JOURNAL OF SOLID STATE CHEMISTRY **88,** 571–576 (1990)

Synthesis and Crystal Structure of SrD_2 and SrND and Bond Valence Parameters for Hydrides

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Received February 14, 1990; in revised form June 7, 1990

A mixture of SrD_2 and SrND was obtained from a reaction of Sr_2N and D_2. Their structures were refined using time-of-flight neutron diffraction data. SrD_2 and SrND crystallize with the $PbCl_2$ and rock salt structures, respectively. For SrND the space group is *Fm3m*, a = 5.4474(1) Å. The diffraction data confirm the composition SrND and indicate a rotationally disordered ND group. For SrD_2, the prototype of the *C*29 structure type, the space group is *Pnma*, a = 6.3706(4) Å, b = 3.8717(2) Å, c = 7.3021(4) Å. The structure differs only in minor details from the *C*23 ($PbCl_2$) type.

Introduction

All discussions of strontium nitrides have been plagued by controversy, since the most stable stoichiometries are unexpected ones. The compositions Sr_2N, Sr_3N_2, and SrN have all been reported; although it has been claimed that these are contaminated with oxygen and/or hydrogen.

Diffraction patterns from materials with the normal composition Sr_3N_2 show striking similarities to a mixture of "SrN" and Sr_2N (*1*). "SrN" and Sr_2N crystallize with the rock salt (*2*) and anti-$CdCl_2$ structures (*3*), respectively. Brice, however, claims that Sr_2N is actually Sr_2NH_x (which, if stoichiometric, would crystallize with a distorted rock salt structure) and that "SrN" is actually $SrNH_x.SrO$ (*4*).

We recently showed that Sr_2N with the anti-$CdCl_2$ structure can be made as a stoichiometric compound free from any hydrogen contamination (*5*). In an effort to study hydrogen intercalation between the Sr_2N layers, we reacted the nitride with D_2 gas. Instead of forming Sr_2ND_x as expected on the basis of previous reports (*6, 7*), a mixture of SrD_2 and SrND was produced. As the two phases have small unit cells a simultaneous structure determination of both phases were carried out by powder methods. We confirm that the composition of the face-centered cubic phase is SrND as originally suggested (*8*).

We also show that the original proposal (*9*) for the structure of SrD_2 (the *C*29 structure) was incorrect and that the structure is essentially that of the *C*23 ($PbCl_2$) type as previously shown to be the case for CaD_2 (*10*) and BaD_2 (*11*).

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0022-4596/90 $3.00

Experimental

(*a*) *Synthesis*

An Al_2O_3 jacket (Coors porcelain) was soaked in nitric acid, rinsed thoroughly with deionized water, and heated to 900°C under flowing oxygen then vacuum (10^{-3} Torr). A quartz tube was cleansed for 2 min in an acid solution (87 ml 48% HF, 332 ml 70% HNO_3, 20 g Alconox, and 405 ml distilled H_2O), rinsed repeatedly with distilled water, and heated to 900°C under air and then under vacuum (10^{-3} Torr). The Sr_2N sample previously used for neutron powder diffraction (*5*) was loaded into the tube in a dry box. The sample was then evacuated to 10^{-5} Torr, and the system was back-filled with oxygen-free D_2 from a gas bulb (99.5% isotopic purity, Airco). The tube was heated by a small furnace and the pressure monitored by a Baratron gauge. Reaction began at 400°C and was rapid at 470°C. The vacuum line was refilled twice with D_2 during the course of reaction. The amount of D_2 taken up was consistent with the reaction stoichiometry:

$$Sr_2N + 3/2\ D_2 \rightarrow SrD_2 + SrND$$

Mass spectral analysis of the residual gases revealed exclusively the presence of D_2 and in particular the absence of N_2 and ND_3.

(*b*) *Structural Study*

A Rigaku D/Max-IIB X-ray powder diffractometer with an environmental cell was used for phase identification. All the observed peaks in the spectrum could be indexed with a combination of an orthorhombic cell with a = 6.3706(4) Å, b = 3.8717(2) Å, c = 7.3021(4) Å (assigned to SrD_2) and a face-centered cubic cell with a = 5.4474(1) Å.

Pulsed neutron diffraction data were collected at room temperature on the High Intensity Powder Diffractometer (HIPD) of the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos National Laboratory. The powder data were refined with use of the General Structure Analysis System (GSAS), a Rietveld profile analysis code (*12*). Only data from the $2\theta = +153°$ and $+90°$ detector banks were used. The structure of CaH_2 (with refined lattice parameters of SrD_2) was used as a starting model for the structure of SrD_2 which refined in a straightforward manner.

