JOURNAL OF SOLID STATE CHEMISTRY 71, 205–213 (1987)

A Preparatory and X-Ray Diffraction Study of the $SrCl_2$–$NdCl_3$ System

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Received February 25, 1986; in revised form February 3, 1987

The $SrCl_2$–$NdCl_3$ system was examined over the full composition range by the Guinier powder X-ray diffraction technique. A solid solution, $Sr_{(1-x)}Nd_xCl_{(2+x)}$, was found for the composition region $0 < x < 0.18$. Beyond the solid solution region two intermediate chloride phases were identified: $Sr_{0.80}Nd_{0.20}Cl_{2.20}$ (Sr_4NdCl_{11}) and $Sr_{0.643}Nd_{0.357}Cl_{2.357}$ ($Sr_9Nd_5Cl_{33}$). Orthorhombic Sr_4NdCl_{11} is isostructural with vernier-type Sr_4DyCl_{11}; lattice parameters are $a = 7.230(5)$; $b = 35.292(18)$, and $c = 6.826(4)$ Å. The phase $Sr_9Nd_5Cl_{33}$ exhibits hexagonal symmetry with lattice parameters $a = 12.908(6)$ and $c = 24.823(10)$ Å and is isostructural with $Nd_{14}Cl_{33}$. © 1987 Academic Press, Inc.

Introduction

The $SrCl_2$–$NdCl_3$ system has been characterized by differential thermal studies effected by two research groups (*1*, *2*). Both groups reported the presence of one phase, Sr_3NdCl_9 ($MCl_{2.25}$), with a melting temperature of 618 (*1*) or 600°C (*2*). A phase of similar composition was reported for the $SrCl_2$–$RECl_3$, RE = Pr and Sm systems. Neither research group provided either X-ray powder diffraction or analytical data to support its claim. The system $SrCl_2$–$RECl_3$, where RE = La, Sm, Gd, and Yb, was examined recently by both differential thermal and X-ray powder diffraction analysis procedures (*3*), and a series of Sr_2RECl_7 ($MCl_{2.33}$) isotypic compounds was reported. These compounds are stated to have an X-ray powder diffraction pattern related to that of Sm_3Cl_7 (*4*), but again no X-ray diffraction data are reported. For the systems with RE = La, Sm, and Gd, a second phase of the approximate composition $Sr_{0.8}RE_{0.2}Cl_{2.20}$, which decomposes peritectically, was hypothesized. Since the ionic radius of CN8 Sr^{2+} (1.40 Å) is similar to that of the comparably coordinated divalent lanthanoids Nd^{2+} (1.43 Å), Sm^{2+} (1.41 Å), Eu^{2+} (1.39 Å), and Dy^{2+} (1.33 Å) (*5*), the crystal chemistry of the strontium–lanthanoid(III) halide systems should be comparable to that of the lanthanoid(II)–lanthanoid(III) halide systems. The phases $SmCl_{2.33}$ ($SmCl_3 \cdot 2SmCl_2$), $SmCl_{2.31}$ ($4SmCl_3 \cdot 9SmCl_2$) and $SmCl_{2.20}$ ($SmCl_3 \cdot 4SmCl_2$) have been reported in the $SmCl_2$–$SmCl_3$ system (*4*). Two neodymium phases characterized as $NdCl_{2.27}$ and $NdCl_{2.37}$ were originally reported in the $NdCl_2$–$NdCl_3$ system (*6*), but more recent work lists one

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0022-4596/87 $3.00

phase, $Nd_{14}Cl_{33}$ or $Nd_{14}Cl_{32}O$ (*7*). The phases Eu_4Cl_9, Eu_5Cl_{11}, and $Eu_{14}Cl_{33}$ have been characterized in the $EuCl_2$–$EuCl_3$ system (*8*), and Sr_4DyCl_{11} has been found to be isostructural with Dy_5Cl_{11} (*9*).

The investigation reported herein was undertaken because the behavior reported for the title system differed significantly from that expected by comparison to mixed-valent lanthanoid systems.

