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Synthesis and Characterization of the Rocksalt Phases (Ca,Th)(N,O) and (Sr,Th)(N,O)

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Alkaline-earth rich (Ca,Th)(N,O) and (Sr,Th)(N,O) can be prepared from reactions of the binary nitrides at 1000°C. Th_2N_2O impurities in the starting material, Th_3N_4, resulted in oxygen incorporation in the final compound. The black products crystallize in the rocksalt structure type in which the cations are disordered (a = 5.101(5) Å and a = 5.241(2) Å, respectively). They exhibit semiconducting behavior. © 1995 Academic Press, Inc.

INTRODUCTION

Despite the remarkable stability of Th_3N_4, there are only a handful of ternary thorium nitride compounds known. There are but two pure nitride phases, Li_2ThN_2 (1, 2) and $BeThN_2$ (2, 3), although there are several mixed anion systems, including $ThNX$(X = F, Cl, Br, I) (4, 5), Th_2N_2Q (Q = O, S, Se, Te, Bi, Sb) (6, 7), and the many thorium amide–imide nitrides (8, 9). Stable ternary nitrides often contain metals that themselves form stable binary nitrides (10), so it seemed reasonable to embark on an exploration of the reactivity of thorium in ternary nitride systems.

SYNTHESIS

Pressed pellets of Th_3N_4 and A_3N_2 (A = Ca, Sr) heated to 1000°C in welded Ta containers, jacketed in evacuated quartz tubes, produced the rocksalt phases. Th_3N_4 was produced from a reaction of $ThCl_4$ with $LiNH_2$ in liquid ammonia. The $Th(NH_2)_4 \cdot nNH_3$/LiCl mixture was washed 6–10 times with liquid ammonia. The resultant amorphous material was heated to 900°C under purified, flowing N_2 to yield Th_3N_4 and some Th_2N_2O (est. <10 mole%), as identified by X-ray diffraction. Oxygen was probably introduced during the high-temperature heating, due to outgassing of the system or small leaks in the O-ring sealed system. Excess LiCl condensed at the cold end of the tube. Thermogravimetric analysis in air suggested bulk compositions of Th_3N_4 and Th_2N_2O which could be written as $ThO_{2-x}N_{2x}/3$ with x = 1.69–2.00; only materials with $x >$ 1.8 were used in making the ternary compounds. Ca_3N_2 and SrN/Sr_2N ("Sr_3N_2") mixtures were produced from reactions of the elements at 600°C. All materials were handled in an Ar-filled drybox or standard Schlenk ware.

We tried other alkaline earth nitride reactions as well. Mg_3N_2 and Ba_3N_2 do not react with Th_3N_4 to form ternary compounds under the above conditions. The chemistry is probably complicated by the fact that Ba_3N_2, and possibly Mg_3N_2, decompose before Th_3N_4 is significantly reactive; Ba metal is present in the reaction product mixture. Similarly, the group 4 transition metals do not react with the alkaline earth nitrides to form ternaries under the same or similar conditions. Only binary nitrides resulted from all combinations other than those to form (Ca,Th)(N,O) and (Sr,Th)(N,O).

Since the products are single-phased and since there was some Th_2N_2O in the starting materials, it seems reasonable to assume there is oxygen in the product. A three-fold excess of calcium with respect to thorium was required to form single-phased materials, since some of the calcium nitride reacts with the Ta tubing. This makes the task of discerning the Ca : Th ratio difficult. Chemical analysis revealed 20.8, 64.7, and 8.7 wt.% for Ca, Th, and N, respectively. The sum of these weight percentages is 94.2%. Complete combustion and digestion of the sample is difficult, so the analysis results in numbers that are a little low. Taking the analysis numbers at face value, a composition of $(Ca_{0.65}Th_{0.35})N_{0.78}$ is obtained. However, we expect that the presence of oxygen will make up some of the difference in "missing mass." To balance charge requires $(Ca_{0.65}Th_{0.35})(N_{0.78}O_{0.18})$, a slightly anion-deficient composition and certainly within experimental error of a fully-occupied model.

Excess strontium nitride was also used to form the Sr analog. Only nitrogen analysis was performed on this compound (6.7 wt.%), a mole percent of nitrogen similar to the (Ca,Th)(N,O) phase.

