Crystal Structure of the Brownmillerite-Related Phase LaCaCUGaO₅

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A new compound, LaCaCuGaO₅, of the brownmillerite-type structure [$a = 16.022(3)$, $b = 5.4979(7)$, $c = 5.3366(9)$ Å] has been synthesized. The phase was investigated by means of X-ray powder diffraction and electron microscopy, together with energy-dispersive spectrometry (EDS) analysis. The structure was refined by the Rietveld method using the space group $Imcm$ (No. 74 in a non-standard setting) and a statistical distribution of the La and Ca atoms.

Recently, Vaughey et al.,[1] Cava et al.[2] and Dabrowski et al.[3] reported a new family of cuprate superconductors containing gallium, $Ln_{1-x}Ca_xSr_2Cu_2GaO_7$ (Ln = a lanthanide or Y). The perovskite-like structure of these compounds is closely related to that of $YBa_2Cu_3O_{7-\delta}$,[4] where one copper atom per unit cell is replaced by a gallium atom tetrahedrally coordinated to oxygen, so that an ordered distribution of two B-cations, copper and gallium, occurs.[1,5]

Synthesis and structure investigations of the brownmillerite-related compound, LaSrCuGaO₅, have also been published.[6–9] In this structure there are infinite CuO₂ sheets alternating with chains of gallium–oxygen tetrahedra. Results from a partial substitution of La by Sr have also been reported.[9] It was shown that solid solutions with high formal copper valence, $La_{0.8}Sr_{1.2}CuGaO_5$, can be prepared at low temperature in an oxidizing atmosphere. The $\rho(T)$ dependence found indicated a marked tendency towards metallic behaviour, but the substituted compound still remained non-superconducting.

The present paper describes the synthesis and structure of an analogous calcium compound, LaCaCuGaO₅.

Experimental

A polycrystalline sample of LaCaCuGaO₅ was synthesized by the solid-state reaction of La_2O_3, $CaCO_3$, CuO and Ga_2O_3 in appropriate ratios. The mixture was ground in an agate mortar, pressed into a pellet and heated in air at 1050°C for 50 h with one intermediate grinding.

X-Ray powder diffraction (XRD) investigations were carried out with Cu $K\alpha_1$ radiation ($\lambda = 1.540\,5981$ Å)

using a Guinier–Hägg focusing camera with subtraction geometry. Finely powdered silicon ($a = 5.430\,880$ Å at 25°C)[10] was used as internal standard. The films were evaluated by means of an automatic film scanner.[11] The unit-cell parameters were refined with the program PUDER.[12] Powder data for structure determination were collected on a Stoe STADI/P diffractometer with a rotating sample in the symmetric transmission mode. A germanium crystal monochromator and scintillation counter were used. Step intensities in the 2θ-range 10–95° were used in the refinement (step length $\Delta 2\theta = 0.02°$). Full-profile Rietveld refinement of the structural parameters was carried out with the program DBW3.2S.[13]

Three types of electron microscope were used for characterizing the sample: a JEOL 820 scanning electron microscope (SEM) with microanalysis equipment (LINK QX200) and two transmission electron microscopes, viz. JEOL 200CX and JEOL 2000FX. The latter is equipped with an energy-dispersive spectrometry (EDS) system (LINK QX200), with the detector in the high-angle (70°) position. For investigation in a transmission electron microscope (TEM), parts of the sample were crushed in butanol and the crystal fragments were placed on a metal grid covered with an amorphous holey carbon film. Simulations of high-resolution (HREM) images were made with the program SHRLI.[14]

The oxygen content was determined by iodometric titration of the copper ions, according to Graboy et al.[15]

Results

A polycrystalline sample of LaCaCuGaO₅ was found to be monophasic by X-ray powder diffraction. Energy-dispersive spectrometry (EDS) analysis carried out on the SEM confirmed the composition of the prepared compound. The average metal ratio La : Ca : Cu : Ga = 25.0(7) : 25.3(9) : 25.6(6) : 24.1(9) was obtained for 15

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measurements on 10 crystallites. The formal valence of the copper ions determined by iodometrical titration was shown to be 2.0. Therefore, LaCaCuGaO$_5$ is the correct formula for the phase, and the oxygen off-stoichiometry is zero.

