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S. Kemmler-Sack and A. Ehmann

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16. Abstract

In the system $BaFe_{1-x}Ru_xO_{3-y}$, 3 phases, sepd. by immiscibility gaps, are present: an Fe-rich phase ($x = 0-0.75$) with hexagonal $BaTiO_3$ structure ($6H$; sequence $(hcc)_2$), a Ru-rich phase ($x = 0.9$) of hexagonal $4H$-type (sequence $(hc)_2$), and the pure Ru compd. $BaRuO_3$ with rhombohedral $9R$ structure (sequence $(hhc)_3$). By vibrational spectroscopic investigations in the $6H$ phase a transition from n-type semiconduction (Fe-rich O-deficient compds.) to good, metal-like conduction (Ru-rich compds. with complete O lattice) can be detected. The $4H$ and $9R$ stacking polytypes are good, metal-like conductors. The lattice parameters are given.

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THE BARIUM IRON RUTHENIUM OXIDE SYSTEM

S. Kemmler-Sack* and A. Ehmann
Institut für Anorganische Chemie der Universität Tübingen
Auf der Morgenstelle 18, D-7400 Tübingen, West Germany

Introduction

Stoichiometric $BaFeO_3$ can only be prepared at high oxygen
pressures; it crystallizes in the rhombohedral 12-layer type
(reaction rate $R\bar{3}m$ [1, 2]). An isotopic compound with a phase
breadth $BaFeO_{2.75-2.90}$ was similarly obtained under
pressurized oxygen by Zanne and Gleitzer [3]. Compounds with
deficient oxygen form at standard pressure: $BeFeO_{3-y}$. For
$y < 0.5$, perovskiet is produced with cubic, tetragonal,
monoclinic, or triclinic deformations, depending on the
conditions of formation, along with compounds with hexagonal
$BaTiO_3$ structure [4-9]. The latter are formed by heating a
stoichiometric mixture of $BaCO_3$ and Fe_2O_3, which has
previously been heated to 1100-1200°C, to temperatures between
650 and 850°C [7, 8]. The hexagonal $BaTiO_3$ type (6H; sequence
$(hcc)_2$) has a phase breadth of $BaFeO_{2.67-2.95}$, for which the
lattice constants decline with decreasing oxygen deficiency
[7]. According to neutron diffraction studies of 6H-$BaFeO_{2.79}$
[8], the majority of oxygen lattice defects are located in the
hexagonally packed layers ($BaO_{2.5}$ composition), while
stoichiometric $BaO_{2.835}$ is present in the cubically packed
layers; tetrahedral coordination could thereby be produced for a
part of the iron in the flatly connected double tetrahedrons
[8]. On the other hand, the corresponding Ru compound,
$BaRuO_3$, can be produced stoichiometrically at even standard
pressure; it crystallizes in a rhombohedral 9-layer structure
(9R: sequence $(hhc)_3$ [10]).

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*Author to whom correspondence should be addressed.
**Numbers in the margin indicate pagination in the foreign text.

Previously in the $BaFe_{1-x}Ru_xO_{3-y}$ system, a quaternary oxide which belongs to the 6H type, $Ba_3FeRu_2O_9$ (x = 0.667), could be formed [11]. Further studies showed that this reaction involves a member of an extended 6H phase (x = 0 to 0.75); in addition, a compound with hexagonal 4-layer structure (4H, sequence $(hc)_2$) exists for x = 0.9. The phase <u>/367</u> relationships and property variations in the $BaFe_{1-x}Ru_xO_{3-y}$ series are given.

Experimental Part

Initial products were $BaCO_3$ (p.A.; Merck), Fe_2O_3 (20 m^2/g of $Fe(CO)_5$; BASF), and Ru (99.97%; Heraeus). Sintered alumina, Degussit Al 23, served as crucible material.

Concentrations were fixed at 22.2°C with n-octane as sealing fluid.

To produce radiographs (Cu Kα-radiation), Philips Corporation used a recording goniometric counter tube. The IR (infrared) spectra (KBr compacts; 4000-250 cm^{-1} range) were recorded with a Beckman spectrograph IR 20A, and the FIR (far infrared) spectra (polyethylene compacts, 650-50 cm^{-1}) with a Fourier device from the company Bruker IFS 114c. Raman spectra could not be obtained from the black compounds.

