

dissymmetry. Furthermore this length is certainly an overestimate since coiling of chains and/or cross linking would result in a decrease in the longest dimension of the particle.

The results of the present study seem to be best summarized by a hydrolytic process for thorium whereby a continuous series of aggregates are formed above  $\bar{n} = 1.0$ , beginning with the formation of dinuclear and trinuclear species near hydroxyl number 1.5–2.0 and leading to the formation of very large particles prior to precipitation of hydrous oxide or basic salts above hydroxyl number 3.0. Although no measurements were made between hydroxyl numbers 2.0 and 3.0, the existence of polymers of intermediate molecular weight seems quite likely in this range. Such a continuous polymerization scheme for hydrolysis would lend cre-

dence to the hypothesis that hydrous oxide or basic salt structures are approximated in solution prior to precipitation, but the validity of this theory and the general nature of this phenomenon are subject to the results of considerable further work along these lines.

Finally, the results of this work are believed to be of the usual accuracy obtained in light-scattering work, the polymerization numbers reported being most likely accurate to within less than  $\pm 10\%$ .

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## The Phase Equilibria and Crystal Chemistry of the Rare Earth Group VI Systems. III. Neodymium-Tellurium<sup>1</sup>

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The phases occurring in the neodymium-tellurium system are: NdTe, f.c.c.  $a = 6.278 \text{ \AA}$ , m.p. 2040°. A solid solution series  $\text{Nd}_3\text{Te}_4$ - $\text{Nd}_2\text{Te}_3$  which has a high temperature,  $\text{Th}_3\text{P}_4$ -type structure, whose cubic lattice constant varies from 9.434 to 9.424  $\text{ \AA}$ , respectively; a phase transition occurs at 1000° to an orthorhombic modification, Pbnm,  $a = 11.94 \text{ \AA}$ ,  $b = 12.24 \text{ \AA}$ ,  $c = 4.407 \text{ \AA}$ ;  $\text{Nd}_2\text{Te}_4$  melts at 1680° and  $\text{Nd}_2\text{Te}_3$  melts at 1620°. A solid solution series exists over the composition range  $\text{NdTe}_{1.74}$  to  $\text{NdTe}_2$ ; the tetragonal unit cell for  $\text{NdTe}_2$  has dimensions  $a = 4.419 \text{ \AA}$ ,  $c = 9.021 \text{ \AA}$ , space group  $P^{+4}_1/\text{mmm}$ , and the compound melts at 1270°. The phase  $\text{Nd}_2\text{Te}_5$  is orthorhombic, pseudotetragonal,  $a = b = 4.380 \text{ \AA}$ ,  $c = 44.0 \text{ \AA}$ , space group Bmmb, and melts incongruently at 910°.  $\text{NdTe}_3$  is orthorhombic, Bmmb, and the dimensions of the pseudotetragonal cell are  $a = 4.350 \text{ \AA}$ ,  $c = 25.8 \text{ \AA}$ . The compound melts incongruently at 830°.

### Introduction

Two intermediate phases in the neodymium-tellurium system, NdTe and  $\text{Nd}_2\text{Te}_3$ , have been reported. Iandelli<sup>2</sup> found that NdTe was isostructural with NaCl, and  $\text{Nd}_2\text{Te}_3$  has been shown by Miller, *et al.*,<sup>3</sup> to exhibit solid solubility ranging to the composition  $\text{Nd}_3\text{Te}_4$ . The body-centered cubic  $\text{Th}_3\text{P}_4$ -type structure, which is frequently observed for rare earth-group VI compounds having the 2:3-3:4 composition range, is observed for  $\text{Nd}_2\text{Te}_3$ , although Miller<sup>3</sup> and Flahaut, *et al.*,<sup>4</sup> report a phase transformation to the orthorhombic system below 1000°. No complete investigation of the binary phase diagram has been reported and the aim of this investigation is to determine all the intermediate phases

which exist in this system and to study their crystal chemistry.