The diffraction pattern of LaCaCuGaO$_5$ was indexed according to an I-centered orthorhombic unit cell with the parameters $a = 16.022(3)$, $b = 5.4979(7)$, $c = 5.3366(9)$ Å. The indexed pattern is listed in Table 1. Electron diffraction studies confirmed the space groups $Ima2$ or $Imcm$. Selected-area electron diffraction patterns of the [010], [001] and [011] zone directions are shown in Fig. 1. A weak streaking along a^* was frequently noticed in different zone directions, indicating that there could be some disorder of the structure.

To refine the structure of LaCaCuGaO$_5$ it is possible to use a few slightly different models, all of which result in very similar parameters. The model presented here, using the space group $Imcm$, has some advantages which will be discussed below. Crystallographic data of the Rietveld powder refinement and final R-values obtained for the parameters listed in Table 2 can be seen in Table 3. Observed and difference X-ray Rietveld patterns are shown in Fig. 2. Because of serial correlation, as indicated by Durbin–Watson statistics,[16] the standard deviations obtained in the least-squares refinements have been multiplied by a factor 2.0. Selected interatomic distances and angles are presented in Table 4.

The occupation parameter for the atoms in the perovskite A-position was set to $g = 0.5$La$ + 0.5$Ca, since the result of EDS analysis indicated equal amounts of La and Ca, in accordance with the initial composition. The isotropic thermal parameter of the split atom O3 is abnormally high. This may be related to the disorder (see below). The thermal parameters of light atoms have little physical significance in powder refinements, however.

The structure of LaCaCuGaO$_5$ is of the brownmillerite type[17] (Fig. 3a). It can be described as an anion-deficient perovskite structure $A_2BB'O_5$ ($A = $ La, Ca; $B = $ Cu; $B' = $ Ga), where one of the oxygen atoms per formula unit is missing compared to perovskite. The Ga atoms in the oxygen-deficient layers have a tetrahedral coordination.

Table 1. Observed and calculated d-values for the Guinier powder diffraction pattern of LaCaCuGaO$_5$.

N	h	k	l	d_{obs}	d_{calc}	$(I/I_0)_{obs}$	$(I/I_0)_{calc}$
	2	0	0	8.06	8.01	9.5	9.7
2	1	1	0	5.21	5.20	1.6	1.6
3	3	1	0	3.834	3.831	8.4	8.0
	0	1	1		3.829		
4	2	1	1	3.458	3.455	4.2	4.3
5	5	1	0	2.768	2.769	100.0	99.7
	4	1	1		2.768		
6	0	2	0	2.749	2.749	27.6	26.9
7	6	0	0	2.668	2.670	34.2	34.2
	0	0	2		2.668		
8	1	2	1	2.415	2.416	2.8	1.8
9	4	2	0	2.267	2.267	4.2	4.2
10	4	0	2	2.221	2.221	3.7	3.1
11	6	1	1	2.190	2.190	17.4	17.2
	3	1	2		2.190		
12	8	0	0	2.003	2.003	10.9	11.4
13	6	2	0	1.9141	1.9154	32.9	27.8
	0	2	2		1.9147		
14	6	0	2	1.8868	1.8875	4.5	3.5
15	2	2	2	1.8615	1.8622	3.3	2.9
16	3	3	0	1.7334	1.7334	3.9	3.7
	0	3	1		1.7333		
17	7	2	1	1.6704	1.6706	1.9	1.7
18	8	2	0	1.6185	1.6187	4.7	4.3
19	10	0	0	1.6018	1.6022	7.1	6.7
	8	0	2		1.6019		
20	5	3	0	1.5907	1.5909	14.4	13.5
	4	3	1		1.5907		
21	4	1	3	1.5586	1.5590	14.0	14.5
22	10	1	1	1.4781	1.4781	5.9	5.1
23	6	3	1	1.4540	1.4539	5.6	5.2
	3	3	2		1.4536		
24	6	1	3	1.4293	1.4295	2.4	2.4
25	10	2	0	1.3841	1.3843	8.9	8.5
	8	2	2		1.3840		
26	0	4	0	1.3743	1.3745	3.1	2.6
	10	0	2		1.3736		
27	5	3	2	1.3668	1.3664	1.1	1.1
28	2	4	0	1.3545	1.3547	1.1	1.1