To determine the oxidation level, about 150 mg of the substance under a CO_2 stream in a closed apparatus were exposed to concentrated HCl (p.A.), the resulting Cl_2 was collected in an ice-cooled KI solution, and the formed I_2 was titrated with 0.1 n $Na_2S_2O_3$ solution with intensity as an indicator. A gravimetric determination of Ba as $BaSO_4$ was subsequently performed.

Production and Structure

To make the exclusively black preparations of the $BaFe_{1-x}Ru_xO_{3-y}$ system, the mixture of $BaCO_3$, Fe_2O_3, and Ru was carefully pulverized in an agate mortar, heated in air inside a corundum crucible, and finely repulverized one or two days later; the reaction process was monitored radiographically. On the Fe-rich side ($x \leq 0.2$), heating at 900-1100°C for two to three days followed by heating at lower temperatures (700-800°C; two to ten days) was shown to be effective for producing the 6H phases[1] of interest, while the materials richer in Ru ($x = 0.333$ to 0.75) were heated at 800-900°C for a full 6 days and at 1000-1100°C for six to ten days. Experiments for the example where $x = 0.667$ showed that longer heating at low temperatures (1000°C), as well as briefer heating at higher temperatures (1300°C), does not affect purity, cell dimensions, or oxygen content. However, a preparation richer in Fe ($x = 0.45$) was similarly homogeneous after heating at 1300°C for three days but showed a greater oxygen deficiency ($y = 0.125$; average oxidation level +3.75 in comparison to $y = 0.06$ after heating at 1000°C), whereby the lattice constants increased to $a = 5.73_3$ angstroms and $c = 14.1_0$ angstroms.

In the Ru-rich range ($x = 0.8$ to 1.0), after six to eight repetitions of two-day heating to 1300°C, another compound with 4H structure, whose isolation was achieved in material with $x = 0.9$ after a total of 7×2 days at 1300°C, formed beside the member of the 6H phase richest in Ru, $BaRuO_3$. On the other hand, counting-tube recordings of preparations with lower Ru levels ($x = 0.89$; 0.88) always show weak indications of the strongest 6H reflexes, and those of preparations with higher Ru levels ($x = 0.92$; 0.95) always weakly show the most intensive 9R lines of $BaRuO_3$.

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[1] No tests were conducted to produce compounds with cubic, tetragonal, or monoclinic perovskite structure by heating longer at lower temperatures.

According to radiographic studies, preparations with x = 0 to 0.75, 0.9, and 1.0 are homogeneous. Lattice constants, analysis data, and concentration values are given in Table I.

For x = 0 to 0.75, compounds in the 6H structure crystallize. The cell dimensions for x = 0 are approximately equal to the listed values of Mori [7] for about the same

TABLE I

Lattice Constants (angstroms),[a] Average Oxydation Level, Barium Content and Concentration Values in the System $BaFe_{1-x}Ru_xO_{3-y}$

x	a	c	Average Oxidation Level	Ba (%)		S (g/cm³)	
				meas.	calc.	meas.	calc.
0	5.68_3	14.0_2	+3.55	57.9	57.81^b	—	6.03_6^b
0.01	5.68_6	14.0_3	+3.48	57.6	57.83^b	—	6.01_6^b
0.05	5.69_7	14.0_3	+3.57	57.7	57.22^b	5.8_3	6.05_6^b
0.1	5.69_6	14.0_3	+3.61	57.0	56.61^b	—	6.11_6^b
0.2	5.70_4	14.0_6	+3.75	55.4	55.33^b	—	6.24_2^b
0.333	5.72_4	14.0_6	+3.85	53.7	53.85^b	6.1_3	6.35_6^b
0.45	5.72_4	14.0_7	+3.88	52.6	52.51	6.2_4	6.52_7
0.5	5.73_2	14.0_7	+3.98	51.9	52.06	—	6.56_5
0.667(11)	5.72_6	14.0_6	+4.01	50.5	50.62	6.3_9	6.77_1
0.75	5.72_4	14.0_7	+4.04	50.0	49.92	6.4_9	6.86_5
0.9	5.73_4	9.51_0	[c]	[c]	48.72	6.6_7	6.91_4

[a] ±0.002 (a); ±0.005 (c).

[b] calculated with consideration of experimentally determined oxygen deficiency.