Experimental

The entire composition range was investigated. Samples were prepared from anhydrous $SrCl_2$ and $NdCl_3$. Anhydrous strontium dichloride was obtained from AESAR (Johnson Matthey, Inc., Seabrook, NH) and was melted under vacuum prior to use. Neodymium trichloride was prepared from 99.9% Nd_2O_3 (Michigan Chemical Co., principal impurity 500 ppm Ca) by the ammonium halide matrix method (*10*) and was purified further by distillation under high vacuum. X-ray diffractograms of the reactants indicated only reflections assignable to pure cubic $SrCl_2$ (*11*) and hexagonal $NdCl_3$ (*12*). Lattice parameters of all phases are listed in Table I.

All manipulations of reactants and products were performed in an argon-filled glove box which was continuously purged of both oxygen (BASF catalyst) and water (molecular sieves). Samples were transported between the glove box and the reaction systems in either evacuated containers or under a dry argon atmosphere. Samples to be analyzed by powder X-ray diffraction were coated with paraffin oil dried over elemental sodium to minimize reaction with moisture during transfer to the Guinier camera, which during exposure was evacuated by a mechanical pump.

The principal preparatory procedure involved heating, as described later, intimately ground mixtures of strontium dichloride and neodymium trichloride prepared from powders according to

$$(1-x)SrCl_2 + xNdCl_3 \rightarrow Sr_{(1-x)}Nd_xCl_{(2+x)}. \quad (1)$$

Samples of 25 and 40 mole% neodymium were also prepared by a second procedure which involved coprecipitation. The appropriate molar amounts of $Sr(OH)_2$ (J. T. Baker Chemical Co.) and Nd_2O_3, together with a 6 × molar excess of NH_4Cl (Fisher Scientific Co.) were dissolved in dilute HCl, evaporated slowly to dryness, and converted to the anhydrous halide by the ammonium halide matrix method (*10*).

Three heating methods were utilized in this work. In the first procedure 1- to 2-g quantities of the selected compositions were mixed thoroughly by grinding with an agate mortar and pestle, then placed in Alundum boats which were sealed under high vacuum (10^{-7} Torr) in silica tubes. These sealed tubes were placed in a three-zone Minibrute furnace whose temperature was controllable to ±0.2°C, and then heated to 880°C, above the melting points of both reactants (*13*). They were subsequently cooled to 400°C at a linear rate over the course of 14 days, then cooled to room temperature over a 12-hr period. In the second procedure approximately 1-g quantities of the reactants, mixed as described above, were placed into 7-mm-i.d. previously outgassed quartz ampoules which were evacuated to a pressure of 10^{-4} Torr and sealed. Samples prepared by the coprecipitation procedure were also sealed in outgassed quartz ampoules under similar conditions. These specimens were heated below the melting point of the reactants (550 ± 5°C), maintained at that temperature for ~600 hr, and then cooled slowly to room temperature over a 3- to 8-day period. In some instances the ampoules were opened and a portion of the contents was examined by X-ray diffraction. The remainder was resealed in quartz under vacuum and annealed further. In the third procedure the reactants, again confined in 7-mm-i.d. outgassed quartz ampoules evacuated to 10^{-4} Torr, were melted with a hand-held torch, and then air-quenched.

The products from all the preparatory procedures were analyzed by X-ray diffraction. The 14-day preparations were analyzed by X-ray fluorescence (XRF) with tungsten radiation for Sr and Nd on a Norelco spectrograph by an external standard procedure. Powder X-ray diffraction data were obtained with an evacuated 114.6-mm-diameter Guinier–Haegg camera using $CuK\alpha_1$ radiation with NBS standard Si reference material (a_0 = 5.430825(36) Å) as internal standard. Reflection positions were determined with a Super film reader modified slightly to improve readability. Intensities of the diffraction reflections were either estimated visually or measured on a Philips APD 3720 diffractometer system equipped with a diffracted beam monochromator, a θ compensating slit, and a sample spinner.

X-ray powder reflection intensities were calculated on a VAX 11/750 with the program POWD 12 (*14*). Polynomial scattering factors integral to the program were used in the calculations with thermal parameters estimated to be 1.0 for cations and 1.5 for anions unless indicated otherwise. A correction was made for the Guinier camera incident beam monochromator or the APD system diffracted beam monochromator. An absorption correction was not included. The choice of atomic positional parameters is described where appropriate in the text.