### Experimental

Neodymium ingots of 99.9% purity were obtained from the Nuclear Corporation of America and tellurium of 99.99% purity was obtained from the American Smelting and Refining Co. The region of the phase diagram 60–100 atom % Te was investigated by sealing the appropriate compositions of the elements in evacuated silica tubes and allowing them to react for at least 2 weeks at temperatures below 700°. Extensive reaction between neodymium metal and the silica surfaces occurred if the reaction temperature exceeded 700°. The intermediate phases  $\text{NdTe}_3$ ,  $\text{Nd}_2\text{Te}_5$ , and  $\text{NdTe}_2$ - $\text{NdTe}_{1.74}$  were prepared in this manner. Mixtures containing less than 60% tellurium did not yield satisfactory results because at temperatures below 700° equilibrium could not be established and higher temperatures caused the formation of  $\text{Nd}_2\text{O}_3$ . In order to prepare the neodymium-rich compounds the mixtures were allowed to prereact in silica tubes for approximately 100 hr. and then sealed into tantalum tubes. These specimens were then heated in a vacuum induction furnace at approximately 2000° for 2–5 min. This procedure was very satisfactory for the preparation of  $\text{Nd}_2\text{Te}_3$  and its solid solution compositions and for NdTe. The reacted, neodymium-rich, compositions can be equilibrated in silica tubes

(1) This work is being sponsored by a grant from the U. S. Air Force Office of Scientific Research.

(2) A. Iandelli, *Gazz. chim. ital.*, **85**, 881 (1955).

(3) J. F. Miller, F. D. Reid, C. K. Matson, S. W. Moody, R. D. Baxter, and R. C. Himes, Technical Documentary Report No. AL TDR 64-239, Office of Technical Service, U. S. Department of Commerce, Washington, D. C., 1964.

(4) J. Flahaut, L. Domange, M. Guittard, M. P. Pardo, and M. Patrie, *Compt. rend.*, **257**, 1530 (1963).

at high temperatures and no attack on the container surfaces occurs. Although no visible reaction with the quartz container surfaces took place, minute amounts of oxygen contamination in the samples cannot be ruled out.

Single crystal and powder X-ray diffraction techniques were used to identify the phases. Microscopic examination of the reacted materials was very useful because the differences in color of the various phases served as a good criterion for their identification. The chemical composition of the specimens was determined by a chelometric titration of neodymium,<sup>5</sup> and tellurium was determined by the sodium thiosulfate procedure. The densities of the materials were determined by the displacement method using acetone as the liquid.

## Results

**Phase Diagram.**—The condensed phase diagram for the Nd-Te system is shown in Figure 1. The solid lines represent that portion of the diagram which was located from a study of quenched samples and the dashed lines represent areas which are uncertain. The solid dots of Figure 1 represent the compositions

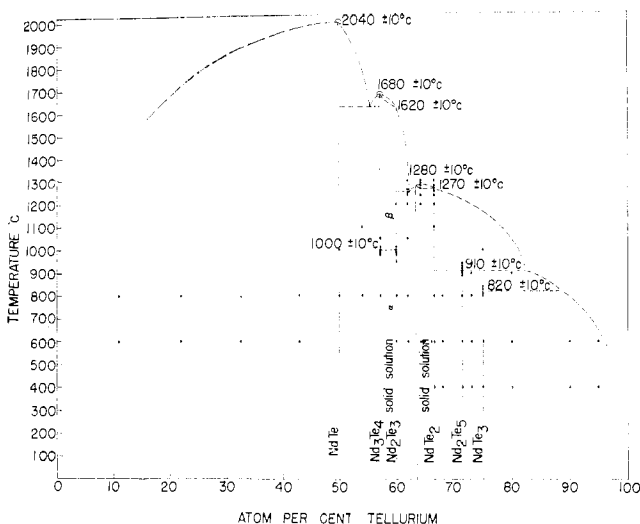


Figure 1.—The condensed phase diagram, Nd-Te. Full circles represent quench data; open circles are observed melting points. The dashed lines indicate uncertain phase boundaries.

which were quenched at those temperatures and the open circles represent melting point observations. The system has five intermediate phases and two regions of continuous solid solubility. Two of the phases melt incongruently and one phase displays a phase transition.