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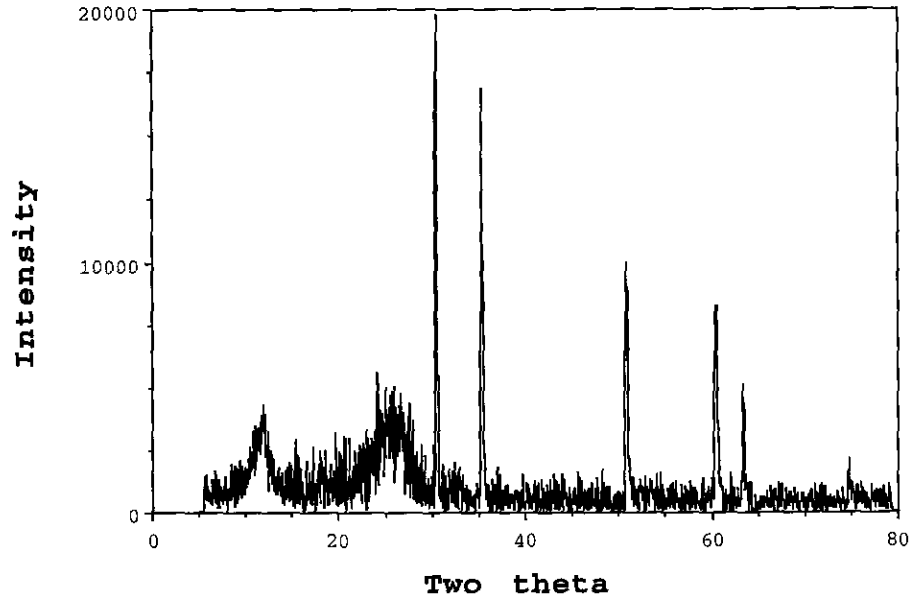

FIG. 1. X-ray diffraction data for (Ca,Th)(N,O).

RESULTS

X-ray diffraction patterns were collected from a Scintag XDS2000 θ–θ diffractometer, fitted with a solid-state detector. The samples were protected from the atmosphere by a mylar film during the data collection, as they are moisture-sensitive. The peaks from an automatic peak-finding routine that uses the Pearson VII function were indexed on cubic cells, a = 5.101(5) Å and a = 5.241(2) Å, for (Ca,Th)(N,O) and (Sr,Th)(N,O), respectively. The diffraction patterns are shown in Figs. 1 and 2. Variations in the final temperature and loading composition resulted in multiple phases, but lattice parameters within 1–2 e.s.d.'s of those stated above were always obtained for the rock-salt phases.

The diffraction pattern intensities were calculated with

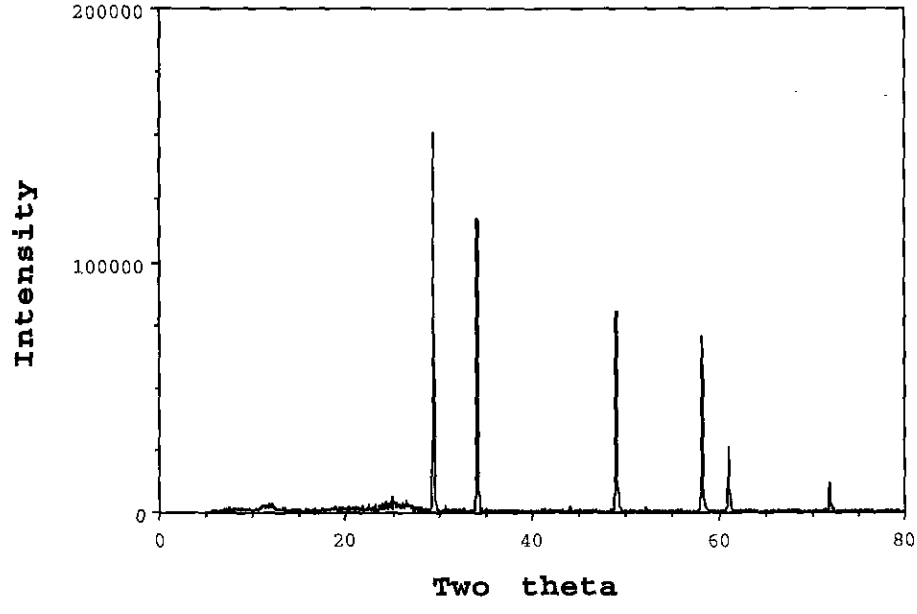

FIG. 2. X-ray diffraction data for (Sr, Th)(N, O).

