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The Phase Equilibria and Crystal Chemistry of the Rare Earth–Group VI Systems. IV. Lanthanum–Tellurium[1]

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The phases occurring in the lanthanum–tellurium system are LaTe, f.c.c., $a = 6.436$ Å., m.p. 1720°; a solid solution series La_3Te_4–La_2Te_3 which has the Th_3P_4-type structure, the cubic lattice constant for the two end members are $a = 9.628$ and 9.619 Å., respectively, and they melt at 1515 and 1485°; a solid solution series $LaTe_{2.0}$–$LaTe_{1.7}$, the tetragonal unit cell for $LaTe_{2.0}$ has dimensions $a = 4.506$ Å., $c = 9.13$ Å. and melts incongruently at 1450°; and finally the phase $LaTe_3$, orthorhombic, with a pseudo-tetragonal cell $a = b = 4.41$ Å., $c = 26.1$ Å., which melts incongruently at 835°.

Introduction

The intermediate phases which have been reported for the system La–Te are LaTe,[2] La_2Te_3,[3,4] La_3Te_4,[4] $LaTe_2$,[5] and $LaTe_3$.[6] These compounds were produced and investigated as part of a study on a particular stoichiometry Ln_yX_z, where Ln represented a series of rare earth elements and X was an element of group VI of the periodic table. We have systematically investigated the intermediate phases which exist in the binary rare earth–group VI systems[7–9] in order to determine their crystal chemistry and physical properties,[10,11] and the study of the La–Te system is part of this continuing investigation.

Experimental

Lanthanum metal of 99.9% purity and tellurium of 99.99% purity were used in the preparation of the intermediate phases. Metal turnings were used initially in the preparations but oxide contamination was always extensive and metal chunks were therefore preferred for the reactions. The lanthanum ingots were mechanically cleaned while immersed in mineral oil to remove adhering oxide and then stored under mineral oil. Prior to use, the metal was washed with trichloroethylene. The reactions were first carried out in a horizontal Vycor tube in which lanthanum and tellurium were kept at opposite ends of the tube, and by suitable choice of the furnace temperatures vapor–solid and vapor–liquid reactions took place. This technique produced intermediate phases which were identified by powder X-ray diffraction techniques and served as standard patterns for compounds produced in the equilibrium investigation. The latter was carried out by sealing the appropriate compositions of the elements in evacuated silica tubes and allowing them to react at 600° for 3 days. The samples were then held at various temperatures up to 1000° for 2 weeks and quenched in oil or water baths. This procedure worked well for the preparations of $LaTe_3$ and the $LaTe_2$ solid solution series, but for compositions richer in lanthanum equilibrium conditions could not be achieved at 1000°. These reacted mixtures were sealed into tantalum tubes and heated in a vacuum induction furnace at approximately 2000° for several minutes. These compositions were then equilibriated at various temperatures for 2 weeks prior to quenching.

Single crystal and powder X-ray diffraction techniques were used primarily to identify the phases, although thermal and metallographic analyses were also used. The chemical composition of the specimens was determined by a chelometric titration of lanthanum,[12] 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 La–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 points of Figure 1 represent the compositions which were quenched at those temperatures and the open circles represent melting point observations at atmospheric pressure and in an inert environment. At compound melting points, the solid points are shown, although the temperatures were obtained by quenching as well as by melting in an inert atmosphere. The system has four intermediate phases and two regions of solid solubility.

The melting point of tellurium was verified by differential thermal analysis to be 450°, and this technique was also used to establish a eutectic point at approximately 400°; the eutectic composition is estimated to be more than 97 atom % Te. Quenching studies carried out between 75 and 95 atom % Te indicate only $LaTe_3$ and a melt in the region below 835°, and specimens quenched above that temperature showed the presence of $LaTe_2$ and melt. $LaTe_3$ undergoes a peritectic decomposition at 835°, but the composition of the peritectic point is uncertain because the melts in the region of about 90 atom % Te could not be quenched rapidly enough to prevent crystallization. An attempt to obtain cooling curves was made in the