X-Ray diffraction powder patterns of samples quenched at 400° containing 95, 90, and 80 atom % Te showed the presence of Te and NdTe<sub>3</sub>, while these compositions quenched at 600° showed the presence of NdTe<sub>3</sub> and melt. No attempts were made to define a eutectic point precisely.

Quenching studies of single phase NdTe<sub>3</sub> specimens at various temperatures and subsequent X-ray diffraction and microscopic examination showed that this phase melts incongruently at 820 ± 10°. Specimens, with tellurium compositions between 75 and 71.4 atom %, which were quenched at temperatures below

820° contained Nd<sub>2</sub>Te<sub>5</sub> and NdTe<sub>3</sub> in equilibrium, while observations on such samples between 820 and 910° showed Nd<sub>2</sub>Te<sub>5</sub> and melt. The determination of the melting point of Nd<sub>2</sub>Te<sub>5</sub> by quenching studies of the single phase material shows that the compound undergoes a peritectic decomposition to NdTe<sub>2</sub> and melt at 910 ± 10°. X-Ray diffraction patterns obtained from compositions containing 71.4 to 66.7 atom % Te and quenched below 910° reveal the presence of NdTe<sub>2</sub> and Nd<sub>2</sub>Te<sub>5</sub>.

Specimens containing 66.7 atom % Te as well as samples prepared with slightly lower Te contents had identical X-ray patterns, except that the diffraction lines shifted their positions. The lattice parameters of the end members of this solid solution series were determined from specimens quenched from the two-phase regions NdTe<sub>2</sub>-Nd<sub>2</sub>Te<sub>5</sub> and NdTe<sub>2-x</sub>-Nd<sub>2</sub>Te<sub>5</sub>. The composition of the tellurium-deficient end member was established as NdTe<sub>1.74</sub> by preparing samples which varied in steps of 0.1 atom % Te and determining the shifts of the lattice parameters. After the appearance of the second phase, Nd<sub>2</sub>Te<sub>5</sub>, no further shifts in the lattice parameters take place, Figure 2. Samples of

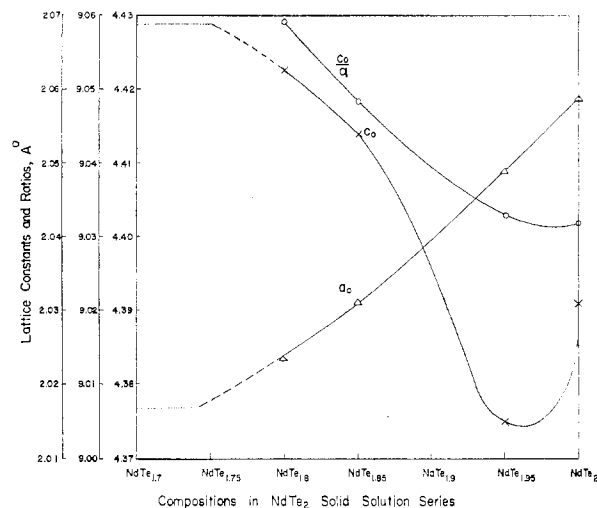


Figure 2.—Room temperature variation of lattice constants,  $c$ ,  $a$ , and  $c/a$  as a function of composition in NdTe<sub>2</sub> solid solution.