[c] insoluble in mineral acids.

oxidation level. As x increases, a increases at first and then progresses through a flat maximum for x approximately equal to 0.5; however, the c measurements do not change much. The average oxidation level of iron and ruthenium, which must amount to +4.00 for a completely filled oxygen lattice ($BaFe_{1-x}Ru_xO_3$), falls below this value on the Fe-rich

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side; i.e., there is an oxygen deficiency. With increasing x, the average oxidation number rises, and consequently the oxygen content increases; with +3.98 for x = 0.5, the limiting value of +4.00, which is maintained up to x = 0.75, is practically reached. Pycnometric densities determined in the 6H region lie in the range of error of the values calculated for 6 $BaFe_{1-x}Ru_xO_{3-y}$ formular units.

The counting-tube recording of x = 0.9 is subject to complete, hexagonal labeling with a = 5.73_4 angstroms and c = 9.51_0 angstroms (see the labeling in Table II). A 4-layer structure results from the magnitude of c: for 2.38 angstroms the average distance between layers, L = c/4, lies in the normal range (see, for example, [12]). For the configuration of the densely packed barium-oxygen layers, there is only one possibility ($(hc)_2$; reaction rate $P6_3/mmc$ [13]). Thus, for the first time, isotypy is to be assumed for the high temperature modification of the localized 4H type [14] of $BaMnO_3$. With respect to the Fe:Ru proportions, as well as to the oxygen level, there could be no phase breadth, since, on the one hand, the 4H lattice constants determined for the two-phase products lie within the range of error limits for the listed values, and, on the other hand, the thermal treatment (open air quenching from 1300°C to room temperature; oven cooling within one day to 200°C as well as 3-day heating to 800°C and 7-day to 600°C) has no measurable effect. The pycnometric densities are close to the value calculated for 4 formular units.

Pure Ru bonding can acquire no recognizable Fe components. For a = 5.75_0 angstroms and c = 21.6_0 angstroms, lattice constants defined in the two-phase, Fe-poorer products correspond to the values listed for $BaRuO_3$ (a = 5.75 angstroms and c = 21.60 angstroms [10]).

TABLE II

X-ray interference of $BaGe_{0.1}Ru_{0.9}O_3$ ($x = 0.9$);
Counter tube recording with CuK-alpha radiation;
Hexagonal: $\underline{a} = 5.734 \pm 0.002$ angstroms; $\underline{c} = 9.510 \pm 0.005$ angstroms

Int[a]	$\sin^2\theta \times 10^4$ meas.	$\sin^2\theta \times 10^4$ calc.	hkl	Int[a]	$\sin^2\theta \times 10^4$ meas.	$\sin^2\theta \times 10^4$ calc.	hkl
s	241	241 ā	100	m	2888	2887 α₁	220
ss	307	307 ā	101	m − s	2901	2902 α₂	
st	503	504 ā	102	ssss	3082	3083 α₁	116
ssss	590	591 ā	003	ssss	3099	3099 α₂	
sst	722	723 ā	110	m	3324	3324 α₁	215/206
st	832	832 ā	103	m − s	3341	3341 α₂	
sss	1030	1030 ā	201	s	3391	3390 α₁	312
m − s	1050	1050 α₁	004	ss	3409	3407 α₂	
s	1056	1055 α₂		m − s	3718	3718 α₁	313
st	1225	1225 α₁	202	s	3735	3737 α₂	
m − st	1231	1231 α₂		sss	3937	3936 α₁	117
m	1291	1290 α₁	104			3937 α₁	224
m − s	1297	1297 α₂		ssss	3959	3956 α₂	117/224
m − st	1553	1553 α₁	203	m − s	4046	4046 α₁	216
m	1561	1561 α₂		s	4065	4066 α₂	
ssss	1686	1687 ā	210	s	4112	4112 α₁	402
ssss	1771	1771 α₁	114	ss	4132	4132 α₂	
ssss	1781	1780 α₂		ss	4176	4177 α₁	314/207
m	1883	1881 α₁	105	m	4198	4198 α₂	314/207
m − s	1891	1890 α₂				4198 α₁	008
m	1947	1947 α₁	212	m − s	4220	4219 α₂	008
m − s	1956	1956 α₂		s	4441	4439 α₁	108
m − s	2011	2012 α₁	204			4440 α₁	403
s	2020	2022 α₂		ss	4462	4461 α₂	108
m − st	2167	2165 α₁	300			4462 α₂	403
m	2177	2176 α₂		s	4766	4768 α₁	315
m − st	2275	2275 α₁	213	ss	4791	4792 α₂	
m	2286	2286 α₂		s − ss	4833	4834 α₁	322
ssss	2360	2362 α₁	115/006	ss	4857	4858 α₂	
ssss	2374	2373 α₂	006	ss	4898	4899 α₁	404/217
		2374 α₂	115	m − s	4921	4929 α₁	118
m	2603	2602 α₁	205/106			4923 α₂	217
m − s	2615	2615 α₂				4924 α₂	404
m − s	2735	2734 α₁	214	s	4944	4945 α₂	118
s	2748	2747 α₂		m − s	5054	5053 α₁	410
				s	5077	5978 α₂	

[a] st = strong; m = medium; s = weak; sst = very strong; ss = very weak, etc.

