JOURNAL OF SOLID STATE CHEMISTRY 52, 156–162 (1984)

Preparatory and X-Ray Diffraction Studies of the $SrCl_2$–SrI_2, $EuCl_2$–EuI_2, and $EuBr_2$–EuI_2 Systems[1]

EWA K. HODOROWICZ,[2] STANISLAW A. HODOROWICZ,[2]
AND HARRY A. EICK[3]

Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824

Received September 7, 1983; in revised form November 30, 1983

Preparatory and crystallographic studies of the $SrCl_2$–SrI_2, $EuCl_2$–EuI_2, and $EuBr_2$–EuI_2 systems over the full composition range are described. The $SrCl_2$–SrI_2 and $EuCl_2$–EuI_2 systems are similar with only limited solid solution regions and, at the 1 : 1 anion composition, pure EuClI and SrClI phases. The $EuBr_2$–EuI_2 system exhibits seven distinct regions: for $EuBr_{2-x}I_x$, when $0 \leq x \leq 0.2$, a $SrBr_2$-type solid solution region; when $0.4 \leq x \leq 1.2$, a $PbCl_2$-type solid solution region; for $x = 1.6$ a monoclinic phase with a basic structural arrangement close to that of the monoclinic and orthorhombic modifications of EuI_2, and when $1.8 \leq x \leq 2.0$ an orthorhombic EuI_2-type solid solution region. Two-phase regions separate these four structure types. The $EuBr_{0.4}I_{1.6}$($Eu_5Br_2I_8$) phase appears to be metastable. All three MXI phases (X = Cl, Br) exhibit $PbCl_2$-type anion-ordered structures, as was expected from high pressure studies of the parent phases.

Introduction

The crystal structures of strontium and europium(II) halides are well-characterized at normal temperatures and pressures (*1*, *2*), and are as follows: $SrCl_2$ (CaF_2-type), $SrBr_2$ and $EuBr_2$ ($SrBr_2$-type), SrI_2 (SrI_2-type), $EuCl_2$ ($PbCl_2$-type), and EuI_2 (SrI_2- and *m*-EuI_2-types). Under high pressure, both strontium chloride and europium dibromide transform to the more dense $PbCl_2$-type structure (*3*). The diiodides of these elements undergo a high pressure transition to a $PbCl_2$-type structure whose lattice parameters indicate an unusually large amount of covalent character; SrI_2 undergoes a second transition to an unknown structure (*4*).

Previous studies of mixed halide systems (*5–7*) have indicated that substitution of a different sized anion into a crystal lattice has the effect of creating an internal pressure and yielding over a limited composition range the high pressure modification, the more dense anion-ordered $PbCl_2$-type structure. Thus the MCl_2–MI_2 systems, for M = Sr and Eu, would be expected to behave similarly and to exhibit near their midpoint a single phase anion-ordered $PbCl_2$-type structure, probably existing over a limited composition range, and separated from the parent phases by a two-phase region of unknown size. Although the diiodides transform under pressure into an un-

---

[1] A preliminary report of this work was presented at the 16th Rare Earth Research Conference, Tallahassee, Florida 1983.

[2] On leave from Department of Chemistry, Jagiellonian University, Poland.

[3] To whom correspondence should be addressed.

0022-4596/84 $3.00

usual variant of the $PbCl_2$-type structure (*4*), studies of the $SrBr_2$–SrI_2 (*6*) and $PbBr_2$–PbI_2 (*8*) systems indicated only the expected $PbCl_2$-type phase with surrounding two-phase regions. However, the anion occupancy is random in the former and ordered in the latter. In view of this behavioral difference and with the hope of getting a better understanding of the ordering phenomenon, we undertook a detailed study of the $EuBr_2$–EuI_2 system and cursory studies of the MCl_2–MI_2 systems for M = Sr and Eu. The results of these studies are reported here.

Experimental

The analytical grade reactants $SrCl_2$ and SrI_2 (Cerac, Inc., Milwaukee, Wisc.) were heated at 400°C under vacuum before use. The europium dihalides were prepared from the oxide by the method of Taylor and Carter (*9*) with, in the case of the chloride, subsequent reduction by dried ultrapure hydrogen. The X-ray powder diffraction patterns of all reactants indicated them to be pure.

Sample manipulations were performed in a glove box in which the recirculated argon atmosphere was purged of water [$Mg(ClO_4)_2$, molecular sieves, and phosphorus pentoxide].