[a] $(I/I_0)_{obs}$ and $(I/I_0)_{calc}$ are normalized integrated intensities of reflections from diffractometer data and theoretical calculations, respectively. All reflections with $(I/I_0)_{obs} < 1.0$ and $2\Theta_{obs} > 70°$ are omitted. The refined unit cell parameters are $a = 16.022(3)$, $b = 5.4979(7)$, $c = 5.3366(9)$ Å, space group $Imcm$, $M(20) = 58.3$.
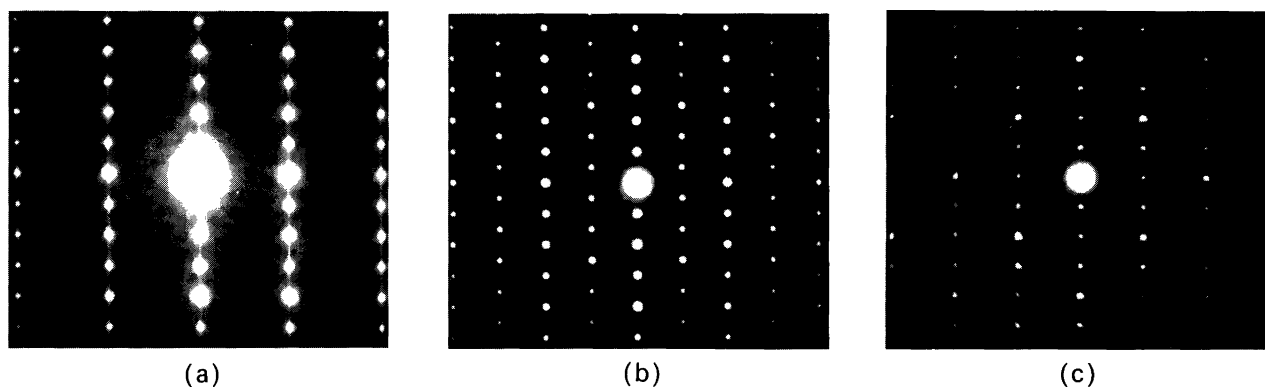

(a)   (b)   (c)

Fig. 1. Selected-area electron diffraction patterns of LaCaCuGaO$_5$ along [010] (a), [001] (b) and [011] (c) zone directions.
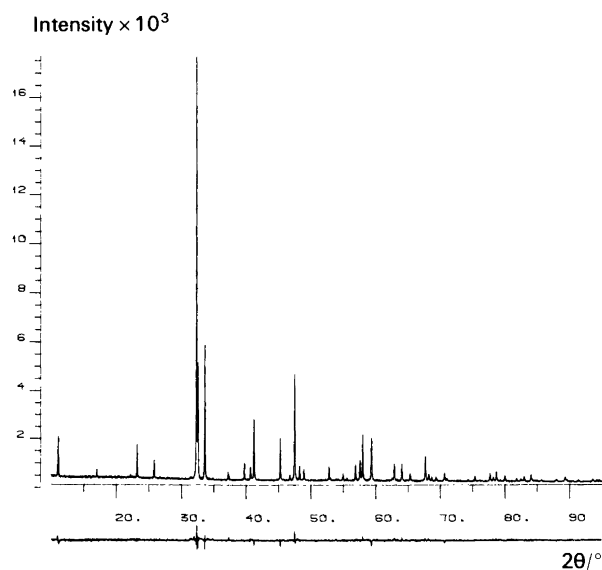
Intensity × 10³

2θ/°

Fig. 2. Observed X-ray powder diffraction pattern and (obs. − calc.) difference obtained after Rietveld refinement.