Vibrational Spectroscopic Research

A differentiation between metal-like, conductive, oxidic solids and semiconductors or insulators can be made with vibrational spectroscopic methods, since the former group shows a continuous absorption throughout the IR while the second group

shows discrete oscillations [15-20]; as expected, it absorbs throughout the IR [20]. In contrast, the pure Fe-phase, $6H-BaFeO_{3-y}$, shows semiconductivity of n-type [4]. As indicated by Diagram 1, the required discrete oscillations for $6H-BaFeO_{2.775}$ (x = 0) appear in the IR.

Diagram 1 shows the IR spectra of some bonds of the $BaFe_{1-x}Ru_xO_{3-y}$ system. For the Ru-rich phase (x = 0.9), a continuous absorption is observed--analagous to $BaRuO_3$-- indicative in both cases of conductivity similar to that of a metal.

In the 6H range (x = 0 to 0.75), striking differences can be seen as a function of x in the IR spectra: starting with the pure Fe bond, the spectra show clearly separated bands up to x = 0.33. The structuring already regresses for x = 0.5; for x = 0.667, its presence is only suggested; and for x = 0.75, its disappearance is virtually complete. Thus the transition from a semiconductor (x = 0) to a metal-like conductor (x = 0.75) is shown by the spectra. In comparison, a systematic progression of the band positions with respect to x cannot be established (see Table III).

Moreover, it is noteworthy that no bands appear in the higher frequency range for bonds with oxygen deficiencies (x $<$ 0.5). In the presence of FeO_4 tetrahedrons, which are discussed by Jacobson for $6H-BaFeO_{2.79}$ in the case of an ordered distribution of defects [8], their highest frequency IR-active oscillation would be expected at about 700-800 cm^{-1} [23]--similar to that of MO_4 tetrahedrons in II-IV and I-II-V spinels.

A factor group analysis is necessary for the band configuration on the Fe-rich side. Assuming a statistical distribution of Fe and Ru, as well as oxygen and defect <u>/371</u> sites (reaction rate $P6_3/mmc$: Ba(1) in 2b, BA(2) in 4f;
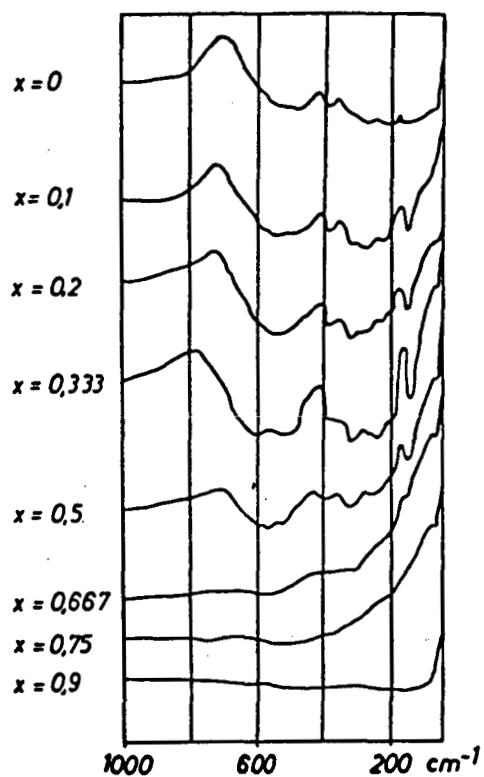
DIAGRAM 1

IR Spectra

TABLE III: IR Spectra[a]; Band Position (cm^{-1})

x =													
0	640sh		560st		480st	440sh	385st	330sh	275st	215st,b		140st,b	80sh
0,1	660sh	600sh		530st	480sh	440sh	385st	320st	285st	220st		160st	90sh
0,2	660sh	600sh		545st	485sh	440sh	385st	320st	275sh	230sh	200sh	160st	80sh
0,333	660sh	610st		520st	460sh		375st	320st	265sh	240st	200sh	150st	80sh
0,5	660sh	600sh	570st	525st	460sh		390st	320st		240sh,b	200sh	150st	80sh