Since so few Bragg peaks were attributable to the rock salt phase, we were limited in the number of parameters for refinement. A preliminary refinement of several models (see below) showed that the composition must be close to SrND and the N–D bond length close to 1 Å (the neutron scattering lengths of Sr, N, and D are all comparable). The final model for the imide which was chosen fixed the ND center of mass at the origin of the unit cell, the composition at SrND, and the N–D bond length at 1.01 Å. No evidence for a rock salt superstructure (i.e., Sr_2ND) as suggested by Brice (*13*) was found in either the X-ray or neutron data.

The final refinement included 708 reflections in the range $0.56 < d < 3.68$ Å (3691 profile points) for the backscattering data and 620 reflections in the range of $0.58 < d < 3.77$ Å (3881 profile points) for the 90° data. The 56 variables refined included 18 background coefficients used in a cosine Fourier series technique, an absorption factor for each bank of data (*14*, *15*), a profile coefficient for each bank (σ_1) (*16*), diffractometer zero constants, lattice parameters, 8 atomic position parameters (including 2 for the N–D rigid body rotation), and thermal parameters (12 anisotropic for SrD_2 and 2 isotropic for SrND). The final conventional agreement indices are R_p = 0.030 and R_{wp} = 0.041 with a reduced χ^2 = 3.84. An analysis of agreement factors versus parity class revealed no unusual trends.

The final Rietveld refinement profile fit is displayed in Fig. 1. Crystallographic data

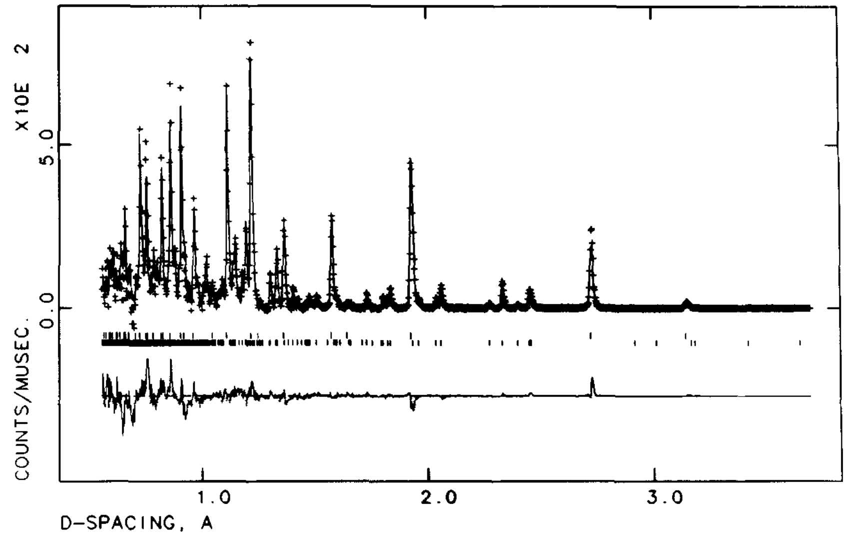

FIG. 1. Neutron diffraction profile fit for the refinement. The data points are shown as '+,' and the solid line is the calculated profile. The upper tick marks are those denoting the SrND phase and the lower ones are those for SrD_2. The difference curve at the bottom is on the same scale. The background has been subtracted.

for SrND are given in Table I and for SrD_2 in Table II. Structure amplitudes are given in Table III.[2]

Discussion

(*a*) SrND

We found several plausible models for the SrND phase (including two sets of 3) which allow for varying amounts of rotational disorder. Each ND dipole can be pointing toward the vertex, edge, or face of the Sr_6

TABLE I

POSITIONAL PARAMETERS FOR SrND[a]

Atom	Site	x	y	z	100 U
Sr	4 *b*	1/2	1/2	1/2	2.35(7)
N	192 *l*	−0.0071(4)	0.0072(5)	0.02087(4)	2.86(7)
D	192 *l*	0.050(3)	−0.051(4)	−0.1460(3)	2.86(7)

[a] Space group $Fm3m$, a = 5.4474(1) Å.

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR SrD_2[a]

	Sr	D(1)	D(2)
x	0.2438(6)	0.3570(4)	−0.0307(6)
y	1/4	1/4	1/4
z	0.1108(3)	0.4281(5)	0.6825(4)
U_{11}	0.024(1)	0.027(2)	0.029(2)
U_{22}	0.0033(7)	0.027(2)	0.032(2)
U_{33}	0.019(1)	0.032(2)	0.043(2)
U_{13}	−0.004(1)	−0.005(1)	−0.019(2)

[a] Space group $Pnma$ a = 6.3706(4) Å, b = 3.8717(2) Å, c = 7.3021(4) Å. $U_{12} = U_{23} = 0$.