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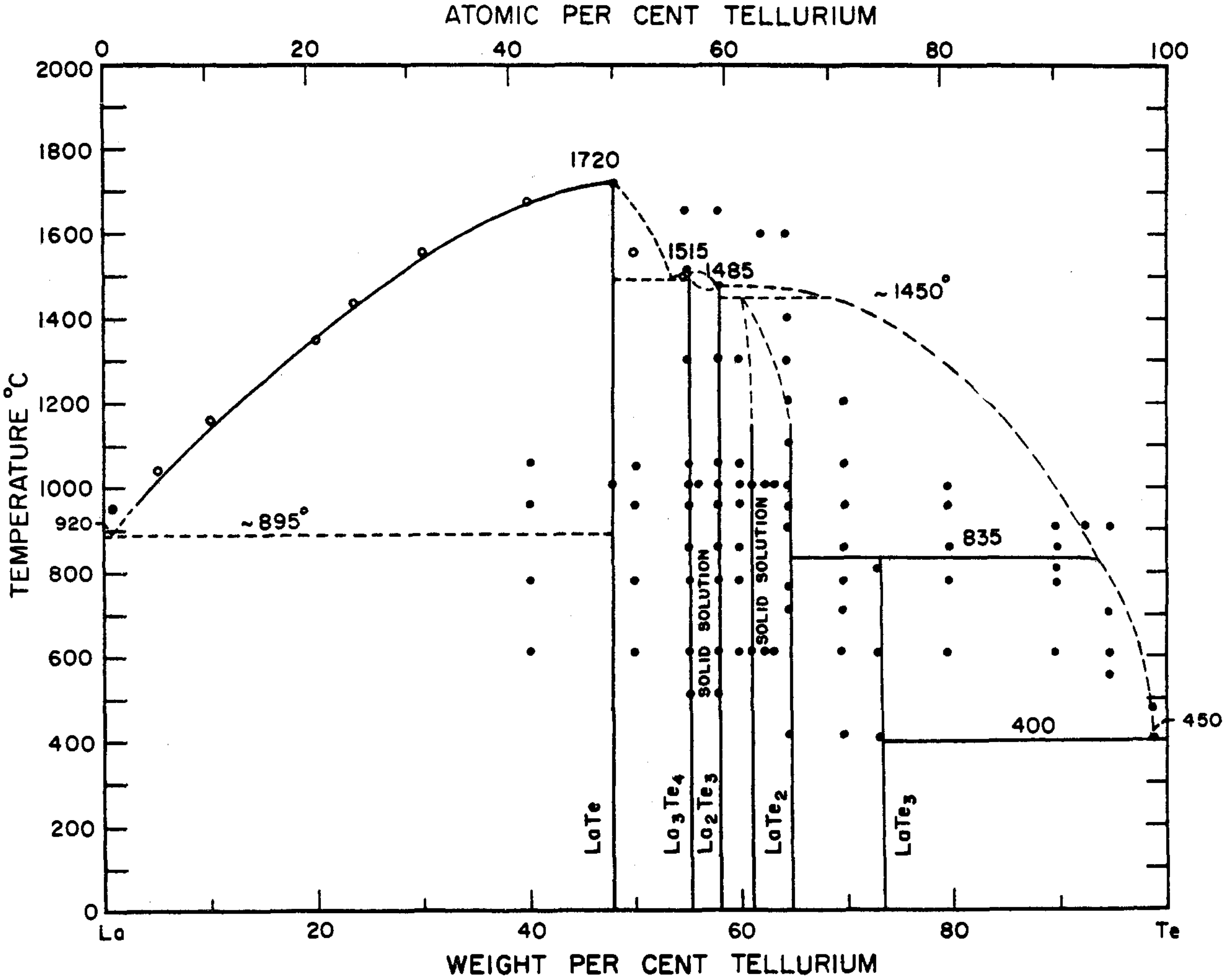

Figure 1.—The condensed phase diagram, La–Te. Full circles represent quench data; open circles are observed melting points. The dashed lines indicate uncertain phase boundaries.

region below 1000°, but the poor thermal conductivity of the silica ampoules prevented the observation of definite thermal arrests. No lattice parameter variations were observed for $LaTe_3$ crystallizing from various compositions and no evidence of a phase transition was seen.