[a] sh = shoulder; st = strong; b = breadth

Fe and Ru in 2a and 4f; 0 and ☐ in 6h and 12k), it offers, for k = 0, the irreducible preparations [24]

$$\Gamma_{tot} = 5A_{1g} + 2A_{2g} + 6B_{1g}$$
$$+ B_{2g} + 6E_{1g} + 8E_{2g} + A_{1u} + 7A_{2u}$$
$$+ 2B_{1u} + 6B_{2u} + 9E_{1u} + 7E_{2u}$$

and, after deduction of Ba translations, as well as the acoustic branch,

$$(A_{1g} + 2B_{1g} + E_{1g} + 2E_{2g} + 2A_{2u} + B_{2u} + 2E_{1u} + E_{2u})$$

$$(B_{1g} + E_{2g} + A_{2u} + E_{1u})$$

the following oscillations within the framework of Fe- and Ru-oxygen octahedrons:

$$\Gamma_{Octoh.Skelet.} = 4A_{1g} + 2A_{2g} + 3B_{1g}$$
$$+ B_{2g} + 5E_{1g} + 5E_{2g} + A_{1u} + 4A_{2u} + 2B_{1u}$$
$$+ 5B_{2u} + 6E_{1u} + 6E_{2u}$$

Thus 10 IR-active oscillations are expected within the octahedral framework.

Given a lack of couplings, separation of frequencies of the octahedral framework from the barium translations can be undertaken, since the latter are always found as characteristic oscillations in a similar frequency range (100-150 cm^{-1} [25]). Spectra of the Fe-rich bonds show a relatively intensive band in this range at approximately 150 cm^{-1} next to a weaker shoulder at approximately 90 cm^{-1}. For x = 0.1 to 0.333, two further, distinctly separated band groups (range 180-410 cm^{-1} and 430-660 cm^{-1}) are adjoined here, and these could be coordinated with the ranges of the IR-active, asymmetric deforming and stretching vibrations. Accordingly, nine to ten of the ten oscillations predicted by the factor group analysis would be

observable (Table III). Above all, the question remains whether the intensive band at approximately 150 cm^{-1} actually corresponds to a pure translation of barium. The observed structuring in the low-frequency region also could represent the result of couplings between translations and energy-poor framework vibrations of the same type. If this is the case, an increase of couplings with decreasing x may be inferred from the separation around approximately 180 cm^{-1} which becomes less and less distinct with increasing Fe content ($x \leq 0.33$).

Discussion

Among the applied reaction conditions in the $BaFe_{1-x}Ru_xO_{3-y}$ system, there are three hexagonal perovskite stack variants of differing sequence, each separated from the others by two-phase regions:

x = 0 to 0.75:	6H;	sequence $(hcc)_2$;
		33.3% h-bonding,
x = 0.9:	4H;	sequence $(hc)_2$;
		50% h-bonding,
x = 1.0:	9R;	sequence $(hhc)_3$;
		66.7% h-bonding.

With rising Ru levels, the proportion of h-packed layers per sequence increases. In the same direction, the average layer separation L increases from about 2.35 angstroms (6H) through 2.38 angstroms (4H) to 2.40 angstroms (9R). The increase of L results from the fact that each h-stacking implies face-coupled linkage of the octahedrons, which leads to a shorter separation between the central metal ions in comparison to corner-coupled linkage (for c-stacking). The cations attempt to avoid this electrostatically unfavorable configuration (3rd Pauling rule) by moving away from the octahedral centers, thus increasing the separation distance, so that a growing h-proportion is

accompanied by lattice extension. Even systems with only one transition metal (e.g. $BaMnO_{3-7}$ [26] and $Ba_{1-x}Sr_xMnO_{3-y}$ [27]) show a similar process.