TABLE 1
Observed and Calculated X-Ray Diffraction Intensities for $Ca_{1-x}Th_xN$

h	k	l	2θ	I(obs)	$I(x = 0.3)$	$I(x = 0.4)$	$I(x = 0.5)$	$I(x = 0.75)$
1	1	1	30.32	1000	1000	1000	1000	1000
2	0	0	35.16	853	925	846	792	712
2	2	0	50.57	503	626	582	551	505
3	1	1	60.11	417	464	467	469	472
2	2	2	63.08	259	208	195	187	173
4	0	0	74.32	110	96	90	87	82
		$\Sigma \lvert(I_{obs} - I_{calc})\rvert/\Sigma\ (I_{obs})$			0.098	0.070	0.081	0.099

Note. The diffraction pattern calculated for composition $Ca_{0.6}Th_{0.4}N$ best matches the observed.

LAZY-PULVERIX (11) for the compositions $Ca_{1-x}Th_xN$ and $Sr_{1-x}Th_xN$. The first 3 reflections [(111), (200), and (220)] are particularly sensitive to compositional changes. These calculated intensities are given in Tables 1 and 2 and Figs. 3 and 4. The closest matches are for the compositions $Ca_{0.6}Th_{0.4}X$ and $Sr_{0.6}Th_{0.4}X$, in reasonable agreement with the chemical analysis. The intensities are insensitive to the nature and concentration of the anion X = N, O.

Since the lattice parameters of Th metal and (Ca,Th)(N,O) are very close, we wanted to confirm the presence of both metals in the material. Powdered samples of (Ca,Th)(N,O) and (Sr,Th)(N,O) were transferred to a JEOL 733 microprobe using a custom-designed interface (12) without being exposed to air. Indeed the appropriate metal atoms were detected and found uniformly distributed in each material on length scales of 1 μm or larger. A predominance of alkaline earth metal was indicated for both materials, as indicated previously.

Four-probe electrical conductivity experiments were carried out on $\frac{5}{16}''$ pellets, previously heated at 1100°C for 4 days in welded Ta containers. The pellets flattened during the heat treatment; obvious cracks indicated that the materials did not melt, however. The pellets were brittle. The measurements versus temperature indicate semiconducting behavior, as seen in Figs. 5 and 6, with activation energies on the order of 10^{-2} eV. The absolute differences in the resistivities are mainly attributed to variable impurity and compositional variations, intergrain versus bulk conductivity, and difficulty in defining the pellet size (±20%). The shapes and temperature variations are consistent, however, with semiconducting behavior in both cases. This would indicate that the cations are fully oxidized or that low levels of Th^{3+} result in trapped carriers. In the former case, any potential reduction by the substitution of oxygen for nitrogen is compensated by the cation ratio.

DISCUSSION

At first glance, it is surprising that the other alkaline earths do not react with Th_3N_4. To form a stable mixing of cations in a rocksalt structure, one would expect their bond lengths to be similar. This is the case for (Ca,Th)(N,O) and (Sr,Th)(N,O) but not for $BeThN_2$, $MgThN_2$, or $BaThN_2$ (expected $d(M\text{–}6N)$ = 2.49, 1.90, 2.25, 2.54, 2.63, 2.87 Å for M = Th, Be, Mg, Ca, Sr, Ba (10)). In fact, the bond lengths from calcium and strontium to nitrogen

TABLE 2
Observed and Calculated X-Ray Diffraction Intensities for $Sr_{1-x}Th_xN$

h	k	l	2θ	I(obs)	$I(x = 0.3)$	$I(x = 0.4)$	$I(x = 0.5)$	$I(x = 0.75)$
1	1	1	30.32	1000	1000	1000	1000	1000
2	0	0	35.16	776	801.3	770	745	699
2	2	0	50.57	533	554.1	536.5	522	497
3	1	1	60.11	466	464.9	466.9	469	472
2	2	2	63.08	177	186.8	181.9	178	171
4	0	0	74.32	76	86.8	84.8	83	81
		$\Sigma \lvert(I_{obs} - I_{calc})\rvert/\Sigma\ (I_{obs})$			0.023	0.008	0.018	0.043

Note. The diffraction pattern calculated for composition $Sr_{0.6}Th_{0.4}N$ best matches the observed; the intensities are much less sensitive than for the Ca analog.