Results

The mass loss experiments indicated minimal sample loss during the course of the heatings. The fact that the melts separated cleanly from the quartz heating tube was taken as an indication that reaction with the container had not occurred. The XRF analyses indicated that the composition of the specimens heated for 14 days agreed with that of the initial mixture to within 3%. The solid products obtained after melting of the initial components exhibited a slight green coloration. The products obtained by the coprecipitation procedure were identical to those obtained from the grinding/heating method. The results were consistent and were independent of heating procedure.

Over the composition range 0 to 18 mole% $NdCl_3$ and independent of the preparatory procedure, the unit cell parameters decreased slightly from those of pure $SrCl_2$ (see Table I). This slight decrease was interpreted as an indication of a solid solution region. The reflection intensities of the X-ray powder diffraction patterns also changed somewhat over this region. Reflections of the type *hkl* ($h + k + l$ = an odd multiple of 2, i.e., 2, 6, 10, . . .) which are extinct in $SrCl_2$, increased in intensity with increasing neodymium content. At 10 mole% neodymium the following relative intensities, with associated Miller indices in parentheses, were observed: (111),68; (200),2; (220),100; (311),53; (222),2; (400),22; (331),25; (420),2 and (422),56. Reflection intensities were calculated with the cations assumed to occupy the face-centered positions randomly, and with the excess chloride ion content located at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) as proposed by Brauer and Mueller (*15*). The calculations yielded the following reflection intensities, with corresponding Miller indices in parentheses, for a flat diffractometer specimen: (111),68; (200),2; (220),100; (311),37; (222),1; (400),17; (331),16; (420),2; and (422),33.

The initial experiments on compositions greater than 20 mole% $NdCl_3$ yielded a plethora of reflections, indicative of the presence of intermediate chloride phases in addition to the fluorite-type solid solution. Compositions of 40 or more mole% $NdCl_3$ exhibited in addition to reflections assign-

TABLE I

CRYSTALLOGRAPHIC DATA FOR STRONTIUM CHLORIDE–NEODYMIUM CHLORIDE PHASES (THE STANDARD DEVIATION OF THE LEAST SIGNIFICANT DIGIT IS INDICATED IN PARENTHESES)

$NdCl_3$ (mole%)	Symmetry	Lattice parameter (Å) *a*	*b*	*c*	Refs.
0		6.979(2)			(*11*)
		6.978(1)			This work
10	Cubic	6.977(2)			
15		6.973(3)			
20(Sr_4NdCl_{11})	Ortho	7.230(4)	35.29(2)	6.826(4)	
36($Sr_9Nd_5Cl_{33}$)	Hex	12.908(6)		24.82(1)	
100	Hex	7.392(3)		4.235(1)	
		7.398(8)		4.242(3)	(*12*)

able to $NdCl_3$ those common to the 20–40 mole% $NdCl_3$ composition region.

The powder diffraction reflections of the phase which coexisted with the $SrCl_2$ solid solution region were indexed in three stages. In the initial stage, Miller indices of the first 12 reflections were determined by the method of Lipson and Steeple (*16*). These reflections were then used to determine the initial values of coefficients in the quadratic formulation. Next, 20 observed reflections were indexed with the program ITO (*17*) by using the method proposed by de Wolff (*18*) and programmed by Visser (*17*). When indexing was complete it was noted that parameters for this orthorhombic phase, $a = 7.056(1)$, $b = 7.222(2)$, and $c = 6.828(1)$ Å were similar to those reported for the Sr_4DyCl_{11} pseudocell, $a = 7.036(1)$, $b = 7.210(1)$ and $c = 6.768(1)$ Å (*9*). Reflection intensities were then calculated with the program POWD 12 in space group $P2_1/m$ by using the positional and thermal parameters reported for Dy_5Cl_{11} (*9*). For these calculations Sr^{2+} ions were located in cation positions 1, 2, 3, and 5, Nd^{3+} ions were located in cation position 6, and Sr^{2+} and Nd^{3+} ions occupied cation position 4 equally. With the intensity data available, some weaker reflections which were not indexed initially could now be accounted for satisfactorily. The final values of lattice parameters were determined by least-squares refinement of all observed reflections. Lattice parameter data are presented in Table I and observed and calculated interplanar *d*-spacing and intensities are presented in Table II.