NdTe<sub>2</sub> which were sealed into evacuated quartz ampoules and quenched above 1100° are believed to be deficient in Te because the lattice parameters were observed to shift. The observed changes did not indicate that the end members tend toward the same composition as the melting point is approached, but this possibility cannot be excluded. It is assumed that if initially the compound had been contained under atmospheric pressure it would not have dissociated, and therefore the lines in Figure 1 representing the end members of the solid solution series are shown vertical. Specimens quenched at 1260° showed no change in appearance and were recovered as granular powders, while specimens quenched at 1270° and above were recovered as buttons and had obviously been molten. The quenching did not proceed rapidly enough because the melted material gave the diffraction patterns of the

(5) J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, *Anal. Chem.*, **30**, 1111 (1958).

TABLE I  
 CRYSTALLOGRAPHIC DATA FOR COMPOUNDS IN THE NEODYMIUM-TELLURIUM SYSTEM

Compound	Space group	Unit cell dimensions, Å.	X-Ray density, g./cc.	Measd. density, g./cc.	Molecules per unit cell	M.p., °C.	Color
NdTe <sub>3</sub>	Bmmb	$a = b = 4.350$ $c = 25.8$	7.17	7.00	4	820 <sup>b</sup>	Gold
Nd <sub>2</sub> Te <sub>5</sub>	Bmmb	$a = b = 4.380$ $c = 44.0$	7.29	7.10	4	910 <sup>b</sup>	Dark gold
NdTe <sub>2</sub> <sup>a</sup>	P <sup>4</sup> / <sub>n</sub> mm	$a = 4.419$ $c = 9.021$	7.53	7.35	2	1270	Black
NdTe <sub>1.74</sub> <sup>a</sup>	P <sup>4</sup> / <sub>n</sub> mm	$a = 4.377$ $c = 9.060$					Silver-gray
Nd <sub>2</sub> Te <sub>3</sub> <sup>a</sup>	I $\bar{4}$ 3d	$a = 9.424$	7.10	7.30	5.33	1620	Silver-gray
Nd <sub>3</sub> Te <sub>4</sub> <sup>a</sup>	I $\bar{4}$ 3d	$a = 9.434$	7.46	7.33	4	1680	Black
Nd <sub>2</sub> Te <sub>3</sub> -Nd <sub>3</sub> Te <sub>4</sub> Low-temperature form	Pbnm	$a = 11.94$ $b = 12.24$ $c = 4.407$			4	1000 <sup>c</sup>	
NdTe	Fm3m	$a = 6.278$	7.30	7.5	4	2040	Purple

<sup>a</sup> Solid solution series. <sup>b</sup> Incongruent. <sup>c</sup> Phase transition.

crystalline compound. It is considered that melting occurred congruently because the liquid appears to have had the same composition as the solid, and the behavior is indicated in Figure 1 as analogous to the melting of the Nd<sub>2</sub>Te<sub>3</sub>-Nd<sub>3</sub>Te<sub>4</sub> solid solution.

A region of solid solubility exists between the limits 60-57.1 atom % Te. The phase transformation of the high-temperature, Th<sub>3</sub>P<sub>4</sub>-type structure to the low-temperature, orthorhombic structure occurs at 1000 ± 10°. The melting points of Nd<sub>2</sub>Te<sub>3</sub> and Nd<sub>3</sub>Te<sub>4</sub> were determined by a procedure previously described<sup>6</sup> and are considered to be congruent because the molten material after solidification always had the X-ray diffraction pattern of the crystalline solid.

Only one additional intermediate compound, NdTe, exists. The procedure to establish the melting point and the evidence for believing that it is congruent are the same as for Nd<sub>2</sub>Te<sub>3</sub>.

**Crystal Data.**—The crystallographic and physical parameters for the intermediate phases are summarized in Table I. The X-ray powder diffraction data are given in Table II.