Compositions between $66^2/_3$ and 75 atom % Te quenched below 835° show $LaTe_2$ and $LaTe_3$ in equilibrium. Specimens containing slightly less than $66^2/_3$ atom % Te had identical X-ray patterns, but the diffraction lines shifted their positions indicating the existence of a solid solution region. The lattice parameters of the end members of this solid solutions series were determined from specimens quenched from the two phase regions $LaTe_2$–$LaTe_3$ and $LaTe_{2-x}$–La_2Te_3; the tellurium-deficient end member has the composition $LaTe_{1.70\pm0.02}$.

Specimens of $LaTe_{2.0}$ which were sealed into quartz capillaries under reduced pressure and quenched from temperatures up to 1000° did not show any differences in their X-ray diffraction patterns. Specimens quenched from temperatures above 1000 and up to 1400° gave powder patterns which showed that they had lost tellurium, and the quartz tubes were seen to be coated with it. Figure 1 shows the lines denoting the end members of the solid solution as vertical up to approximately 1100° and turning toward lower Te compositions above it. The loss of Te at higher temperatures is probably a sensitive function of the initial pressure under which the sample was sealed, and since this was not investigated the lines are shown dashed.

The specimen of initial stoichiometric $LaTe_{2.0}$ composition quenched at 1400° produced a tellurium-deficient composition, $LaTe_{2-x}$, while a sample containing approximately 61 atom % Te and quenched at 1400° contained $LaTe_{2-y}$ and some La_2Te_3. These two compositions were also sealed in tantalum tubing and heated to about 1600°. The specimens quenched at that temperature showed no evidence of $LaTe_2$, but due to undercooling mixtures of LaTe and La_2Te_3 were observed to be present. No evidence of congruent melting of the $LaTe_2$ phase was seen and therefore the compound is shown as melting incongruently at about 1450°.

A region of solid solubility exists between the limits 60 and 57.1 atom % Te, La_2Te_3 to La_3Te_4. No phase transformations were observed for specimens quenched at 500° and above. The melting points of La_2Te_3 and

Table I

Physical and Crystallographic Properties of Lanthanum–Tellurium Compounds

Compd.	Crystal system	Space group	Lattice constants, Å.	Molecules per unit cell	Density X-Ray	Density Measd.	M.p., °C.	Color and luster
$LaTe_3$	Orthorhombic	Bmmb	$a_0 = 4.41 \pm 0.01$	4	6.92	6.88	835 ± 15	Gold, metallic
	pseudo-tetragonal		$c_0 = 26.1 \pm 0.1$				incongruent	
$LaTe_2$[a]	Tetragonal	$P^4/_nmm$	$a_0 = 4.506 \pm 0.005$				1450 ± 25	Black, metallic
$LaTe_{1.7}$			$c_0 = 9.13 \pm 0.01$	2	7.06	6.86	incongruent	
La_2Te_3[a]	Cubic	$I\bar{4}3d$	$a_0 = 9.619 \pm 0.001$	$5^1/_3$	6.57	6.57	1485 ± 25	Gray-black, dull metallic
La_3Te_4			$a_0 = 9.628 \pm 0.001$	4	6.90	6.90	1515 ± 25	Black, metallic
LaTe	Cubic	Fm3m	$a_0 = 6.436 \pm 0.002$	4	6.64	6.66	1720 ± 25	Purple, metallic

[a] Solid solution series.

La_3Te_4 were determined by a procedure previously described[7] and are considered congruent because the molten material after solidification always had the X-ray diffraction pattern of the crystalline solid.

Only one other intermediate compound, LaTe, was observed. The determination of the melting point and the reason for believing that it is congruent are the same as for La_3Te_4. Specimens quenched at various temperatures and investigated by powder X-ray diffraction techniques show that no phase transition occurs. Alloys of LaTe and La were prepared by melting them in an inert atmosphere on tantalum strips and remelting them to determine the liquidus melting points. X-Ray diffraction and metallographic examinations of such compositions showed only the presence of LaTe and melt.

Crystal Data

The crystallographic and physical parameters for the intermediate phases are summarized in Table I.