By using the procedure described above, reflection data for the second phase were indexed with orthorhombic symmetry and cell parameters of 6.441, 12.882, and 16.656 Å. However, a smaller, more reasonable cell consistent with these parameters could not be identified in any related system. These lattice constants were analyzed with the program TRACER (*19*) to identify a reduced cell, but none could be found. Only when we became aware of the structure determination of the phases $Nd_{14}Cl_{33}$ and $Nd_{14}Cl_{32}O$ (*7*) were we able to interpret the data satisfactorily. By using lattice parameters for $Eu_{14}Cl_{33}$ (*8*), the more intense reflections could be indexed. Subsequent least-squares refinement of these data, coupled with intensity calculations (*14*) effected with the $R\bar{3}$ space group positional parameters for $Nd_{14}Cl_{33}$ (*7*) (Table III) permitted all remaining reflections to be indexed. Intensity data were calculated for $Sr_9Nd_5Cl_{33}$ with both ordered and random cationic arrangements. The low-angle re-

TABLE II

OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS AND INTENSITIES FOR ORTHORHOMBIC Sr_4NdCl_{11}

d_{obs}	d_{calc}	I_{obs}	I_{calc}	ΣI_{calc}[a]	*h k l*
17.68	17.65	vvw	9	5	0 2 0
6.71	6.70	vvw	5	3	0 1 1
4.958	4.963	m	38	20	1 0 1
4.057	4.060	vs	192	100	1 5 1
3.605	3.614 3.596	m	14 5	10	2 0 0 2 1 0
3.525	3.529	m	20	10	0 10 0
3.411	3.413	m	13	7	0 0 2
3.348	3.350	vw	4	2	0 2 2
3.211	3.217	w	10	5	2 5 0
3.176	3.181	w	8	4	2 1 1
3.069	3.074	m	11	6	1 1 2
2.942	2.941 2.938	m	12 4	8	0 12 0 2 7 0
2.906	2.904	m	12	6	0 11 1
2.872	2.876	m	27	14	1 10 1
2.805	2.807	m	24	13	2 6 1
2.733	2.733	m	26	14	1 6 2
2.699	2.699 2.698	vvw	2 3	3	0 8 2 2 7 1
2.592	2.587	vvw	1	1	2 8 1
2.525	2.525	s	46	24	2 10 0
2.481	2.481	s	34	18	2 0 2
2.470	2.475	m	15	8	2 1 2
2.453	2.453	s	78	41	0 10 2
2.425	2.425	vw	5	3	1 9 2
2.400	2.399	w	13	7	2 11 0
2.341	2.341	m	35	18	2 5 2
2.279	2.281	vw	7	4	2 12 0
2.270	2.272	m	33	17	3 0 1
2.161	2.163	w	10	5	3 5 1
2.125	2.126	s	47	24	1 15 1
2.116	2.119	w	12	6	3 6 1
2.075	2.074	s	57	30	1 5 3
2.030	2.030	w	11	6	2 10 2
1.9719	1.9719	m	15	8	2 15 0
1.9102	1.9106	m	18	9	3 10 1
1.8812	1.8813	vvw	4	2	2 4 3
1.8557	1.8559	vvw	3	2	0 11 3
1.7979	1.7982 1.7980	vvw	1 2	2	3 12 1 4 2 0
1.7639	1.7646	w	10	5	0 20 0
1.7505	1.7509	vw	5	3	4 5 0
1.7076	1.7074	vw	5	3	2 15 2
1.6585	1.6590	vw	4	2	1 1 4
1.6323	1.6322 1.6318	vw	3 5	4	1 4 4 0 21 1
1.6106	1.6108	vvw	2	1	3 5 3
1.5953	1.5953	m	14	7	1 15 3
1.5830	1.5828	vw	6	3	3 16 1
1.5672	1.5675	vw	5	3	0 20 2
1.5578	1.5579	m	9	5	4 5 2
1.5430	1.5432	vw	3	2	2 0 4
1.5363	1.5363	vw	5	3	0 10 4
1.5081	1.5076	w	8	4	2 5 4
1.4977	1.4980	m	14	7	3 10 3
1.4378	1.4381	m	10	5	2 20 2
1.4137	1.4139 1.4134	m	6 5	6	2 10 4 5 1 1
1.4038	1.4036	vvw	3	2	4 12 2
1.3939	1.3938	vw	7	4	3 20 1
1.3752	1.3753	vvw	2	1	5 6 1
1.3695	1.3692	w	4	2	1 20 3
1.3528	1.3533	vvw	2	1	3 15 3
1.3299	1.3306	vw	4	2	5 9 1
1.3214	1.3215	vw	4	2	4 15 2
1.3177	1.3179	w	8	4	1 5 5

[a] Overlapping intensities are summed, then scaled to 100.