The desired anion compositions were obtained by mixing appropriate ratios of MX_2 (X = Cl or Br) and MI_2. The composition parameter x was varied in steps of 0.10. The reactants were ground intimately in an agate mortar, transferred to quartz ampoules which were evacuated and sealed, and heated to temperatures about 50°C above the melting points of both reactants. All specimens were cooled at a constant rate of 15°C/hr.

Reaction products were subjected to X-ray powder diffraction analysis as described previously (*5–7*). Platinum powder (a = 3.9237(3) Å at t = 24 ± 2°C) was employed as internal standard; lattice parameters were determined by a linear regression program written locally.

Quantitative intensity data were obtained with a Siemens X-ray diffractometer with Ni-filtered Cu$K\alpha$ radiation. Samples were prepared by sifting the specimen through a 325-mesh screen onto a glass slide coated with paraffin oil. Calculated intensities were obtained with the program ANIFAC (*10*). Scattering factors, including the appropriate dispersion correction terms, were taken from the International Tables (*11*). Because of the geometry of the diffractometer an absorption factor was not included in the calculations.

Results and Discussion

The structure types and lattice parameters for the various compositions of the $SrCl_2$–SrI_2 and $EuCl_2$–EuI_2 systems are summarized in Table I and an overview is presented in Fig. 1. The cell dimensions of our reactants agree well with literature values. In practice, in both systems investigated, there is no solubility near the end members, $SrCl_2$ and $EuCl_2$ on one side, and SrI_2 and EuI_2 on the other, respectively. At the 1 : 1 composition only pure $PbCl_2$-type $MClI$ (M = Sr and Eu) phases are observed. The lattice parameters of these phases show only limited solubility in either

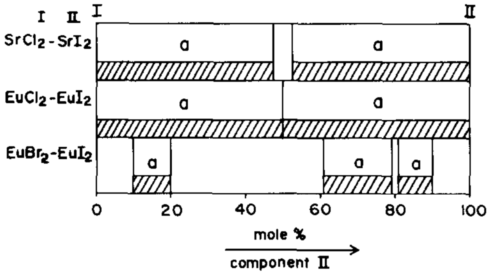

FIG. 1. Phase relationships in some MX_2–MI_2 systems. The clear areas represent solid solution regions and the hashed areas (labeled "a") represent two-phase regions.

TABLE I

CRYSTALLOGRAPHIC DATA FOR $SrCl_2$–SrI_2, $EuCl_2$–EuI_2, and $EuBr_2$–EuI_2 SYSTEMS