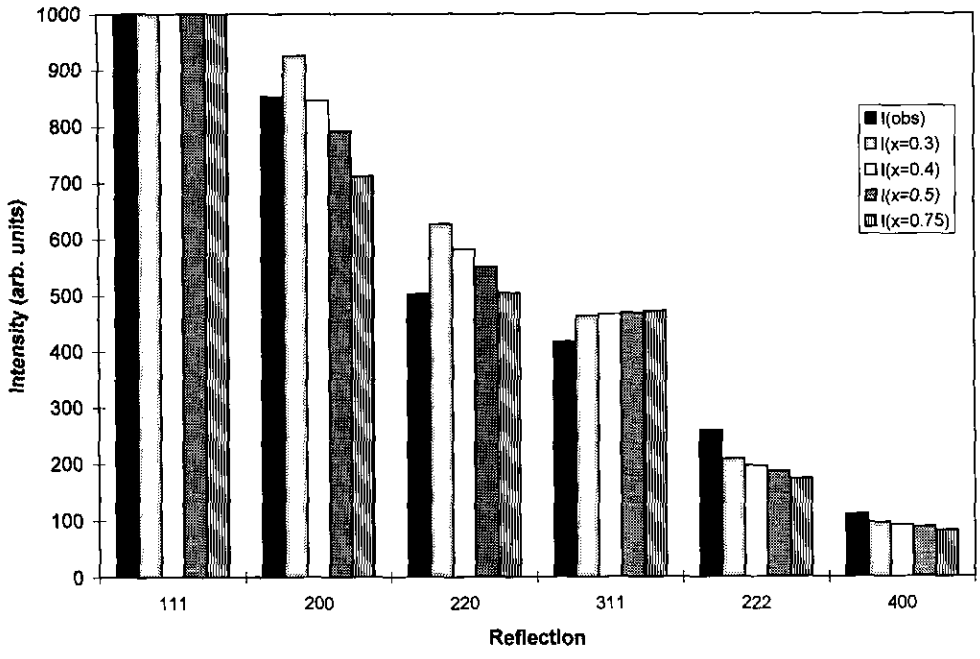

FIG. 3. Calculated and observed diffraction intensities for $Ca_{1-x}Th_xN$.

have a smaller difference than any other alkaline earth pair. This island of similarity corresponds to their chemical reactivity as well.

One could predict cubic lattice parameters for these $ATHN_2$ materials by using the sum of their expected bond lengths (see Fig. 7). For $CaThN_2$ and $SrThN_2$, one finds $a = 5.03$ Å (obs. 5.101 Å) and $a = 5.12$ Å (obs. 5.241 Å), respectively. These deviations of 1.4 and 2.3% suggest that the structure is "forced" to be more open than expected, perhaps due to metal–metal repulsions. An excess of alka-

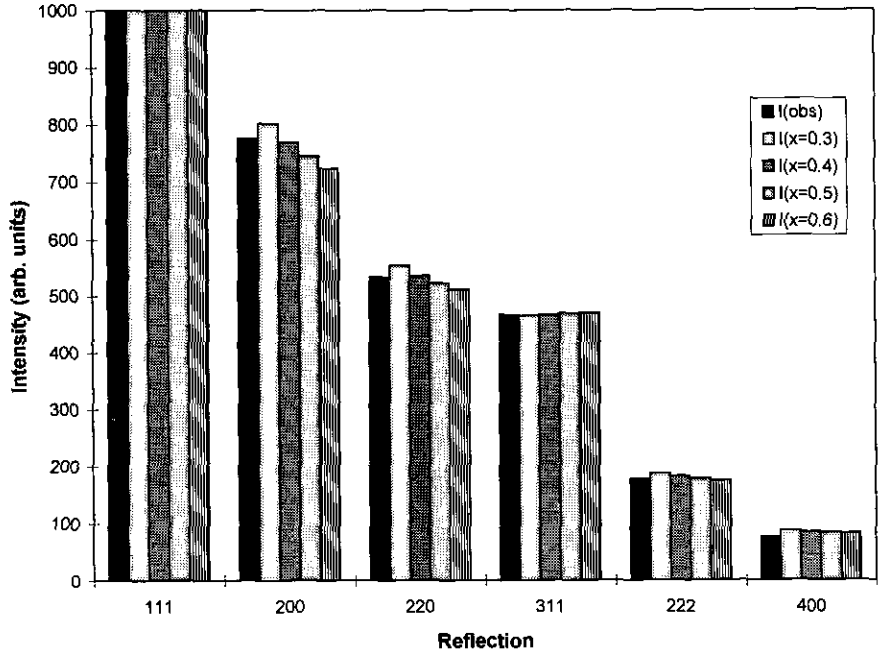

FIG. 4. Calculated and observed diffraction intensities for $Sr_{1-x}Th_xN$.