TABLE III

ATOMIC PARAMETERS USED IN SPACE GROUP $R\bar{3}$ FOR CALCULATING X-RAY POWDER DIFFRACTION INTENSITIES OF $Sr_9Nd_5Cl_{33}$ (*7*)

Atom	No. of atoms in position	Coordinate		
		x/a	*y/b*	*z/c*
Sr(1) Nd(1)	3.132 1.741	0.0	0.0	0.7561
Sr(1′) Nd(1′)	0.725 0.403	0.0	0.0	0.7286
Sr(2) Nd(2)	11.57 6.426	0.0990	0.4486	0.5793
Sr(3) Nd(3)	6.838 3.800	0.2639	0.2124	0.5879
Sr(3′) Nd(3′)	4.732 2.629	0.2469	0.1978	0.5806
Cl(1)	6.	0.0	0.0	0.8785
Cl(2)	18.	0.3145	0.4363	0.6291
Cl(3)	18.	0.4879	0.3924	0.5444
Cl(4)	18.	0.2334	0.1805	0.7036
Cl(5)	18.	0.2187	0.3302	0.4999
Cl(6)	18.	0.0389	0.1842	0.6122
Cl(7)	3.	0.0495	0.0583	0.4936

flections were particularly sensitive to the occupancy parameter. The ordered arrangement in which the Sr^{2+} atoms occupied the sites designated as divalent by Eitel could be rejected readily on the basis of severe intensity mismatch. The random occupancy arrangement listed in Table III gave the best fit. Observed and calculated interplanar *d*-spacings and intensity data are presented in Table IV; lattice parameter data are presented in Table I.

TABLE IV

OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS AND INTENSITIES FOR HEXAGONAL $Sr_9Nd_5Cl_{33}$

d_{obs}	d_{calc}	I_{obs}	I_{calc}	$\Sigma I_{calc}{}^a$	*h k*	*l*
10.208	10.193	vvw	1	1	1 0	1
6.446	6.454	w	4	4	1 1	0
5.446	5.453	w	2	2	0 2	1
5.087	5.096	vw	1	1	2 0	2
4.137	4.137	s	43	38	0 0	6
3.998	3.999	vs	1	89	1 2	2
			100		2 1	−2
3.720	3.726	vw	1	2	3 0	0
	3.712		1		2 0	5
3.492	3.493	s	39	35	2 1	4
3.398	3.398	vw	3	3	3 0	3
3.222	3.218	vvw	1	1	1 2	5
3.007	3.007	m	1	8	2 2	3
			8		2 2	−3
2.774	2.777	m	7	19	4 0	1
	2.774		9		3 1	−4
	2.769		5		0 3	6
2.718	2.716	m	7	12	2 1	7
			6		1 2	−7
2.630	2.630	m	9	9	3 1	5
			1		1 3	−5
2.547	2.548	w	2	6	4 0	4
	2.545		5		2 2	6
2.504	2.511	vs	10	100	2 3	2
			4		3 2	−2
	2.501		3		1 2	8
			94		2 1	−8
2.438	2.439	vs	87	77	1 4	0
2.340	2.340	w	2	4	4 1	3
			3		4 1	−3
2.280	2.279	vw	1	2	2 3	5
			1		3 2	−5
2.228	2.227	vw	3	3	0 5	1
2.217	2.217	vw	1	2	3 0	9
	2.212		1		0 1	11
2.197	2.195	vvw	1	2	4 0	7
	2.193		1		3 1	8
2.142	2.140	s	32	28	2 1	10
2.103	2.101	s	24	44	1 4	6
			24		1 4	−6
			1		4 1	6
			1		4 1	−6
2.080	2.082	m	22	22	4 2	2
			3		2 4	−2
2.0002	1.9999	w	1	5	2 4	4
			5		4 2	−4
1.9768	1.9768	vw	2	4	2 3	8
			2		3 2	−8
1.9101	1.9104	vw	2	2	5 1	5

Because Eu_4Cl_9 has been characterized, the existence of Sr_3NdCl_9 seemed probable. Consequently, a search was made for reflections which might be assignable to this phase. A consistent reflection set could not be identified in any of the X-ray photographs of compositions between $MCl_{2.18}$ and $MCl_{2.25}$.