Composition x in $MA_{2-x}I_x$	Compound[a]	a (Å)	b (Å)	c (Å)	β (deg)	Comment[b]	Reference[c]
0.0	$SrCl_2$	6.976(7)					(*12*)
		6.979(2)				*Fm*3*m*	(*13*)
		6.974(6)					(*14*)
		6.975(2)					
0.10	$SrCl_2$	6.976(1)				Two-phase	
0.90	SrClI	9.436(1)	8.231(4)	4.735(3)		Two-phase	
1.00	SrClI	9.458(2)	8.248(1)	4.738(1)		*Pbnm*	
1.10	SrClI	9.466(4)	8.248(4)	4.739(3)		Two-phase	
1.90	SrI_2	15.268(2)	8.251(3)	7.895(8)		Two-phase	
2.00	SrI_2	15.268(4)	8.252(1)	7.896(3)			
		15.273(8)	8.249(5)	7.898(4)		*Pbca*	(*15*)
		15.22(6)	8.22(3)	7.90(3)			(*16*)
0.0	$EuCl_2$	8.965(2)	7.538(1)	4.511(1)			(*17*)
		8.86(1)	7.46(2)	4.44(3)		*Pbnm*	(*18*)
		8.914	7.499	4.493			(*19*)
		8.973(3)	7.542(2)	4.512(3)			
0.10	$EuCl_2$	8.974(3)	7.543(2)	4.512(2)		Two-phase	
0.90	EuClI	9.398(3)	8.184(2)	4.690(3)		Two-phase	
1.00	EuClI	9.395(3)	8.185(1)	4.691(2)		*Pbnm*	
1.10	EuClI	9.397(1)	8.186(2)	4.694(0)		Two-phase	
1.90	*m*-EuI_2	7.618(3)	8.233(1)	7.874(2)	98.0(2)	Two-phase	
2.00	*m*-EuI_2	7.619(3)	8.234(1)	7.875(2)	98.0(1)		
		7.62(2)	8.23(2)	7.88(2)	98.0(6)	$P2_1/c$	(*20, 21*)
0.0	$EuBr_2$	11.574(6)		7.098(5)			(*22*)
		11.567(7)		7.094(5)		*P*4/*n*	(*23*)
		11.562(2)		7.087(1)			
0.10	$EuBr_{1.9}I_{0.1}$	11.601(3)		7.110(2)			
0.20	$EuBr_{1.8}I_{0.2}$	11.652(1)		7.140(1)			
0.30		Two-phase region					
0.40	$EuBr_{1.6}I_{0.4}$	9.570(2)	8.182(1)	4.770(1)			
0.60	$EuBr_{1.4}I_{0.6}$	9.603(3)	8.240(2)	4.783(1)			
0.80	$EuBr_{1.2}I_{0.8}$	9.669(1)	8.303(2)	4.788(1)		*Pbnm*	
1.00	EuBrI	9.711(1)	8.341(1)	4.820(2)			
1.20	$EuBr_{0.8}I_{1.2}$	9.824(2)	8.414(2)	4.856(1)			
1.30 – 1.50		Two-phase region					
1.60	$EuBr_{0.4}I_{1.6}$	15.004(2)	7.654(4)	7.985(1)	95.4(2)		
1.70		Two-phase region					
1.80	$EuBr_{0.2}I_{1.8}$	15.065(3)	8.167(2)	7.786(2)			
1.90	$EuBr_{0.1}I_{1.9}$	15.086(2)	8.174(2)	7.801(4)		*Pbca*	
	r-EuI_2	15.12(3)	8.18(2)	7.83(2)			(*21*)
2.00	*m*-EuI_2	See above section					(*20, 21*)

[a] Formula of compound whose parameters are presented.

[b] Single phase, except as noted, with space group of single-phase region.

[c] This work, except as noted.

dichloride or diiodide, and for 5, 45, 55, and 95 mole% MI_2, two-phase regions are observed. Both $MClI$ phases crystallize in orthorhombic symmetry with lattice parameters close to those of similar $PbCl_2$-type mixed halides of lead (*8*, *24*) and strontium (*25*, *5*, *6*). The observed and calculated *d*-spacings are presented in Table II. These results are consistent with the general observation that the size disparity between the Cl^- and I^- ions strongly limits their substitution ability. A similar result has been obtained for the $PbCl_2$–PbI_2 system (*8*).

The phase behavior of the $EuBr_2$–EuI_2 system is very different from that of the chloride–iodide systems. The structure types and the lattice parameter-composition data are listed in Table I, and a system overview is presented in Fig. 1. Seven discrete regions were identified. In the composition range $0 \leq x \leq 0.20$ the $EuBr_{2-x}I_x$ phase crystallizes in the tetragonal $SrBr_2$-type structure. If the iodine concentration is increased beyond $x = 0.20$ (10 mole% EuI_2), a two-phase region consisting of the $SrBr_2$-type phase and an orthorhombic $PbCl_2$-type phase appears.

When 20 mole% EuI_2 is reached, only the $PbCl_2$-type phase is observed. This phase