The chains of GaO_4 tetrahedra running along the c-axis are of two types (Fig. 3b) related by a mirror plane. The Cu atoms possess an octahedral oxygen coordination, forming infinite layers of (CuO_2) with the Cu–O1 distances equal to 1.92 Å. These planes are distorted because the copper–oxygen octahedra are strongly tilted. The atoms in the A-positions have an eight-fold oxygen coordination $(4 + 3 + 1)$. This open polyhedron can be closed into a
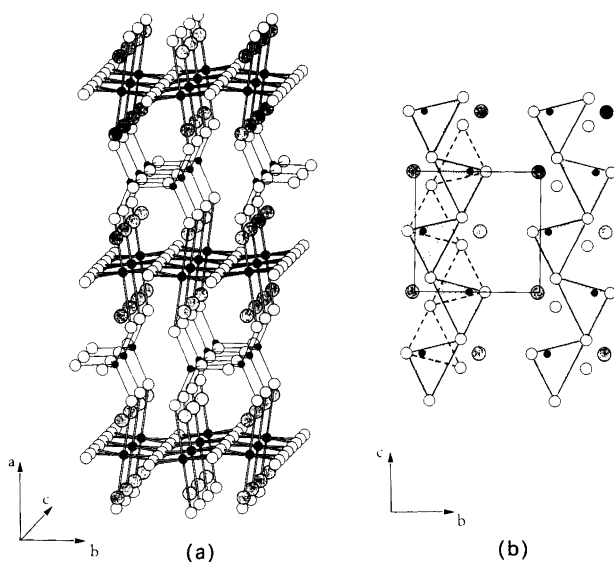

Fig. 3. Crystal structure of $LaCaCuGaO_5$ (a) and projection on the bc-plane (b). In (b) the two possible types of placement of chains of tetrahedra (related by a mirror plane) are indicated by full and broken lines (see text). The La/Ca atoms are shown as large grey spheres and the oxygen atoms as empty ones. Smaller black spheres with tetrahedral and octahedral coordinations are gallium and copper atoms, respectively.

Table 2. Positional and thermal parameters from the powder data Rietveld refinement of $LaCaCuGaO_5$.

Atom	Site	x	y	z	$B/Å^2$
M^a	$8h$	0.6069(2)	0.0178(8)	0	1.5(1)
Ga	$4e$	1/4	0.4358(15)	0	3.1(2)
Cu	$4b$	0	1/2	0	2.2(2)
O1	$8g$	0.490(2)	1/4	1/4	0.7(5)
O2	$8h$	0.1485(11)	0.565(4)	0	3.6(6)
$O3^b$	$8i$	1/4	0.133(7)	0.115(7)	5.7(11)

^{a} $g(M) = 0.5La + 0.5Ca$. ^{b} Split from special position $4e$ $(1/4, y, 0)$; $g(O3) = 0.5$.

Table 3. Summary of crystallographic data.

Formula	$LaCaCuGaO_5$
Space group (proposed)	$Imcm$ (No. 74)
$a/Å$	16.022(3)
$b/Å$	5.4979(7)
$c/Å$	5.3366(9)
Cell volume/$Å^3$	470.1
Z	4
No. of atoms in cell	36
Radiation, $\lambda/Å$	Cu $K\alpha_1$, 1.5405981
Diffractometer	Stoe STADI/P
Mode of refinement	Full profile
No. of atom sites	6
No. of free parameters	24
2θ range/°	10.0–95.0
Reflections used in refinement	133
R_p, R_{wp}, R_{Bragg}, R_F	0.045, 0.059, 0.065, 0.080
Goodness of fit	1.23

nine-coordinated one $(4 + 4 + 1)$ if the O2 atom at a distance of 3.25 Å also is included (Table 4).

