through approximately 48° about it. Such residual density, naturally, can be treated as a consequence of crystal twinning. A similar domain structure was formerly found in KLiSO_4 crystals [8].

The studied samples of RbLiCrO_4 crystals in the G_3 phase can contain any of the following variants of twin domains: xyz , xyz , xyz , xyz . This corresponds to twinning by plane, the two-fold axis or the centre of inversion. We refined all structural models with allowance for possible twinning according to those three laws. In order to take twinning into account the twin

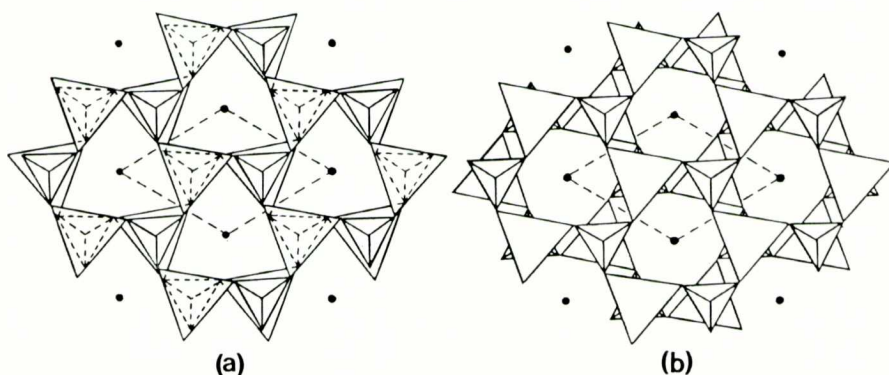


Fig. 1. Structures of RbLiCrO_4 in phase $P31c$ (a) and phase $P6_3$ (b). View along $[001]$. Small tetrahedra – $[\text{CrO}_4]$ groups; large tetrahedra – $[\text{LiO}_4]$ groups; full circles – Rb atoms. The unit cell is shown by dashed lines.

volume ratio should be determined and the contribution of the largest in volume component to observed structure amplitudes should be selected. In other words, the parameter $p = V_1/V_2$ should be introduced into the refinement procedure. These problems were solved according to the technique described in [9].

For sample I at 293 K and sample II at 428 K and 493 K the lowest R_w were obtained for the variant when the domain orientations were related by the symmetry plane $m \perp [001]$, and hkl and $hk\bar{l}$ reflections from different twin domains overlapped, the twin volume ratio being $V_1 : V_2 = 3.4 : 1$ and $8.3 : 1$, respectively. For sample III at 523 K the lowest R_w was obtained for such twinning when domain orientations were related by the symmetry operation $2 \parallel [001]$ and the total twin volume ratio was $V_1 : V_2 = 1.2 : 1$. Refinement of structural models with the addition of a third component led to a zero volume of that third component. We may suppose that within the accuracy of our measurements and calculations, the three samples studied contain twin components of only two orientations.

In studies of KLiSO_4 crystals [8, 10, 11] special attention was paid to disorder in the arrangement of O(1) and O(2) atoms. In the course of structure refinement both the statistic disorder in the atomic arrangement and the true anharmonicity of atomic thermal motion are manifested roughly similarly. We refined anharmonic thermal vibrations for all Rb, Cr, O(1), O(2) atoms, except Li, using the Gram-Charlier formalism [12]. In the course of structure refinement we took into account sequentially tensors in the temperature factor transform up to the fourth order.

As a result of refinement of anharmonic thermal parameters of Rb atom we obtained the only physically meaningful parameter C^{111} of the Rb atom. Figure 2 shows a difference electron density map constructed at the stage of refinement of harmonic thermal parameters of the Rb atom. Figure 3 shows a section of the difference probability density function (PDF) of Rb atom displacement from its equilibrium position on the three-fold axis, which shows the contribution of anharmonic parameters and is calculated from the results of the refinement of parameter C^{111} of Rb atom. The sections are given for $T = 428$ K. At other temperatures the distributions are identical to those shown in figures 2 and 3. Our attempts to reveal deviations from the harmonic law of thermal motion of the O(1), O(2) and Cr atoms in the G_3 phase of RbLiCrO_4 crystals did not lead to physically meaningful anharmonic parameters.