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR MXI PHASES

SrClI					EuClI					EuBrI			
d_{hkl}		Intensity			d_{hkl}		Intensity			d_{hkl}		Intensity	
Obs.	Calc.	Obs.	Calc.	*hkl*	Obs.	Calc.	Obs.	Calc.	*hkl*	Obs.	Calc.	Obs.	Calc.
6.209	6.216	10	13	110	6.169	6.164	10	8	210	4.207	4.196	15	14
4.721	4.729	5	4	200	4.696	4.684	1	2	111, 120	3.832	3.834	9	13
4.238	4.236	5	5	101	—	4.194	—	0	211, 220	3.162	3.164	83	74
4.098	4.102	12	9	210	4.068	4.065	22	26	021		3.154		13
3.772	3.768	16	14	111	3.732	3.732	34	31	310	3.018	3.018	22	21
3.102	3.110	70	9	021	3.077	3.083	65	12	121	3.001	2.999	100	100
	3.108		10	220		3.083			301	2.682	2.687	40	29
	3.101		69	211		3.072		51	130		2.673		18
2.951	2.955	100	100	121	2.927	2.929	100	100	311, 320	2.557	2.557	24	28
	2.945		28	310		2.918		19	400	2.425	2.427	10	13
2.640	2.640	10	13	130	2.620	2.623	8	10	230	2.409	2.412	58	27
2.625	2.625	12	14	301	2.601	2.599	15	18	002		2.410		36
2.500	2.501	12	17	311	2.476	2.477	20	22	131	2.341	2.338	10	10
2.376	2.376	25	20	230	2.361	2.359	20	25	321	2.259	2.259	16	14
2.368	2.369	38	29	002	2.344	2.345	34	28	330	2.111	2.109	6	5
	2.364		10	400		2.342		13	411, 420	2.095	2.098	6	6
2.306	2.306	1	4	131	2.286	2.287	6	8	212	2.086	2.089	10	4
2.114	2.114	12	9	321	2.194	2.194	8	12	040		2.085		5
2.072	2.072	5	8	330	2.057	2.055	6	6	222	1.9178	1.9171	2	4
2.061	2.062	4	7	040	2.046	2.046	6	8	312	1.8830	1.8832	8	9
2.050	2.051	8	4	420	2.031	2.032	13	3	132	1.7893	1.7899	8	9
	2.051			212		2.031		8	511, 520	1.7607	1.7609	6	4
	2.049		9	411		2.030		6	402	1.7108	1.7104	20	8
2.007	2.008	1	1	122	—	1.988	—	1	431	1.7098	1.7098		11
1.8905	1.8907	6	3	041	1.8758	1.8757	4	4	232	1.7055	1.7052	15	16
	1.8901		2	240		1.8757			521	1.6536	1.6538	5	10
1.8842	1.8841	6	4	222	—	1.8662	—	2					
1.8456	1.8459	8	12	312	1.8281	1.8278	6	8					
1.7629	1.7632	4	6	132	1.7474	1.7473	5	5					
1.6774	1.6779	14	12	232	1.6625	1.6627	16	15					
	1.6767		9	431		1.6619		6					
1.6160	1.6162	10	10	521	1.6010	1.6012	10	10					

persists over the solid solution region, $EuBr_{2-x}I_x$ for $0.4 \leq x \leq 1.2$. Observed and calculated *d*-value and intensity data for this phase at $x = 1$ (EuBrI) are reported in Table II. A comparable $PbCl_2$-type phase also exists in the $PbBr_2$–PbI_2 system (*8*) at $PbBr_{2-x}I_x$, for $x = 0.8$, but the solid solution limits are very narrow, less than ±0.1. Hirsch (*26*) prepared from aqueous solution a metastable compound, $PbBr_{1.6}I_{0.4}$ ($Pb_5I_2Br_8$) whose X-ray diffraction pattern, while not interpreted, was very different from that of $PbCl_2$. A comparable europium compound does not appear to exist.

When the iodine concentration exceeds $x = 1.2$ (60 mole% EuI_2), a two-phase region which is composed of the $EuBr_{0.8}I_{1.2}$ and $EuBr_{0.4}I_{1.6}$ phases appears. The powder diffraction pattern of the latter phase can be indexed on monoclinic symmetry (see Tables I and III). Its narrow composition region indicates minimal solid solution effects, and it can be described as $Eu_5Br_2I_8$. A sample of $EuBr_{0.4}I_{1.6}$ aged about 2 weeks was found to produce an X-ray diffraction pattern which was different from that of a freshly prepared specimen. Some reflections broadened and additional ones appeared in the aged sample. A diffraction pattern comparable to that of the aged samples was observed in specimens in which the iodine concentration was 85 mole% EuI_2 ($x = 1.7$). The additional reflections are characteristic of the $EuBr_{0.2}I_{1.8}$ phase, which is isostructural with the orthorhombic modification of EuI_2 (see Tables I and III). On the basis of these observations, the $EuBr_{0.4}I_{1.6}$ phase must be regarded as metastable. It is of interest to note that this anion composition ($MBr_{0.4}I_{1.6}$) is the opposite of that in the metastable lead phase reported by Hirsch (*26*) ($PbBr_{1.6}I_{0.4}$). Further comment on this relationship would be speculative.