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[2] See NAPS document No. 04789 for 36 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or $12.55 for photocopy. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

octahedron. Azides and other linear ions are generally oriented toward places of the greatest physical space; therefore we expected orientation toward the triangular faces to be favored. Furthermore, we could fix the N–D center of mass at the origin or could constrain the sum of valences at the N to be 3 (*17–19*). (Note that we fix the N–D bond length to be 1.01 Å which corresponds to a bond of unit valence). It turns out that the position parameters of both models are very similar, and both allow equivalent refinements.

The best refinement was achieved using the greatest amount of rotational disorder. The D and N atoms in the ND dipole were defined as a rigid body and were placed at the general positions 192 *l* with occupancy 1/48. As the N–D bond length is fixed and the center of mass is constrained to lie at 0,0,0 there are two positional degrees of freedom in this model. The refinement did not strongly favor any particular N–D orientation, but this is not surprising for room temperature data. The final model has the N–D dipole directed roughly toward an octahedral face. The thermal parameters for the D atom were now much more reasonable than in any of the other models discussed above. Further, all the SrD_2 anisotropic terms stayed positive using this highly disordered SrND model. The Sr–Sr distance is 3.8519(1) Å ($\sqrt{2}a/2$), N–D is 1.01 Å (fixed), the six shortest Sr–N distances range from 2.6106(2) to 2.8379(2) Å, and the five Sr–D ones from 1.967(2) to 3.117(2) Å.

As a check on the plausibility of our result, we also modeled SrND as an assembly of point ions. The electrostatic energy was calculated as a function of the orientation of the ND group. Again the center of mass was fixed at 0,0,0 and the N–D length was fixed at 1.01 Å. Charges on Sr, N, and D were set equal to 2.0, −3.0, and 1.0, respectively. The electrostatic energy was calculated as a function of θ, the polar angle of the N–H vector with [001], and the azimuthal angle ϕ, the angle with [100] of the projection of that vector in the (001) plane. Flat minima were found in the $\langle 111 \rangle$ directions ($\theta = \cos^{-1}(1/\sqrt{3}) = 54.7°$, $\phi = 45°$) and maxima along $\langle 100 \rangle$, the difference being 0.75 eV per formula unit.

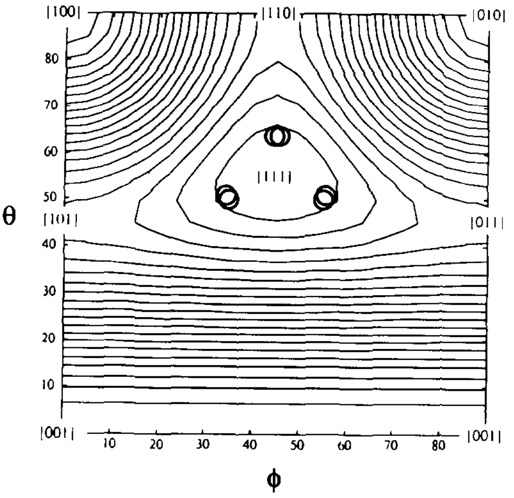

FIG. 2. Contour plot of calculated electrostatic energy for SrND as a function of polar angle (θ) and azimuthal angle (ϕ). The minimum is at [111] and maxima at $\langle 100 \rangle$. Contours are equally spaced at 0.037 eV/formula unit. The open circles show the symmetry-related orientations of the Sr–N-D vector determined from an analysis of the neutron diffraction data.

Figure 2 shows a contour plot of electrostatic energy as a function of θ and ϕ for one octant. Superimposed on the figure are the symmetry-related orientations of the N–D vector determined from the structural analysis. These are considerably closer both in distance and in energy to the minima at $\langle 111 \rangle$ than to the maxima at $\langle 100 \rangle$. Although we do not believe that a simple ionic model will lead to quantitative results, it might be expected to be qualitatively correct and certainly lends credence to our results.

(*b*) *SrD_2*

Structural and thermal parameters are listed in Table II. Sr is nine-coordinated by D with

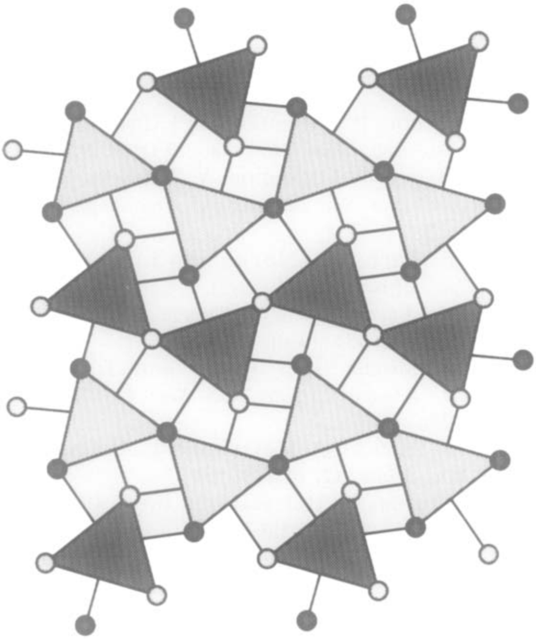

FIG. 3. Projection of the SrD_2 structure down [010]. The shaded circles represent D atoms; the Sr atoms center the tricapped trigonal prisms (represented by triangles). All atoms are at $y = 1/4$ or $3/4$. The a axis is horizontal and the c axis is vertical on the paper.