Refinement of the structural model of the G_2 phase within space group $P6_3$ as well as in the G_2 phase was made with account of a possible twinning by merohedry. There are four possible variants of the orientation of twin domains $xyz, \bar{y}xz, yxz, xyz$ for the phase G_2 . They are related by twinning symmetry elements $m \parallel [001], 2 \perp [001], \bar{1}$. The lowest R_w were obtained

for the variant when domain orientations are linked by symmetry plane $m \parallel [001]$ and hkl and $\bar{k}h\bar{l}$ type reflections from different twin domains overlap. In this twinning variant the twin volume ratio for sample III was $V_1 : V_2 = 1.6 : 1$.

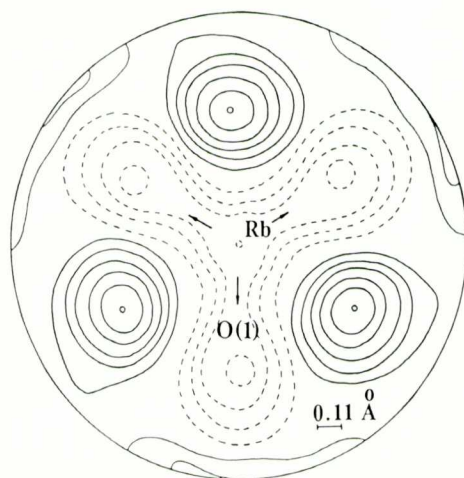


Fig. 2. Residual map in a plane xy through the Rb atom at 428 K. Twinned model. Harmonic approximation of thermal vibrations of Rb atom. Contours at $0.2 \text{ e}/\text{Å}^3$.

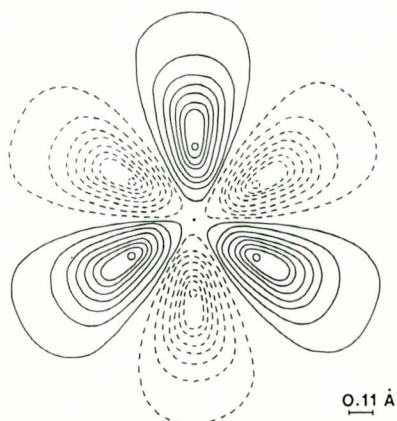


Fig. 3. Section by the xy plane of the difference PDF of the Rb atom at 428 K, which shows the deviations from a purely harmonic PDF and is calculated from the refined third-order anharmonic terms.

Like in the phase G_3 , in the case of phase G_2 the parameters of atomic thermal motion were refined for all the atoms except Li, in anharmonic approximation. The density distribution on difference density maps near the Rb atom site obtained after refinement of the harmonic thermal parameters is similar to the distribution in the G_3 phase shown in figure 2. After refinement of anharmonic thermal parameters of Rb atom we found that the parameters of C^{111} at 553 K, C^{111} and C^{112} at 583 K were physically meaningful. In the G_2 phase we obtained physically meaningful anharmonic parameters C^{111} , C^{113} , C^{133} , C^{123} for the O(2) atom which resulted in "clouds" of difference density of the probability of O(2) atom displacement from its equilibrium position in the plane perpendicular to the three-fold axis, in direct space, that correlates with the displacements of the O(2) atom upon the phase transition. The O(1) and Cr atoms do not exhibit physically meaningful deviation of their thermal vibrations from the harmonic law.

A remarkable anomalous scattering allowed us to establish in all the cases absolute configurations of the structures in each twin domain. If we denote the larger twin domain in sample I as xyz , the second twin domain will be $xy\bar{z}$; accordingly, sample II contains \bar{xyz} and $\bar{xy}z$ twin domains; sample III before the phase transition contains twin domains xyz and \bar{xyz} , after the transition to the G_2 phase $-\bar{yxz}$ and $xy\bar{z}$.

The final positional and thermal parameters of atoms of the $RbLiCrO_4$ structure in the G_3 and G_2 phases are listed in Table 2. Rb atom occupies 2(a) site (000); Li, Cr O(1) atoms occupy sites 2(b) (00z); O(2) atom occupies site 6(c) of the general position. For simplicity, Table 2 lists enantiomorphous modifications of all the samples converted to the xyz configuration of the larger twin domain of sample I. The structural data obtained for $RbLiCrO_4$ crystals evidence that they are isostructural with $KLiSO_4$ [8, 10, 11, 13].