The $EuBr_{0.2}I_{1.8}$ phase persisted over the composition region $1.8 \leq x \leq 2.0$ in $EuBr_{2-x}I_x$. Only at $x = 2.0$ was the pure monoclinic europium iodide diffraction pattern obtained.

The compounds, SrClI and EuClI, and the phase EuBrI, have the same $PbCl_2$-type structure which contains two types of the anion positions, labeled as X(1) and X(2), respectively (*27*). Accordingly, theoretical powder diffraction patterns were calculated as described previously (*5–7*) for the three possible anion structural models, two ordered and one random. Atomic positional parameters for three closely related structural models are available: PbClI, PbBrI (*8*), and $EuCl_{0.5}Br_{1.5}$ (*28*). The anionic atomic parameters of all three are almost identical; the maximum difference between comparable parameters is 0.03. The cationic parameters of the first and third are closely related; those of the second differ appreciably. In view of these relationships the parameters of the europium phase (*28*) were used in the theoretical calculations. The intensities obtained for selected reflections which are most sensitive to anion position indicate clearly that the anions are ordered in all three. The position X(1), surrounded by four cations in a tetrahedral configuration, is occupied by the smaller anion, whereas position X(2), surrounded by five cations in a square pyramidal configuration, is occupied by the iodine ion.

The structure of the metastable $EuBr_{0.4}I_{1.6}$ phase is not known, but on the basis of its lattice parameters it must be closely related to both the monoclinic and orthorhombic modification of EuI_2. As such, the structure must contain a basic structural arrangement typical for these forms. In the orthorhombic modification of EuI_2 the two iodine atoms are trigonally and tetrahedrally coordinated. Based on this modification, numerous theoretical X-ray powder diffraction patterns were calculated for various arrangements of the anions. Since the calculations evidenced only minimal intensity variations for the different models, we can only speculate on the

TABLE III

OBSERVED AND CALCULATED POWDER DIFFRACTION DATA FOR $EuBr_{0.4}I_{1.6}$ AND $EuBr_{0.2}I_{1.8}$

$EuBr_{0.4}I_{1.6}$				$EuBr_{0.2}I_{1.8}$				
	d_{hkl}				d_{hkl}		Intensity	
hkl	Obs.	Calc.	Intensity[a]	*hkl*	Obs.	Calc.	Obs.[a]	Calc.[b]
$30\bar{1}$	4.410	4.411	m	200	7.536	7.528	w	14
120	3.707	3.707	vw	210	5.531	5.530	w	11
012	3.535	3.528	m	211	4.512	4.507	m	75
021	3.441	3.448	vs	002	3.883	3.887	vw	10
$22\bar{1}$	3.176	3.181	w	400, 102 }	3.759	3.764	m	{ 21
212	3.092	3.091	vs	311 }		3.745		28
221	3.075	3.083	vs	220	3.590	3.585	s	42
022	2.760	2.757	vs	121	3.511	3.511	m	34
$12\bar{2}$	2.743	2.743	vs	202	3.453	3.454	s	57
122 }	2.678	2.680	s	410, 112	3.415	3.417	s	70
$41\bar{2}$ }		2.679		221	3.257	3.255	s	55
$20\bar{3}$	2.572	2.575	m	212	3.182	3.180	s	64
$13\bar{1}$	2.405	2.409	w	411	3.129	3.128	s	78
610	2.366	2.367	m	302	3.072	3.073	w	27
303	2.252	2.252	w	022	2.811	2.813	vs	100
$41\bar{3}$	2.174	2.171	m	420, 122	2.767	2.765	s	47
620 }	2.085	2.086	m	402	2.702	2.704	s	49
$50\bar{3}$ }		2.082		222	2.636	2.635	m	39
530	1.9398	1.9400	m	421	2.605	2.605	m	34
$13\bar{3}$ }	1.8384	1.8387	vw	412 }	2.559	2.566	vs	{ 15
033 }		1.8379		230 }		2.556		65
$23\bar{3}$	1.8120	1.8124	vw	113 }	2.432	2.437	m	18
124	1.7351	1.7346	m	231 }		2.428		24
532	1.7026	1.7027	w	213	2.346	2.346	m	27
				611	2.291	2.292	s	66
				313	2.215	2.216	vw	14
				123	2.165	2.164	m	26
				620 }	2.136	2.137	vw	5
				232 }		2.135		12
				612	2.042	2.041	w	18
				800, 702, 204	1.8821	1.8821	w	19
				810, 712, 214	1.8335	1.8339	w	20
				532	1.7906	1.7907	vw	12
				441	1.7465	1.7465	vw	14

[a] Estimated visually from Guinier film. s = strong, m = medium, w = weak, v = very.