Since the stacking sequences with large h-proportions first appear in the $BaFe_{1-x}Ru_xO_{3-y}$ system with high Ru levels, in <u>/372</u> which case a metal-like conductivity is already present, there is the impression that the collective, electrostatically unfavorable h-bonding is additionally stabilized by electron delocalization. Apparently only precious metal electrons can participate in the metal-like conductivity--as in many other polynary oxides with precious metal--and 3d ions [19]. In contrast, the pure Fe-phase of 6H-type belongs to the semiconductors. Semiconductivity is maintained during insertion of smaller Ru proportions up to x = approximately 0.333. An oxygen deficiency is always present, and consequently the possibility of n-conductivity is given. After insertion of about 50% Ru, the disappearance of the oxygen deficiency is practically complete. The observable changes in the IR spectra opposite x = 0.333 can be explained by the appearance of a second, metal-like conductivity mechanism which predominates over the first type, i.e., semiconductivity, and whose proportion rises strongly to x = 0.75. With this composition, modification of the band structure within the 6H phase corresponding to x = approximately 0.5 appears to be finished; further insertion of ruthenium is avoided upon formation of a new structure (4H). The breakdown of the 6H structure for x < 0.75 could be explained by the already large number of conducting electrons supplied by the ruthenium which is no longer suitable for the stacking sequence with only 33.3% h-coupling. A relationship between the formed crystal structure and the available number of conducting electrons would consequently be expected. However, only further research can offer proof of this.

Acknowledgements

REFERENCES

1. Y. Takeda, M. Shimada, F. Kanamura, u. M. Koizuma, *J. Solid State Chem.* **7**, 229 (1973).

2. M. Shimada, Y. Takeda, H. Taguchi, F. Kanamura, u. M. Koizuma, *J. Cryst. Growth* **29**, 75 (1975).

3. M. Zanne u. C. Gleitzer, *Bull. Soc. Chim. Fr.*, 1567 (1971).

4. J. B. MacChesney, J. F. Potter, R. C. Sherwood, u. H. J. Williams, *J. Chem. Phys.* **43**, 3317 (1965).

5. P. K. Gallagher, J. B. MacChesney, u. D. N. E. Buchanan, *J. Chem. Phys.* **43**, 516 (1965).

6. T. Negas u. R. S. Roth, *J. Res. Nat. Bur. Stand. Sect. A* **73**, 425 (1969).

7. S. Mori, *J. Phys. Soc. Japan* **28**, 44 (1970).

8. A. J. Jacobson, *Acta Crystallogr. Sect. B* **32**, 1087 (1976).

9. J. L. Hutchison u. A. J. Jacobson, *J. Solid State Chem.* **20**, 417 (1977).

10. P. C. Donohue, L. Katz, u. R. Ward, *Inorg. Chem.* **4**, 306 (1965).

11. U. Treiber, S. Kemmler-Sack, u. A. Ehmann, *Z. Anorg. Allg. Chem.* **487**, 189 (1982).

12. S. Kemmler-Sack u. M. Herrmann, *Z. Anorg. Allg. Chem.* **480**, 171 (1981).

13. "International Tables for X-Ray Crystallography," Vol. II, p. 347, Kynoch Press, Birmingham (1972).

14. A. Hardy, *Bull. Soc. Chim. Fr.*, 1329 (1961).

15. C. A. Wert u. R. M. Thomson, "Physics of Solids," Chap. 10, McGraw–Hill, New York (1964).

16. J. Gopalakrishnan, G. Colsmann, u. B. Reuter, *Z. Anorg. Allg. Chem.* **424**, 155 (1976).

17. L. Schütte, G. Colsmann, u. B. Reuter, *J. Solid State Chem.* **27**, 227 (1976).

18. V. B. Lazarev u. I. S. Shaplygin, *Russ. J. Inorg. Chem.* **275**, 1769 (1980).

19. V. B. Lazarev u. I. S. Shaplygin, *Russ. J. Inorg. Chem.* **23**, 163 (1978).

20. H.-U. Schaller u. S. Kemmler-Sack, *Z. Anorg. Allg. Chem.* **473**, 178 (1981).

21. A. Callaghan, C. W. Moeller, u. R. Ward, *Inorg. Chem.* **5**, 1572 (1966).

22. T. C. Gibb, R. Greatrex, u. N. N. Greenwood, *J. Chem. Soc. Dalton Trans.* **1973**, 1253.

23. J. Preudhomme u. P. Tarte, *Spectrochim. Acta Part A* **28**, 69 (1972).

24. D. H. Adams u. D. C. Newton, "Tables for Factor Group and Point Group Analysis," Beckman RIIC Ltd., Croydon, England (1970).

25. A. Fadini, I. Jooss, S. Kemmler-Sack, G. Rauser, H.-J. Rother, E. Schillinger, H.-J. Schittenhelm, u. U. Treiber, *Z. Anorg. Allg. Chem.* **439**, 35 (1978).

26. T. Negas u. R. S. Roth, *J. Solid State Chem.* **3**, 323 (1971).

27. T. Negas, *J. Solid State Chem.* **6**, 136 (1973).