DISCUSSION

Our structural study of $RbLiCrO_4$ crystals showed that the phase transition $G_3 \longrightarrow G_2$ is accompanied by a symmetry change from $P31c$ to $P6_3$. Upon the phase transition in pairs of layers forming the structure only one layer is transformed. The triangular bases of the tetrahedra of this layer are rotated through approximately 48° about the three-fold axis. The direction of the main axis of crystal symmetry is retained upon the phase transition and it remains parallel in all the domains before and after the phase transition. The main difference between the twin domains depends on the particular layer where the triangles formed by O(2) atoms are rotated.

Figure 4 shows a temperature dependence of the parameters of atomic

Table 2. Atomic parameters. $B(\text{\AA}^2)$ – equivalent isotropic thermal parameter calculated from the vibrational ellipsoid volume. C^{ijk} – the physically meaningful anharmonic parameters.

parameter	293 K	428 K	493 K	523 K	553 K	583 K
Rb B	1.850(8)	2.712(8)	3.33(1)	3.83(2)	4.03(2)	4.41(3)
C ¹¹¹	0.0045(7)	0.0094(9)	0.013(2)	0.020(4)	0.020(4)	0.024(4)
C ¹¹²	0	0	0	0	0	0.012(6)
Li z	0.182(1)	0.184(1)	0.183(2)	0.180(3)	0.180(4)	0.182(5)
B	2.6(2)	3.8(2)	4.3(3)	4.1(5)	4.4(5)	4.4(6)
Cr z	0.7951(1)	0.7940(1)	0.7931(2)	0.7925(3)	0.7920(3)	0.7917(4)
B	1.010(8)	1.481(8)	1.87(1)	2.12(2)	2.26(2)	2.46(3)
O(1) z	0.9731(4)	0.9721(5)	0.9706(8)	0.9678(9)	0.969(2)	0.970(2)
B	2.85(6)	4.44(7)	5.3(1)	5.8(2)	5.9(2)	6.7(3)
O(2) x	0.3864(5)	0.3922(5)	0.3951(7)	0.3973(9)	0.409(1)	0.401(2)
y	0.3490(5)	0.3537(4)	0.3567(7)	0.3613(9)	0.368(1)	0.365(1)
z	0.2387(4)	0.2372(3)	0.2357(5)	0.2337(7)	0.2345(8)	0.2349(9)
B	2.34(4)	3.32(4)	4.14(7)	5.2(1)	6.2(1)	6.0(2)
C ¹¹¹	0	0	0	0	0.010(2)	0.000(2)
C ¹¹³	0	0	0	0	0.04(1)	0.04(2)
C ¹³³	0	0	0	0	0.033(6)	0.034(7)
C ¹²³	0	0	0	0	0.027(9)	0.024(9)

thermal motion in RbLiCrO_4 . As compared with $T = 293$ K the thermal parameters of all atoms at 428 K increase proportionally to the changes of the absolute temperature. At 493 K and 523 K, close to the phase transition temperature $T_{\text{pt}} = 550$ K, the atomic thermal parameters of RbLiCrO_4 are increased, which may be a manifestation of the temperature dependence of the force constants near the phase transition point. However, even against the background of such an increase in other parameters, the parameters u_2^2 and u_3^2 of the O(2) atom increase quite noticeably. This O(2) atom is rotated about the three-fold axis passing through Cr, O(1), Li atoms during the phase transition. The anharmonic parameters of the O(2) atom obtained in the G_2 phase indicate softening of the effective potential of this atom in the plane perpendicular to the Cr-O(1)-Li line as well. To establish more fine features of the behaviour of thermal atomic parameters depending on the temperature in the above type structures additional neutron diffraction studies are desirable.

The author is indebted to Prof. V.I. Simonov for his constant attention to this work and helpful discussions, to Prof. K.S. Alexandrov for the supplied samples and to I.A. Verin for his assistance in data collection.