**NdTe<sub>3</sub>.**—The compound is easily identified by its striking gold color, metallic luster, and brittleness; it will tarnish slowly when exposed to air. Single crystal X-ray data can be indexed on a pseudo-tetragonal cell, although the diffraction symmetry is orthorhombic and the extinctions place the crystal into space group Bmmb (No. 63) or into one of the other two space groups consistent with these extinctions. The crystal structure appears to consist of layers of neodymium and tellurium atoms which are stacked along the *c* axis. It is isostructural with ErTe<sub>3</sub><sup>6</sup> and LaTe<sub>3</sub>.<sup>7,8</sup> *Anal.* Calcd. for NdTe<sub>3</sub>: Nd, 27.37; Te, 72.63. Found: Nd, 26.6; Te, 72.1.

**Nd<sub>2</sub>Te<sub>5</sub>.**—This compound is similar in color to NdTe<sub>3</sub> but has a darker metallic luster. This similarity

caused difficulty in distinguishing optically between the two compounds in the early part of the study. The X-ray powder pattern is similar to that of NdTe<sub>3</sub> and initially it was thought to be part of a Nd-rich solid solution of this phase. Single crystal diffraction data can be indexed on a pseudo-tetragonal cell. Ordered single crystals are difficult to obtain and most of them display stacking faults, but those which are ordered have diffraction symmetry which is orthorhombic, and *hkl* reflections are present when  $h + l = 2n$ ;  $hk0$  when  $k = 2n$ . The space group is Bmmb or one of the other two space groups consistent with these extinctions. The material tarnishes easily in air and its color turns from dark gold to gray-black within several hours. After several days of exposure to the atmosphere a single crystal mounted on a goniometer head produced only a powder pattern. *Anal.* Calcd. for Nd<sub>2</sub>Te<sub>5</sub>: Nd, 31.14; Te, 68.86. Found: Nd, 30.5; Te, 68.4.

**NdTe<sub>2</sub>-NdTe<sub>1.74</sub>.**—Single crystal X-ray patterns of NdTe<sub>2</sub> can be indexed on the basis of a tetragonal cell and the space group is P<sup>4</sup>/<sub>n</sub>mm. This phase is probably isostructural with Fe<sub>2</sub>As.<sup>9</sup> The limits of solid solubility were established by the procedure described above and the variations in lattice parameters are shown in Figure 2. *Anal.* Calcd. for NdTe<sub>2</sub>: Nd, 36.11; Te, 63.89. Found: Nd, 35.9; Te, 63.0.

**Nd<sub>2</sub>Te<sub>3</sub>-Nd<sub>3</sub>Te<sub>4</sub>.**—The high-temperature modification of this phase has the Th<sub>3</sub>P<sub>4</sub> structure. The cubic lattice parameters for the end members of the solid solution series were determined as 9.424 Å. for Nd<sub>2</sub>Te<sub>3</sub> and 9.434 Å. for Nd<sub>3</sub>Te<sub>4</sub>; Miller<sup>3</sup> reported the corresponding values as 9.439 and 9.456 Å. The small shift in lattice constant with increasing Nd content is typical of these solid solutions.<sup>7,10</sup> The color of Nd<sub>2</sub>Te<sub>3</sub> is silver-gray and gradually turns black as the composition changes to Nd<sub>3</sub>Te<sub>4</sub>. Single crystal X-ray patterns were obtained from both polymorphs and the high-temperature form has space group I $\bar{4}$ 3d; the low-temperature form is orthorhombic, space group Pbnm.

(6) D. J. Haase, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 541 (1965).

(7) T. H. Ramsey, Ph.D. Dissertation, University of Texas, Austin, Texas, 1964.

(8) F. L. Carter, *Metallurgy of Semiconductor Materials*, Interscience Publishers, New York, N. Y., 1961, p. 260.

(9) L. Domange, J. Flahaut, M. Pardo, A. Chirazi, and M. Guittard, *Compt. rend.*, **250**, 857 (1960).

(10) W. H. Zachariasen, *Acta Cryst.*, **2**, 57 (1949).