$LaTe_3$.—The compound is easily identified by its gold color, high metallic luster, and brittleness; when exposed to the atmosphere it is unstable and the rate of disintegration depends on the relative humidity. Single crystal X-ray diffraction data can be indexed on a tetragonal unit cell. The diffraction photographs show that considerable stacking disorder in the direction of the c axis occurs in this structure,[6] but well-ordered single crystals were found and they displayed fourfold symmetry although some of the crystals gave patterns in which the fourfold symmetry apparently was not quite perfect. The conditions for nonextinction of spectra are $l = 2n$ when h and k are both even and $l = 2n + 1$ when h and k are both odd; when h and k are mixed then all values of l are observed. The occasional violation of fourfold symmetry by some of the crystals as well as the nonspace-group extinctions can be explained on the basis of twinning of $LaTe_3$ crystals. If the true symmetry is orthorhombic, B centered, and the unit cell has $a = b$, then a reflection of the reciprocal lattice across (110) will produce the observed extinctions and the tetragonal symmetry. Untwinned diffraction photographs of $ErTe_3$[8] and $NdTe_3$[9] confirmed this explanation and show that all three compounds are isostructural. *Anal.* Calcd. for $LaTe_3$: La, 26.63; Te, 73.37. Found: La, 26.28; Te, 72.90.

$LaTe_2$–$LaTe_{1.70}$.—Single crystal X-ray patterns can be indexed on the basis of a tetragonal cell. The diffraction symmetry is $^4/_mmm$ and systematic absences occur for $hk0$ reflections when $h + k = 2n + 1$, so that the space group is $P^4/_nmm$. This phase is isostructural with $NdTe_2$[9] and they probably have the Fe_2As structure.[5] A single crystal structure analysis to confirm this is now in progress. *Anal.* Calcd. for $LaTe_2$: La, 35.25; Te, 64.75. Found: La, 34.45; Te, 67.00.

La_2Te_3–La_3Te_4.—The cubic lattice constants for the end members of the solid solution series were determined by a Taylor–Sinclair extrapolation of lattice constants obtained from diffraction lines in the back-reflection region and are a = 9.619 Å. for La_2Te_3 and 9.628 Å. for La_3Te_4. The compound has the Th_3P_4 structure. Single crystal X-ray diffraction patterns show that the space group is $I\bar{4}3d$. *Anal.* Calcd. for La_2Te_3: La, 42.05; Te, 57.95. Found: La, 41.8. *Anal.* Calcd. for La_3Te_4: La, 44.95; Te, 55.05. Found: La, 45.3; Te, 53.1.

LaTe.—Single crystal diffraction photographs can be indexed on the basis of a cubic unit cell, space group Fm3m. The compound is isostructural with NaCl.[2] Because the Cu Kα dispersion corrected scattering factors differ only by 3.9 electrons at $\sin\theta/\lambda = 0$, no reflections are observed in which h, k, and l are all odd.

Discussion

The binary phase diagrams of La–Te and Nd–Te[9] are expected to show many similarities. All intermediate phases observed in the former binary system also occur in the latter, and the melting points and melting behavior of three of the phases are similar. However, the compound Nd_2Te_5 does not have a corresponding lanthanum analog and the phase transformation of the Th_3P_4-type structure to the Sb_2S_3-type structure for the Nd_2Te_3 solid solution series does not occur for the lanthanum phase which retains the Th_3P_4 structure over the investigated temperature interval. The slight variation in radius ratio seems to exert a critical influence on the structure of these phases.[13] The limits of solid solubility are determined by the statistical occupancy of metal sites in a structure which is formed by a fixed Te framework (Th_3P_4-type structure) and by the occupancy of metal atoms in the twelve crystallographically independent vacancies which occur in the

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Sc_2S_3-type structure.[7,8,14] The small increase in the lattice constant from La_2Te_3 to La_3Te_4 is due to the change in bond character. The compound La_2Te_3 has the highest electrical resistivity of all the phases in the binary system and can be considered to have the highest percentage of ionic character, while La_3Te_4 is much more conducting and has a more covalent metallic bond. This change decreases the effective ionic radius of tellurium, which nearly offsets the expansion due to the additional lanthanum atoms.