[b] Theoretical data for model in which bromine atoms are distributed randomly. See text.

structure and presume that, similar to the $PbBr_2$–PbI_2 system (*8*, *24*), a completely ordered phase is absent.

The orthorhombic $EuBr_{0.2}I_{1.8}$ and monoclinic form of EuI_2 characteristic for $x = 2.0$ seem to be structurally very closely related. Two of the lattice parameters are similar, and the third is exactly twice that of the other. According to Bärnighausen *et al.* (*23*) the orthorhombic modification of EuI_2 can be derived from the monoclinic one by assuming twinning occurs at the unit cell level. It is likely that the same relationship is adopted by the mixed $EuBr_{0.2}I_{1.8}$ phase and pure monoclinic EuI_2.

Acknowledgment

Support of the National Science Foundation–Solid State Chemistry–DMR 79-15187, is acknowledged gratefully.

References

1. R. W. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 1, Interscience, New York (1963).
2. H. Bärnighausen, "Proceedings, 12th Rare Earth Research Conference, Vail, Col., p. 404, (1976).
3. H. P. Beck, *Z. Anorg. Allg. Chem.* **459,** 72 (1979).
4. H. P. Beck, *Z. Anorg. Allg. Chem.* **459,** 81 (1979).
5. S. A. Hodorowicz and H. A. Eick, *J. Solid State Chem.* **43,** 271 (1982).
6. S. A. Hodorowicz and H. A. Eick, *J. Solid State Chem.* **46,** 313 (1983).
7. S. A. Hodorowicz, E. K. Hodorowicz, and H. A. Eick, *J. Solid State Chem.* **48,** 351, 1983.
8. L. H. Brixner, H.-Y Chen, and C. M. Foris, *J. Solid State Chem.* **40,** 336 (1981).
9. M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.* **24,** 387 (1962).
10. D. T. Cromer, private communication.
11. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
12. H. E. Swanson and R. K. Fuyat, N.B.S. Circular 539, Vol. IV, 40 (1953).
13. A. A. Khan and V. T. Deshpande, *Acta Crystallogr. Ser. A* **24,** 402 (1968).
14. G. Brauer and M. Knausenberger, *Z. Anorg. Allg. Chem.* **320,** 54 (1963).
15. B. Frit and M. Mokail-Chbany, *J. Inorg. Nucl. Chem.* **31,** 2685 (1969).
16. E. Th. Rietschel and H. Bärnighausen, *Z. Anorg. Allg. Chem.* **368,** 62 (1969).
17. H. Bärnighausen, *Rev. Chim. Miner.* **10,** 77 (1973).
18. D. M. Laptev, I. S. Astakhova, N. M. Kulagin, and N. F. Bromko, *Zh. Neorg. Khim.* **21,** 643 (1976).
19. W. Doll and W. Klemm, *Z. Anorg. Allg. Chem.* **241,** 239 (1939).
20. H. Bärnighausen, *J. Prakt. Chem.* **14,** 313 (1961).
21. H. Bärnighausen and N. Schultz, *Acta Crystallogr. Ser. B* **25,** 1104 (1969).
22. J. M. Haschke and H. A. Eick, *J. Inorg. Nucl. Chem.* **32,** 2153 (1970).
23. H. Bärnighausen, H. P. Beck, and H. W. Grueninger, "Proceedings, 9th Rare Earth Research Conference, Vol. I, p. 77, Blacksburg, Va. (1971).
24. J. Goodyear, S.A.D. Ali, and W. J. Duffin, *Acta Crystallogr. Ser. B* **25,** 796 (1969).
25. B. Frit, M. Mokail-Chbany, and P. Hagenmuller, *C.R. Acad. Sci. Paris Ser. C.* **267,** 1046 (1968).
26. H. Hirsch, *J. Inorg. Nucl. Chem.* **40,** 1623 (1978).
27. H. Braekken, *Z. Kristallogr.* **83,** 222 (1932).
28. B. L. Clink and H. A. Eick, *J. Solid State Chem.* **28,** 321 (1979).