TABLE II  
 X-RAY POWDER DIFFRACTION DATA FOR THE INTERMEDIATE PHASES OF THE Nd-Te SYSTEM<sup>a</sup>

NdTe <sub>3</sub>				Nd <sub>2</sub> Te <sub>5</sub>				NdTe <sub>2</sub>			
d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub> *	d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub>	d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub>
3.22	3.225	008	s					3.96	3.97	101	w
3.06	3.058	016	w	3.13	3.136	00,14	s	3.16	3.16	102	w <sup>+</sup>
	3.054	111	vs	3.09	3.100	01,10	w	3.12	3.13	110	w <sup>+</sup>
2.90	2.896	113	vs		3.089	111		3.02	3.01	003	m
2.64	2.642	115	s	2.93	2.950	10,11	vs	2.95	2.95	111	vs
2.36	2.362	117	w		2.921	115		2.56	2.568	112	s
2.18	2.175	200	m	2.62	2.615	119	s	2.48	2.485	103	m
1.868	1.865	11,11	m	2.45	2.447	11,11	w	2.20	2.209	200	m <sup>+</sup>
	1.863	214			2.439	00,18		1.829	1.828	114	vw
1.847	1.843	00,14	w		2.433	10,15		1.805	1.804	005	vw
1.804	1.803	208	m	2.20	2.195	00,20	m	1.786	1.782	203	m
	1.806	10,13			2.190	200		1.670	1.670	105	w
1.669	1.666	218	w	1.855	1.852	11,19	w	1.648	1.651	213	w <sup>+</sup>
	1.668	11,13			1.845	218		1.558	1.562	115	w
	1.663	20,10		1.829	1.829	00,24	vw	1.425	1.424	106	w
1.538	1.538	220	m	1.800	1.795	20,14	m	1.395	1.397	130	vw
1.407	1.415	034	vw band	1.627	1.630	10,25,2018	vw broad		1.400	032	
	1.406	20,14			1.628	12,15			1.397	205	
1.389	1.388	228	w		1.625	11,23	+	1.357	1.355	116	vw
1.360	1.358	313	m	1.556	1.561	12,17	w <sup>+</sup>	1.332	1.333	215	m
	1.361	01& 11,17			1.550	20,20		1.198	1.196	216	w <sup>+</sup>
1.331	1.329	315	w		1.549	220		1.132	1.127	008	vw
1.290	1.289	317, 12,15	w band	1.404	1.404	20,24	vw broad	1.014	1.015	332	w
	1.293	309			1.399	309			1.014	325	
	1.295	20,16			1.398	21,22		1.006	1.004	208	w
	1.296	10,19		1.392	*		w	0.986	.984	333	vw
	1.290	00,20		1.374			w	0.980	.979	218	vw
1.190	1.195	323;12,17;20,18		1.361			w	0.957	.954	119	vw
1.187	1.186	234;31,11	w broad band	1.338			w <sup>-</sup>	0.949	.946	334	vw
	1.182	10,21		1.314			w <sup>-</sup>		.947	317	
1.183	1.181	22, 14		1.290			vw	0.920	.922	415	vw
1.176	1.175	325	w	1.222			vw				
	1.172	216		1.192			w broad				
	1.173	00,22		1.156			w				
1.034	1.034	145	w <sup>+</sup>	1.114			vw				
	1.030	408		1.101			vw				
	1.031	32,13;20,22		1.039			vw				
	1.039	12,21		1.023			w <sup>+</sup>				
1.020	1.025	331,416	w	.984			w <sup>+</sup>				
	1.018	333		.970			w <sup>+</sup>				
	1.019	31,17;03,18		.940			vw				
0.980	0.978	11,25	m <sup>-</sup>	.928			vw				
0.934	0.933	22,22;10,27	w <sup>-</sup>								
0.932	0.931	428;14,13	w								

\*vs=very strong s=strong m=medium w=weak vw= very weak  
 \*Due to the large c axis dimension, many different indices can be assigned to these lines and the resultant ambiguity makes it pointless to list them.