The phase $LaTe_2$ forms a defect solid solution with a maximum deficiency of Te corresponding to a composition near $LaTe_{1.70}$. The compound Fe_2As, with which it is isostructural, also shows a varying deficiency of iron. The atomic sites in the faces of the unit cell are occupied by La and Te, respectively, and the latter need be only 85% of the time occupied and still provide a stable structure. As the tellurium concentration decreases the *a* axis shrinks and the *c* axis increases.[9] The stoichiometric $LaTe_2$ has a high degree of metallic conductivity, while the defect structures have lower conductivities.[11] This behavior indicates that the bonding changes from metallic covalent for the stoichiometric composition to a more ionic type in the tellurium-deficient compounds. The lengthening of the *c* axis can also be considered as reducing the overlap among the orbitals of the remaining atoms. Similar behavior is observed in semiconducting transition metal oxides.[15]

The melting behavior of $LaTe_2$ is quite different from that of the neodymium analog. The two equilibrium diagrams neglect the effect of pressure which is no longer correct at these elevated temperatures. It is quite possible that the vapor pressure above $LaTe_2$ is much higher and that sublimation with subsequent decomposition in the vapor phase takes place, thus giving rise to an apparent incongruent melting point. If the vapor pressure above $NdTe_2$ is lower, then the solid goes through the liquid phase and congruent melting is observed. The effect of pressure on the melting behavior of these compositions needs to be investigated further.

The La–Te bond length derived from the LaTe and $LaTe_2$ structures is 3.22 Å., while this distance is 3.33 Å. in the idealized La_2Te_3 structure if the variable parameter is $^1/_{12}$. A detailed refinement of the La_2Te_3 structure[16] shows that the bond lengths are not equivalent and split into two sets of 3.24 and 3.42 Å. The distortion of the coordination polyhedron in the La_2Te_3 structure probably reflects the more ionic nature of the bonding, and the shorter distance in LaTe and $LaTe_2$ reflects the presence of a metallic covalent bond.

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The Crystal and Molecular Structure of Ruthenium–Sulfur Dioxide Coordination Compounds. I. Chlorotetraammine(sulfur dioxide)ruthenium(II) Chloride

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The Ru–SO_2 complex, $[Ru^{II}(NH_3)_4(SO_2)Cl]Cl$, has an orthorhombic unit cell, $a = 13.962$, $b = 9.308$, $c = 7.312$ Å. The space group is Pnam with four formula weights per unit cell. A three-dimensional crystal structure analysis of the complex yielded the positions of all of the atoms but the hydrogens, with a discrepancy factor of 0.047 for 1054 independent reflections. The SO_2 is a monodentate ligand, coordinated through the sulfur. The bond distances and bond angle in the coordinated SO_2 are approximately the same as in free, solid SO_2 and the Ru–N, Ru–S, and Ru–Cl bond lengths are comparable to those observed in other platinum group complexes. Preliminary X-ray and infrared data on the $[Ru^{II}(NH_3)_4(SO_2)Br]Br$, $[Ru^{II}(NH_3)_5(SO_2)]Cl_2$, and $[Ru^{II}(NH_3)_5(SO_2)]Br_2$ complexes indicate that in each case the SO_2 ligand is coordinated through sulfur.

Introduction

The only metal complexes reported in the literature to contain sulfur dioxide as a ligand are those of the ruthenium–ammine series described by Gleu[2,3] and possibly the products of the reactions of iron carbonyls with SO_2.[4] Vaska[5] has prepared several platinum group complexes containing SO_2 ligands as well as carbonyl and substituted phosphine ligands.

Since the ruthenium ammines are the only well

[1] (a) This paper is based on a part of a thesis submitted by L. H. Vogt, Jr., to the Graduate School of the Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry and was presented in part as paper L7 at the American Crystallographic Association annual meeting, July 1964, at Montana State College, Bozeman, Mont.; (b) N.A.S.A. Predoctoral Trainee; (c) present address: General Electric Research Laboratory, Schenectady, N. Y.

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