An HREM image of $LaCaCuGaO_5$ along [010] is shown in Fig. 4. It was difficult to obtain acceptable HREM photographs because the microcrystallites were unstable under the focussed beam. In some parts of the crystallite one can discern a contrast difference between rows of dark spots, representing columns of the A-atoms, La and Ca. In other parts, however, these rows seem to have a more equal contrast, as shown by arrows in Fig. 4.

Table 4. Selected interatomic distances (in Å) and angles (in °).

M–O1^a	2.52(2) × 2	O2–Ga–O2	132.8(14)
M–O1	2.63(2) × 2	O2–Ga–O3	94.2(4) × 2
M–O2	2.39(2)		112.1(7) × 2
M–O2	2.759(5) × 2	O3–Ga–O3	99.7(11)
(M–O2	3.25(2))^b		
M–O3	2.51(2)		
Ga–O2	1.77(2) × 2		
Ga–O3	1.77(4) × 2	O1–Cu–O1	92.2(1) × 2
			87.8(1) × 2
Cu–O1	1.921(2) × 4	O1–Cu–O2	88.8(9) × 2
Cu–O2	2.41(2) × 2		91.2(9) × 2

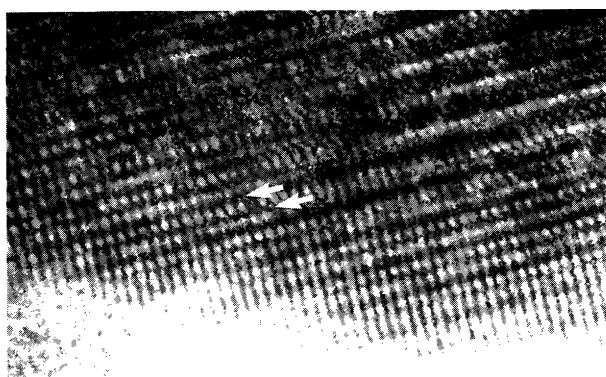^{a} $M = Ca/La$. ^{b} See text.

Fig. 4. HREM image of an LaCaCuGaO$_5$ crystallite in the [010] zone direction. The rows of dark spots of approximately equal contrast, corresponding to a statistical distribution of La and Ca atoms, are indicated by arrows.

Owing to the large difference in the atomic numbers ([57]La and [20]Ca) there should be a larger difference in contrast of the A-atoms in the HREM images if La and Ca were ordered over two sites in the structure. Apparently, a partial ordering of La and Ca atoms can take place to some extent (Fig. 4), but only thin edges of small crystallites are analysed in the HREM studies with a transmission electron microscope. X-Ray analysis, on the contrary, gives an average structure of the compound analysed, and it resulted here in a statistical distribution of those atoms.

In Fig. 5 it can be seen that a calculated image based on parameters from the Rietveld refinement agrees well with the observed one taken along the [011] direction.

Table 5. Structural parameters from Rietveld refinements for two possible models of LaCaCuGaO$_5$.[a]

Atom	Model III, *Imcm*	Model I, *I2cm*
0.5La + 0.5Ca	x	x
	y	y
	0	0.024(4)
Ga	1/4	1/4
	y	y
	0	0
Cu	0	0
	1/2	1/2
	0	0.018(6)
O1	x	x
	1/4	0.257(8)
	1/4	0.304(10)
O2	x	x
	y	y
	0	0.052(9)
O3	1/4	1/4
	y	y
	z	z