αNd <sub>2</sub> Te <sub>3</sub>				βNd <sub>2</sub> Te <sub>3</sub>				NdTe			
d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub>	d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub>	d <sub>obs.</sub> Å	d <sub>calc.</sub> Å	hkl	I <sub>obs.</sub>
4.27	4.27	220	vw					3.12	3.136	200	s
4.13	4.13	101	vw	2.98	2.980	310	vs	2.21	2.218	220	m
3.57	3.576	021	w	2.52	2.518	321	s	1.812	1.812	222	w
3.41	3.406	211	m broad	2.11	2.107	420	w	1.569	1.570	400	w <sup>+</sup>
3.37	3.369	230		2.01	2.009	332	w	1.403	1.404	420	w <sup>+</sup>
3.06	3.060	040	s	1.924	1.924	422	m	1.280	1.281	422	w
2.95	2.954	301	s	1.849	1.848	510, 431	m	1.109	1.110	440	vw
2.90	2.904	131	m	1.530	1.529	611, 532	m <sup>+</sup>	1.046	1.046	600, 442	w <sup>-</sup>
	2.900	410		1.493	1.490	620	w	0.992	0.993	620	w <sup>-</sup>
2.87	2.871	311	m	1.455	1.454	541	w				
2.71	2.723	240	w	1.390	1.390	631	w <sup>-</sup>				
2.67	2.683	420	vs	1.362	1.360	444	vw				
	2.676	231		1.335	1.333	710, 550, 543	vw				
	2.660	321		1.308	1.307	640	vw				
2.46	2.460	141	w	1.283	1.283	721, 633, 552	m <sup>-</sup>				
2.42	2.426	340	vw	1.258	1.259	642	w				
	2.423	411		1.198	1.197	732, 651	w				
2.39	2.393	331	vw	1.128	1.126	653	w <sup>-</sup>				
2.31	2.317	241	vw	1.112	1.111	822, 660	w <sup>-</sup>				
2.28	2.292	421	vw	1.096	1.096	831, 750, 743	w				
2.195	2.204	002	m	1.069	1.067	752	w <sup>-</sup>				
2.054	2.061	530		1.030	1.028	842	vw				
1.879	1.883	540	w	1.018	1.016	921, 761, 655	m <sup>-</sup>				
	1.885	351		0.995	0.993	930, 851, 754	w <sup>+</sup>				
1.839	1.839	322	vw	0.974	0.972	932, 763	vw				
1.815	1.815	360	vw	0.917	0.915	10,40; 864	w <sup>-</sup>				
1.508	1.509	470	vw								
1.501	1.505	371, 532	w								
	1.497	062									

<sup>a</sup> All patterns were obtained with nickel-filtered copper radiation.

**NdTe.**—This phase has been reported as isostructural with NaCl.<sup>2,3</sup> Powder diffraction patterns taken with Cu K $\alpha$  radiation do not show diffraction lines for odd Miller indices. Such lines are due to the difference of the scattering power of the two atoms and with this radiation the difference is further decreased because of the dispersion corrections. The ratio of intensities of (200) to (111) is approximately 10<sup>3</sup> and it is therefore not surprising that (111) is not observed in a powder pattern. A very long exposure of a single crystal of NdTe using Mo K $\alpha$  radiation and a precession camera showed that the (111) reflection was present and confirms the ordered, NaCl-type, arrangement of the atoms.