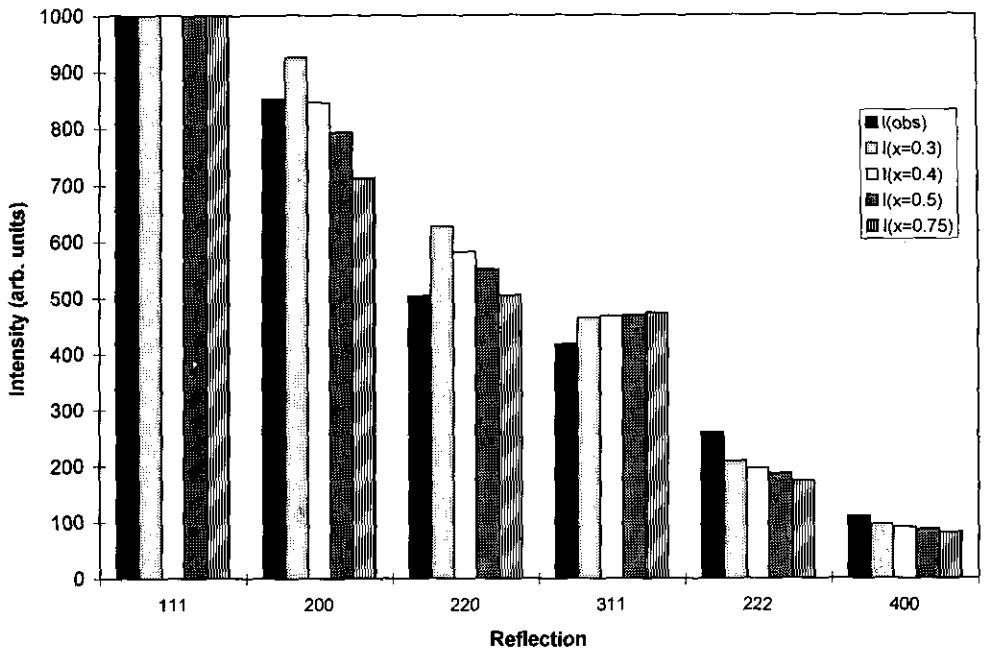

FIG. 5. Conductivity versus temperature for (Ca,Th)(N,O).

line earth would tend to increase the average bond length and lessen these Th–Th repulsions. It is suggestive, therefore, that pure phases only form with excess alkaline earth present.

In the case of "$MgThN_2$," we predict a = 4.74 Å from expected bond lengths, which would force d(Th–Th) = d(Mg–Mg) = 3.35 Å. In eutactic ("close-packed") Th_3N_4, d(Th–Th) is greater than 3.78 Å, while in Li_2ThN_2, d(Th–Th) = 3.70 Å. This suggests that $MgThN_2$ would be forced to form in a different structure type, in order to avoid close

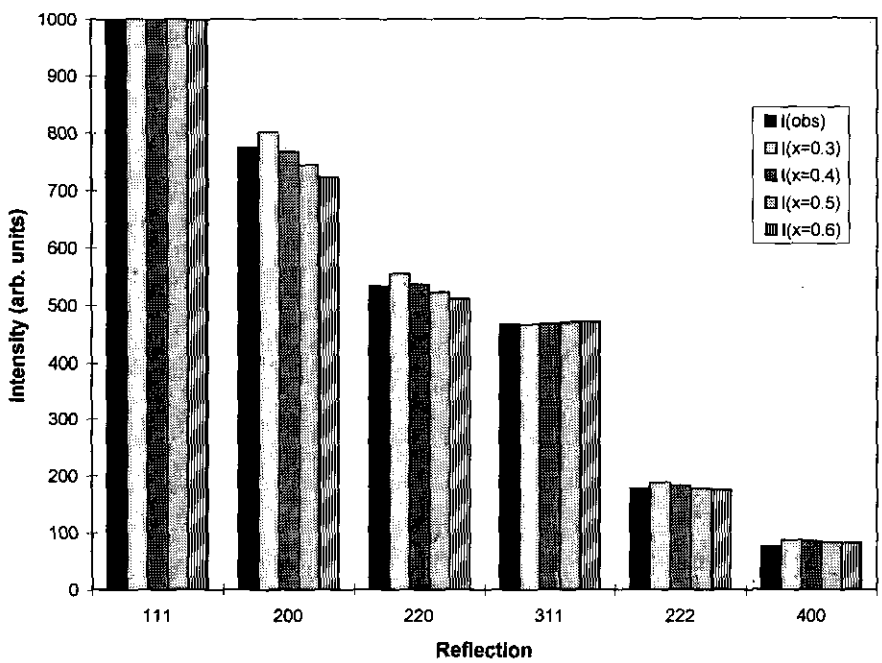

FIG. 6. Conductivity versus temperature for (Sr, Th)(N, O).