[a] In the centrosymmetric space group, *Icmc*, O3 must occupy the four-fold special position (1/4, y, 0), but it was split into an eight-fold one (1/4, y, z), thus having occupancy factor $g = 0.5$.
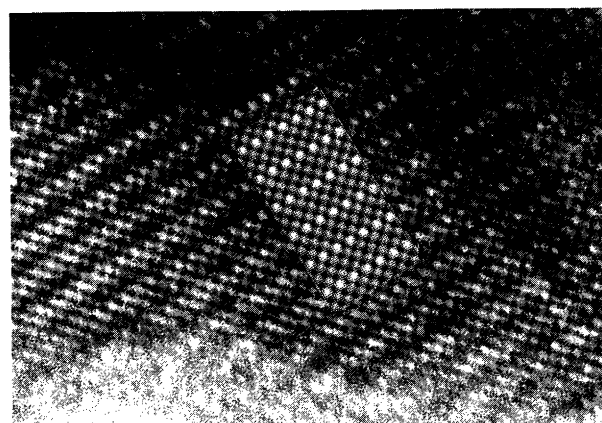

Fig. 5. HREM image of a LaCaCuGaO$_5$ crystallite in the [011] zone direction with simulated image inserted. Defocus value is -250 Å, crystal thickness is ca. 15 Å, $c_s = 1.2$ mm, aperture size corresponds to 0.40 Å^{-1}.

Simulated images of the two other possible structure models (see the following discussion) were approximately the same if a statistical distribution of La and Ca was assumed.

Discussion

As discussed in our previous article[9] concerning the structure and properties of the analogous compound, LaSrCuGaO$_5$, there were two slightly different models for describing that structure. One model (I), from a single-crystal determination by Vaughey *et al.*[6] with space group *Ima2*, has only one position for the La and Sr atoms. In the other model (II), with space group *I2cm*, obtained by X-ray powder data and electron microscopy by us,[9] it was possible to locate these atoms in two different sites. Both models were tried for the present X-ray Rietveld refinement of LaCaCuGaO$_5$, resulting in very similar structures and acceptable R-values ($R_p = 0.045$, $R_F = 0.075$ and 28 refined parameters for *Ima2*; $R_p = 0.043$, $R_F = 0.062$ and 33 refined parameters for *I2cm*). These refinements led to a statistical distribution of La and Ca atoms, and the HREM studies indicated the same. Therefore, there were no reasonable criteria for choosing the second model, in contrast to LaSrCuGaO$_5$. On the other hand, such a statistical distribution of the A-atoms is also compatible with the centrosymmetrical space group *Imcm* (III).

There is no exhaustive evidence for choosing between models I and III to describe the structure of LaCaCuGaO$_5$, but there are some reasons why we believe that the latter (Table 3) is better. One reason is that the refinement gave R-values of approximately the same magnitude but with a smaller number of parameters when the centrosymmetrical space group was used. Moreover, the resulting atom coordinates and temperature factors were the same (taking into account the standard deviations), except for the z-values, which in

space group *Ima*2 converged slowly and ended with large standard deviations. In Table 5 structural parameters obtained are compared for these two models.

Another reason for choosing model III is the more convincing metal–oxygen distances that it provides. In model I the deviations from the symmetrical oxygen positions (Table 5) led to doubtful Cu–O distances in the (CuO_2) sheets [1.79(7) Å × 2 and 2.05(7) Å × 2], while in model III those are necessarily equal owing to the symmetry (1.92 Å × 4). The Ga–O distances are also more appropriate (Table 4), since in model I the distance to one of the bridge oxygens in the tetrahedral chains is abnormally long, $d_{Ga\ O3} = 2.04(4)$ Å.

In model III it was necessary to split the O3 atoms over two slightly different positions. This can be explained by the two possible orientations of the Ga–O chains (Fig. 3b). A similar type of oxygen disordering has been found by neutron diffraction studies of the compounds $YSr_2CoCu_2O_7$[18] and $YSr_2GaCu_2O_7$.[5] As noted there, such a disorder is consistent with two alternative types of tetrahedral chains related by a mirror plane. Together with the statistical distribution of heavy cations, La and Ca, that type of oxygen disordering may also be the reason for the observed streaking in the electron diffraction patterns of $LaCaCuGaO_5$. The occurence of streaking along a^* supports this assumption.