Discussion

It is well-known that some fluorite-type crystals can form solid solutions with trivalent lanthanoid ions. Solid state solution regions have been reported in the systems $SrCl_2$–$LaCl_3$ (*15*), $SrCl_2$–$EuCl_3$ (*20*), $SrCl_2$–$PrCl_3$ (*21*), and $SrCl_2$–$GdCl_3$ (*21*). The $SrCl_2$–$LaCl_3$ and $SrCl_2$–$PrCl_3$ solid solution regions have been examined extensively by neutron diffraction in an effort to locate the excess chloride ions (*22*). According to our X-ray powder diffraction data, the solubility limit of $NdCl_3$ in $SrCl_2$ is about 18 mole%. This result is close to that obtained by Brauer and Mueller (*15*) for the related $LaCl_3$–$SrCl_2$ system—up to 22.5 mole% $LaCl_3$ dissolved into $SrCl_2$ without disrupting the latter's fluorite structure.

The atomic coordinates of Nd^{3+} ions in this solid solution region are not known, but it is generally accepted that trivalent cations occupy a normal cation site in the $SrCl_2$ lattice. This assumption is consistent with recent structural studies on the doped fluoride systems $Ca_{(1-x)}Y_xF_{(2+x)}$ and $Pb_{(1-x)}Zr_xF_{(2+2x)}$ (*23, 24*), and with the neu-

TABLE IV—*Continued*

d_{obs}	d_{calc}	I_{obs}	I_{calc}	$\Sigma I_{calc}{}^a$	$h\ k$	l
1.8171	1.8177	vvw	1	2	0 6	3
			1		6 0	3
1.7458	1.7463	m	23	21	4 2	8
			1		2 4	−8
1.6968	1.6964	vw	2	3	3 3	9
			1		3 3	−9
1.6423	1.6429	vw	2	4	2 5	−6
			1		5 2	6
			1		5 2	−6
1.6091	1.6089	w	11	10	4 2	−10
1.5840	1.5840	m	7	15	0 7	2
			2		5 3	2
			7		3 5	−2
	1.5838		1		4 4	3
1.5613	1.5611	vw	1	4	1 5	−10
			3		5 1	10
1.5469	1.5472	vw	1	2	6 2	1
			1		2 6	−1
	1.5467		1	2	3 5	4
			1		7 0	4
1.5366	1.5365	vvw	1	2	1 6	7
			1		6 1	−7
1.5034	1.5033	vvw	1	3	4 4	6
			3		4 4	−6
1.4938	1.4942	vw	2	4	1 6	−8
			2		6 1	8
1.4567	1.4564	m	19	17	2 1	16
1.4195	1.4200	m	10	18	3 5	−8
			10		0 7	8
1.4082	1.4085	w	9	8	6 3	0
1.3943	1.3941	vw	3	3	1 7	6
1.3432	1.3431	w	4	8	7 0	10
			1		5 3	−10
			4		3 5	10
1.3332	1.3333	w	3	5	6 3	6
			2		6 3	−6
1.3245	1.3242	vvw	1	1	3 4	−13

[a] Overlapping intensities are summed, then scaled to 100.

tron diffraction studies on the $SrCl_2$–$LaCl_3$ and $SrCl_2$–$PrCl_3$ systems (*22*). Brauer and Mueller suggested that the extra chloride ion is positioned in the body center of the unit cell, but that hypothesis is inconsistent with recent results. In the $Ca_{(1-x)}Y_xF_{(2+x)}$ fluorite-related system extra anions are accommodated by transformation from cubic into nearly perfect square antiprism coordination. This change enables solid solution for values of x which can even exceed 0.5 to be accommodated. The neutron diffraction studies of the $SrCl_2$–$RECl_3$ (RE = La and Pr) solid solution regions, including a single-crystal neutron diffraction study of $Sr_{0.9}Pr_{0.1}Cl_{2.10}$, suggested that the excess anions are located at $(\frac{1}{2}vv)$, $v \approx 0.37$, and (x,x,x), $x \approx 0.29$ (*22*). The anion excess fluorite-related phase U_4O_{9-y} has been treated as a cluster arrangement with the excess anions situated in 13-member groups formed by corner sharing of octahedral sets of UO_8 square antiprisms (*25*). This type of arrangement is probably the one present in these anion excess phases, even though the maximum region of solid solution in this $SrCl_2$–$NdCl_3$ system, 0.18 mole%, could be accommodated with any of these models.