Sr–D(1) 2.427(5), 2.437(3)(2×), 2.480(4)
Sr–D(2) 2.580(4), 2.712(4)(2×), 2.860(4)(2×).

It should be noted that the parameters determined are close to those found for CaD_2 (*10*) and for BaD_2 (*11*) and for halides such as $PbCl_2$. Figure 3 shows the structure of SrD_2 in the conventional (*20*) projection on (010). The nine-coordination of Sr by D atoms forming a tricapped trigonal prism is evident.

Other interatomic distances of interest are Sr...Sr 12 distances ranging from 3.776 to 4.134 Å. Sr is in fact approximately in hexagonal eutaxy ("close packing"). D(1) has two D(1) neighbors at 2.863 Å and six D(2) near neighbors at distances of 2.857–3.091 Å.

It is often profitable also to consider structures in terms of the coordination of anions by cations (*21*). D(1) occupies one-half of the tetrahedral sites in the Sr array; the coordination is quite regular: D(1)–Sr = 2.427, 2.437(2×), 2.480 Å and angles Sr–D–Sr = 100.7°, 105.2°, 108.9°(2×), 116.4°(2×).

D(2) atoms are off-center in Sr_6 octahedra, so that their coordination is approximately square pyramidal as shown in Fig. 4. The D(2)–Sr distances are 2.580, 2.712(2×), 2.806(2×), and 3.583 Å. It is interesting that the thermal motion of D(1) is very nearly isotropic (rms amplitudes along the principal axes of the thermal ellipsoid range from 0.16 to 0.19 Å), but there is significant anisotropy in the thermal vibration of D(2) with the largest rms amplitude of 0.24 Å in the mirror plane and directed approximately to the center of the Sr_6 octahedron. The smallest rms amplitude of D(2) is 0.13 Å.

As the structure of MgD_2 (*22*) is also known (rutile structure) we can determine for alkaline–earth/hydrogen bonds the bond valence parameter R appearing in the expression for bond valence,

$$v = \exp[(R - d)/0.37\ \text{Å}], \qquad (1)$$

assuming that the sums of the valences, v, at the cations are equal to 2 (we propose to discuss this point in more detail in a subsequent publication). The results are listed in Table IV and compared with those derived

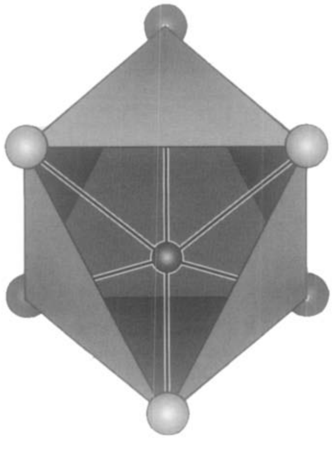

FIG. 4. The environment of D(2) off-center in a Sr_6 octahedron in SrD_2.

TABLE IV

BOND VALENCE PARAMETERS FOR HYDRIDES AND FLUORIDES[a]

	Hydrides	Fluorides
Mg	1.54	1.58
Ca	1.82	1.84
Sr	2.01	2.00
Ba	2.20	2.19

[a] Reference (*17*) except for Sr–F from Ref. (*19*).

for the corresponding fluorides (*17, 19*). It may be seen that *R* for the hydrides and the corresponding fluorides are very close.

Conclusions

The results confirm the existence of strontium imide as a compound in the Sr–N–D system as a rotationally disordered phase similar to high-temperature KOH (*23*). Under the conditions of our experiments (which included rigorous efforts to exclude oxygen contamination) only SrND and SrD_2 are formed by the reaction of D_2 with Sr_2N.

SrD_2 is shown to have the *C*23 structure and it is suggested that the designation *C*29 for SrH_2 be discontinued.

Acknowledgments

This material is based upon work supported under a National Science Foundation Graduate Fellowship to N.E.B. and is part of a continuing program in crystal chemistry supported by the National Science Foundation (DMR 8813524). We have benefited from the use of facilities at the Manuel Lujan, Jr. Neutron Scattering Center, a national user facility, funded as such, by the DOE/Office of Basic Energy Sciences. We thank G. Burr for help with the neutron data collection. The X-ray data were obtained on equipment purchased under National Science Foundation Grant DMR-8406823. Use was made of the Materials Preparation Facility of the Center for Solid State Science.

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