As a final remark, we would like to mention that a partial substitution of calcium for lanthanum is possible with another synthesis technique (precipitation from nitrate solutions followed by sintering at 900°C in oxygen). A sample with the initial composition $La_{0.8}Ca_{1.2}CuGaO_5$ [$a = 15.99(1)$, $b = 5.4828(4)$, $c = 5.303(1)$ Å] has been analyzed in analytical TEM and gave approximately the same metal ratios.

Electrical properties of the prepared compounds are now under investigation and will be published later.

References

1. Vaughey, J. T., Thiel, J. P., Hasty, E. F., Groenke, D. A., Stern, C. L., Poeppelmeier, K. R., Dabrowski, B., Hinks, D. G. and Mitchell, A. W. *Chem. Mater. 3* (1991) 935.
2. Cava, R. J., Van Dover, R. B., Batlogg, B., Krajewski, J. J., Schneemeyer, L. F., Siegrist, T., Hessen, B., Chen, S. H., Peck, Jr., W. F. and Rupp, Jr., L. W. *Physica C 185-189* (1991) 180.
3. Dabrowski, B., Radaelli, P., Hinks, D. G., Mitchell, A. W., Vaughey, J. T., Groenke, D. A. and Poeppelmeier, K. R. *Physica C 193* (1992) 63.
4. Simon, A., Kohler, J., Borrman, H., Gegenheimer, B. and Kremer, R.. *J. Solid State Chem. 77* (1988) 200.
5. Roth, G., Adeldmann, P., Heger, G., Knitter, R. and Wolf, Th. *J. Phys. I 1* (1991) 721.
6. Vaughey, J. T., Wiley, J. B. and Poeppelmeier, K. R. *Z. Anorg. Allg. Chem. 598/599* (1991) 327.
7. Antipov, E. V., Kharlanov, A. L., Kopnin, E. M. and Kovba, L. M. *Report on 15th Congress International Union of Crystallography*, Bordeaux 1990, p. 325.
8. Kovba, L. M., Antipov, E. V., Kharlanov, A. L., Khasanova, N. R. and Kopnin, E. M. *Report on International Symposium MASHTEC'90*, Drezden 1990, Vol. 1, p. 73.
9. Kharlanov, A. L., Antipov, E. V., Bryntse, I., Luzikova, A. V. and Kovba, L. M. *Eur. J. Solid State Inorg. Chem. 29* (1992) 1041.
10. Hubbard, C. R., Swanson, H. E. and Mauer, F. A. *J. Appl. Crystallogr. 8* (1975) 45.
11. Johansson, K. E., Palm, T. and Werner, P.-E. *J. Phys. E 13* (1980) 1289.
12. Eriksson, L. Program PUDER (1991).
13. Wiles, D. B., Sakthivel, A. and Young, R. A. Program DBW3.2S (1987).
14. O'Keefe, M., Buseck, P. R. and Iijima, S. *Nature (London) 274* (1978) 322.
15. Graboy, I. G., Ilushin, A. S., Kaul, A. R., Metlin, Yu. G., Moshchalkov, B. B., Muttik, I. G., Nikanorova, I. A. and Samarin, N. A. *Solid State Phys. (USSR) 15* (1988) 3436.
16. Bérar, J.-F. and Lelann, P. *J. Appl. Crystallogr. 24* (1991) 1.
17. Bertaut, E. F., Blum, P. and Sagnieres, A. *Acta Crystallogr. 12* (1959) 149.
18. Huang, Q., Cava, R. J., Santoro, A., Krajewski, J. J. and Peck, W. F. *Physica C 193* (1992) 196.