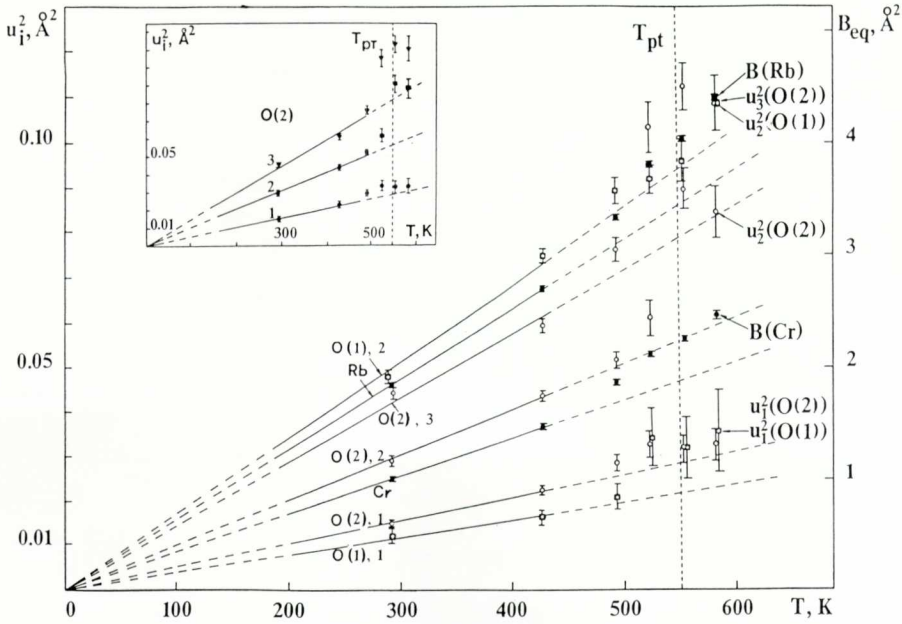


Fig. 4. Equivalent isotropic thermal parameter B_{eq} of Rb, Cr atoms and mean-square displacements u_i^2 of O(1), O(2) atoms as a function of temperature.

ABSTRACT

Crystal structure of $RbLiCrO_4$ crystals of G_3 (sp. gr. $P31c$) and G_2 (sp. gr. $P6_3$) phases has been determined from X-ray diffraction data at $T = 293, 428, 493, 523$ K (for the G_3 phase) and at $T = 553, 583$ K (for the G_2 phase). The $RbLiCrO_4$ crystals exhibit twinning by merohedry according to different twinning laws in the G_3 phase: $2 \parallel [001], m \perp [001], \bar{1}$; in the G_2 phase $m \parallel [001], 2 \perp [001], \bar{1}$. The analysis of reflection intensities with an account of anomalous scattering enabled us to determine unambiguously the twinning laws as well as absolute configurations of twin domains in the three samples studied. The structures were refined with allowance for anharmonic approximation of atomic thermal motion.

REFERENCES

1. KRUGLIC, A.I., MELNIKOVA, S.V., ALEXANDROV, K.S. and GRANKINA, V.A. *Fiz. Tverd. Tela*, 1990, v. 32, No. 10, p. 3029.
2. KRUGLIK, A.I., MELNIKOVA, S.V., TOLOCHKO, B.P., MAKAROVA, I.P. and ALEXANDROV, K.S. Preprint No 680F. Kirensky Institute of Physics, Siberian Department of the USSR Acad. Sci., Krasnoyarsk, 1991.
3. DONNAY, G. and DONNAY, J.D. *Canad Mineral.* 1974. v. 12, p. 422.
4. KLAPPER, H., HAHN, Th. and CHUNG, S.J. *Acta Cryst. B.* 1987. v. 43, N2, p. 147.
5. ZUCKER, U.H., PERENTHALER, E. and KUHS, W.F. et al. *J. Appl. Cryst.* 1983. v. 16. N3, p. 358.
6. *International tables for X-ray crystallography.* v. 4. Birmingham: Kynoch Press. 1974.
7. BECKER, P.J. and COPPENS, P. *Acta Cryst. A.* 1974. v. 30, N2, p. 129.
8. KARPPINEN, M., LUNDGREN, J.O. and LIMINGA, R. *Acta Cryst. C.* 1983. v. 39, N1, p. 34.
9. SIROTA, M.I. and MAXIMOV, B.A. *Kristallografiya*, 1984, v. 29, No 1, p. 34.
10. SCHULZ, H., ZUCKER, U. and FRECH, R. *Acta Cryst. B.* 1985, v. 41, N1, p. 21-26.
11. BHAKAY-TAMHANE, S., SEQUEIRA, A. and CHIDAMBARAM, R. *Acta Cryst. C.* 1984, v. 40, p. 1648-1651.
12. MURADYAN, L.A., SIROTA, M.I., MAKAROVA and I.P., SIMONOV, V.I. *Kristallografiya*, 1985, v. 30, p. 258-266.
13. ZHANG, P.L., YAN, Q.W. and BOUCHERLE, J.X. *Acta Cryst. C.* 1988, v. 44, N3, p. 592.