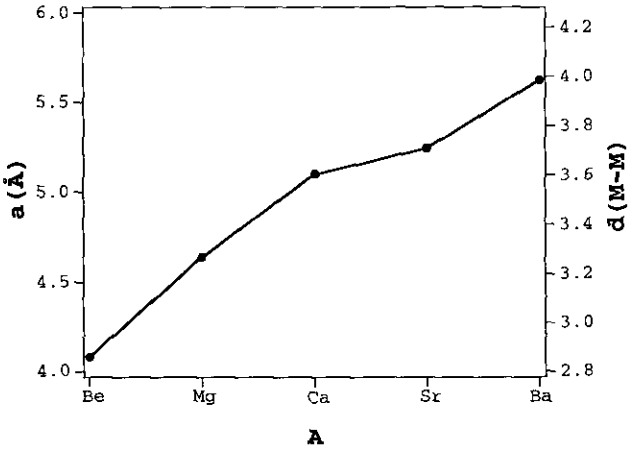

FIG. 7. Predicted cubic lattice parameters for $M\mathrm{ThN_2}$ materials.

Th–Th contacts. Nonetheless, we did not find any evidence of reaction of Mg_3N_2 and Th_3N_4 under several sets of conditions.

Likewise, in "$BaThN_2$," we predict $a = 5.36$ with d(Th–Th) = d(Ba–Ba) = 3.79 Å. While this distance is approaching the minimum acceptable d(Th–Th), the d(Ba–Ba) are becoming quite close. There is precedence for d(Ba–Ba) as close as 3.53 Å in materials like $Ba_9N[N_3][TaN_4]_2$ (13), but it is rarely less than 3.8 Å (e.g., $Ba_4(BN_2)_2O$ (14)). In this case it is difficult to tell which M–M repulsive force prevents the formation of the ternary material.

Thorium is a unique actinide in that it can be completely oxidized by nitrogen. This reactivity leads, in turn, to the stabilization of ternary nitrides. Its large size, however, places minimum size constraints on potential structures. (Ca,Th)(N,O) and (Sr,Th)(N,O) are the first examples of what should prove to be a rich family of ternary thorium nitrides.

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REFERENCES

1. M. G. Barker and I. C. Alexander, *J. Chem. Soc. Dalton Trans.* **2166** (1974).
2. A. Palisaar and R. Juza, *Z. Anorg. Allg. Chem.* **384,** 1 (1971).
3. N. E. Brese and M. O'Keeffe, unpublished results, 1991.
4. R. Juza and R. Sievers, *Z. Anorg. Allg. Chem.* **363,** 258 (1968).
5. R. Juza and R. Sievers, *Naturwiss.* **52,** 538 (1965).
6. R. Benz and W. H. Zachariasen, *Acta Crystallogr.* **21,** 838 (1966).
7. R. Benz and W. H. Zachariasen, *Acta Crystallogr.* ***B26,*** 823 (1970).
8. H. Blunck and R. Juza, *Z. Anorg. Allg. Chem.* **410,** 9 (1974).
9. R. Juza and H. Gerke, *Z. Anorg. Allg. Chem.* **363,** 245 (1968).
10. N. E. Brese and M. O'Keeffe, *Struct. Bonding* **79,** 307 (1992).
11. K. Yvon, W. Jeitschko, and E. Parthé, LAZY-PULVERIX (1977), Laboratoire de Cristallographie aux Rayons-X, Univ. de Geneva, 24 Quai Ernest Ansermet, CH 1211 Geneva 4, Switzerland.
12. G. M. Ehrlich, personal communication, 1993.
13. P. Höhn, R. Kniep, and J. Maier, *Agnew. Chem. Int. Ed. Engl.* **32,** 1350 (1993).
14. J. Curda, U. Herterich, K. Peters, M. Somer, and H. G. von Schnering, *Z. Kristallogr.* **209,** 181 (1994).