### Discussion

The intermediate phases common to this system and the lanthanum-tellurium system<sup>7</sup> are isostructural and also duplicate the melting behavior, except that the lanthanum analogs melt at somewhat lower temperatures. The presence of the Nd<sub>2</sub>Te<sub>5</sub> phase is unique

for this system. The X-ray diffraction patterns for NdTe<sub>3</sub> and Nd<sub>2</sub>Te<sub>5</sub> are very similar and the materials also have the same space group, so that the layer structures are very much alike. The compound NdTe<sub>3</sub> contains two Nd layers and six Te layers in the unit cell which on the average are 3.2 Å. apart. Nd<sub>2</sub>Te<sub>5</sub> results from a substitution of some Te layers by Nd in the NdTe<sub>3</sub> structure so that the ordered structure contains four Nd and ten Te layers in the unit cell which on the average are 3.14 Å. apart. The shrinkage of the layer separation is due to the introduction of a smaller rare earth atom for the metalloid.

The phase transition exhibited by Nd<sub>2</sub>Te<sub>3</sub>-Nd<sub>3</sub>Te<sub>4</sub> solid solution compositions is not observed in the corresponding lanthanum compounds. The low-temperature structure appears to be isostructural with Sb<sub>2</sub>S<sub>3</sub><sup>4</sup> and Sb<sub>2</sub>Se<sub>3</sub>.<sup>11</sup> The occurrence of this transition may be a function of the radius ratio.<sup>4</sup>

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## Crystal Structure of Hexagonal Sodium Neodymium Fluoride and Related Compounds<sup>1</sup>

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A single-crystal X-ray analysis has established the structure of hexagonal NaNdF<sub>4</sub>. The unit cell has  $a = 6.100$ ,  $c = 3.711$  Å.; the space group is P $\bar{6}$ . Fluoride ions lie in triangular arrays at  $z = 0, 1/2$ . Cation sites are of three types: a onefold site occupied by Nd<sup>3+</sup>, a onefold site occupied randomly by  $1/2\text{Na}^+$ ,  $1/2\text{Nd}^{3+}$ , and a twofold site occupied randomly by Na<sup>+</sup> and vacancies. The fluoride coordination about the first two sites is ninefold, a trigonal prism with each vertical face bearing a pyramid, and about the third site is irregular octahedral. It is proposed that this structure becomes the same as that of several other compounds having Nd<sup>3+</sup> replaced by other rare earth ions or Y<sup>3+</sup> and of the mineral gagarinite when the cations of the first two sites are completely intermixed. Bond distances and thermal displacements are given for NaNdF<sub>4</sub>.

### Introduction

Sodium neodymium fluoride is a member of a series of 1:1 compounds existing in the binary systems NaF-MF<sub>3</sub>, in which M is a rare earth or yttrium atom. The phase diagrams for these systems were reported by Thoma<sup>2</sup> and further details are forthcoming. Of interest to the present work is that all of the NaMF<sub>4</sub> compounds have a hexagonal crystalline form, while those for M = Y and Nd to Lu have a high-temperature form with the cubic, fluorite structure. Hund<sup>3</sup> deduced the structure of high-temperature NaYF<sub>4</sub> and concluded that Na<sup>+</sup> and Y<sup>3+</sup> ions are distributed randomly over the cation sites. Recently the low-temperature NaYF<sub>4</sub> was observed to be hexagonal by

Burns<sup>4</sup> and by Roy and Roy,<sup>5</sup> who assigned to it the  $\beta_2$ -Na<sub>2</sub>ThF<sub>6</sub> structure proposed by Zachariasen<sup>6</sup> for NaLaF<sub>4</sub> and NaCeF<sub>4</sub>, and by Sobolev *et al.*,<sup>7</sup> who called it isomorphous with the mineral gagarinite,<sup>8</sup> NaCaMF<sub>6</sub>.

A complete single-crystal structure analysis has been carried out to establish the details of the hexagonal form of NaNdF<sub>4</sub>, to resolve the points of conflict, and to aid in explaining the phase behavior of NaF-MF<sub>3</sub> systems.

### Experimental

A 1:1 mixture of NaF and NdF<sub>3</sub> was melted and allowed to cool slowly; large, violet crystals of NaNdF<sub>4</sub> were obtained. X-Ray

(1) Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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