As expected, the powder intensity values calculated with the extra anions located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for $Sr_{0.9}Nd_{0.1}Cl_{2.1}$ are in only fair agreement with the observed values. The reflections $h + k + l$ = (an odd multiple of 2) are accounted for satisfactorily whether or not excess chloride ion is present in the cell and presumably result from the difference in scattering power of Sr and Nd.

The volume of the fluorite-type $SrCl_2$ cell remains essentially constant as Nd^{3+} (1.249 Å, CN 8) substitutes for Sr^{2+} (1.40 Å, CN 8) (*5*). This absence of a volume change presumably results because of more efficient packing of the anions around the trivalent cations, and has been observed in other mixed-cation systems (*26*).

The lattice parameters derived for Sr_4NdCl_{11} and $Sr_9Nd_5Cl_{33}$ are in good agreement with those reported for the corresponding Eu_5Cl_{11} and $RE_{14}Cl_{33}$ (RE = Nd and Eu) phases (*7*, *8*). Intensities calculated for these phases are also in good agreement with the observed values and every reflection observed in the Guinier photographs could be assigned to one of these phases, to $NdCl_3$, or to

$Sr_{(1-x)}Nd_xCl_{(2+x)}$, $0 < x < 0.18$. It is interesting to note that the cation arrangement in Sr_4NdCl_{11} is ordered, whereas that in $Sr_9Nd_5Cl_{33}$ is random. The reason for this different behavior is not known.

The absence of the M_4Cl_9 phase which was found in the $EuCl_2$–$EuCl_3$ system, is somewhat surprising. To facilitate the search for M_4Cl_9 the expected X-ray powder pattern was calculated (*14*) by using Baernighausen's (*8*) lattice parameters for Eu_4Cl_9 and Loechner's positional and thermal parameters for Nd_4Br_9 (*7*). The Sr^{2+} scattering factor was used for cation positions 5, 6, 7, and 8 which are believed to be occupied by Nd^{2+}; space group number 13, *P2/b*. This ordered arrangement was chosen on the assumption that this vernier structure would be similar to Sr_4NdCl_{11} in cation occupancy. Because of the close relationships among these vernier-type phases and fluorite-type $SrCl_2$, the most intense reflections expected for Sr_3NdCl_9 fall within regions of reciprocal space where potential for reflection overlap is severe. But most of the moderately intense reflections expected for the M_4Cl_9 phase, i.e., ~20 on a scale of 100, fall at reciprocal space locations where phase separation is complete. Consequently, although the presence of the M_4Cl_9 phase as a minor component as a result of disproportionation of a high-temperature stable phase cannot be ruled out on the basis of the X-ray powder diffraction data, its presence is deemed unlikely.

In the $NdCl_2$–$NdCl_3$ system the oxide-containing phase $Nd_{14}Cl_{32}O$ was also characterized. On the basis of our experimental data it is impossible to ensure that the reported hexagonal phase, $Sr_9Nd_5Cl_{33}$, is not actually $Sr_8Nd_6Cl_{32}O$. Although neither oxide nor oxide–chloride was present in the reactants, it is possible that while the specimen was in contact with quartz oxide ions could have replaced the chloride ions, oxidizing the specimen to $Sr_8Nd_6Cl_{32}O$ and simultaneously producing the lower chloride Sr_4NdCl_{11}. But because in this situation a Sr^{2+} ion must be replaced by an Nd^{3+} ion, such an oxidation process would have to overcome a much higher energy barrier than it would in the neodymium system, and consequently is less likely to occur.

In summary, solid strontium dichloride and neodymium trichloride, while not significantly soluble in each other, interact to form two intermediate chlorides: Sr_4NdCl_{11} and $Sr_5Nd_9Cl_{33}$.

Acknowledgments

Support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program DMR-84-00739 is acknowledged gratefully. Numerous helpful criticisms from two anonymous referees are also acknowledged.

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