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Temperature Induced Symmetry Transformation in the Th_3P_4 Type Compounds La_3S_4, La_3Se_4, Pr_3S_4 and Pr_3Se_4

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From X-ray powder diffraction experiments the Th_3P_4 type sulfides and selenides of La and Pr have been shown to undergo a cubic to tetragonal phase transformation with decreasing temperature. The corresponding tellurides show no distortion down to 4.2°K. These results cast some doubt on a possible charge order–disorder mechanism underlying the transition.

Introduction

The lanthanide chalcogenides with the Th_3P_4 structure have been the subject of much interest and study because of possible phase transitions involving vacancy and charge ordering (*1*). X-ray (*2*), Mössbauer (*3*), and transport measurements on Eu_3S_4 have been interpreted on the basis of a transition at low temperatures driven by charge ordering among Eu^{2+} and Eu^{3+} ions. Recent measurements on the analogous sulfides and selenides of La and Pr show the existence of phase transitions in these materials at low temperatures also. In this paper we report powder X-ray diffraction data as a function of temperature for La_3S_4, La_3Se_4, Pr_3S_4, and Pr_3Se_4. A first-order structural phase transition from cubic to tetragonal symmetry is found for each compound. These transitions are similar to those observed for the analogous Eu and Sm sulfides and therefore cast doubt on the charge ordering mechanism as the cause for the transition.

Experimental

Sample preparation consisted of sealing the stoichiometric ratio of elements in an argon flushed and evacuated quartz tube. The constituents were then reacted at 550°C for 18 hr, after which the temperature was raised to 850°C and held for an additional 2 hr. The reacted material was transferred to a tantalum tube and under very high vacuum conditions it was melted at ~2200°C by passing a current through the tube. The tube was then inverted and the contents were remelted and slow cooled to enhance crystal growth. The rare earth elements used were ≥99.9% pure while the other elements were at least 99.99% pure.

The crystalline material was then ground into a fine powder and intimately mixed with powdered silicon, as an internal standard, in a silicone grease medium (*4*). Then the resulting pastelike mixture was spread evenly over the sample block of an Air Products and Chemicals Cryotip diffraction device and mounted on a Philips/Norelco diffractometer. Copper radiation was used ($K\alpha = 1.54178$ Å) along with a bent LiF crystal monochromator on the detection arm of the diffractometer. For each sample, scans were taken over the 2θ range 20–100° at a rate of $\frac{1}{4}$°/min with 1° divergence slit at 298 and 4.2°K. Reflections whose 2θ angles were greater than 100° generally were found to be too weak or overlapping in the tetragonal phase and hence of little value in determining lattice parameters. For those cases where line splittings or anomalous line broadening occurred at 4.2°K, selected reflections were chosen that were

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TABLE I

				La_3Se_4				Pr_3Se_4			
				298°K		4.2°K		298°K		4.2°K	
hkl_{cubic}	I	hkl_{tet}	I	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
2 1 1	*w*	1 1 2	*w*	3.699	3.694	3.678	3.685				
		2 1 1					3.668				
		1 0 3	*s*			2.860	2.861			2.808	2.809
3 1 0	*vs*	3 0 1	*s*	2.862	2.861	2.834	2.839	2.816	2.816	2.797	2.798
		3 1 0					2.837				2.797
		2 1 3	*ms*			2.413	2.412				2.372
3 1 2	*s*	3 1 2	*ms*	2.419	2.418	2.405	2.404	2.381	2.380	2.370	2.367
		3 2 1					2.400				2.365
		2 0 4	*wm*			2.022	2.021			1.988	1.986
4 2 0	*wm*	4 0 2	*wm*	2.023	2.023	2.006	2.009	1.991	1.991	1.980	1.980
3 3 2	*w*	4 2 0		1.929	1.929		2.006	1.899	1.898		1.978
4 2 2	*wm*	2 2 4	*w*	1.847	1.847	1.844	1.843	1.818	1.817	1.813	1.812
		4 2 2	*w*			1.834	1.834			1.808	1.807
		1 0 5	*w*			1.775	1.775				1.743
		3 1 4	*w*			1.770	1.769				1.740
5 1 0	*m*	4 1 3	*w*	1.774	1.774	1.764	1.765	1.747	1.746	1.739	1.738
3 1 4		4 3 1					1.760				1.735
		5 0 1	*w*			1.760	1.760				1.735
5 2 1	*w*	5 1 0		1.652	1.652		1.759	1.626	1.626		1.735
		1 1 6	*wm*			1.468	1.468			1.441	1.442
		3 2 5	*wm*			1.465	1.464				1.440
6 1 1	*m*	5 2 3	*wm*	1.468	1.468	1.458	1.459	1.445	1.444		1.436
5 3 2		5 3 2					1.457			1.433	1.436
		6 1 1	*wm*			1.453	1.455				1.435
		2 0 6	*w*			1.430	1.430			1.405	1.405
6 2 0	*w*	6 0 2	*w*	1.430	1.431	1.417	1.419	1.408	1.408	1.397	1.398
		6 2 0					1.418				1.397
		4 1 5	*w*			1.391	1.392	1.374	1.374	1.368	1.369
5 4 1	*w*	5 1 4		1.396	1.396		1.389				1.367
		5 4 1	*w*			1.388	1.385				1.365
		3 6 1	*vw*			1.332	1.332			1.310	1.309
6 3 1	*w*	6 1 3	*vw*	1.334	1.334		1.325	1.313	1.313		1.305
		6 3 1				1.323	1.323			1.304	1.304
4 4 4	*w*	4 4 4	*w*	1.306	1.306	1.301	1.299	1.285	1.285	1.280	1.279
		4 0 6								1.233	1.231
6 4 0	*w*	6 0 4	*w*	1.255	1.255			1.235	1.235	1.230	1.228
		6 4 0								1.227	1.227
		2 1 7	*w*			1.231	1.231			1.208	1.209
		3 3 6	*w*			1.229	1.228				1.208
7 2 1		5 2 5	*w*			1.226	1.226				1.206
6 3 3	*m*	6 3 3		1.231	1.231		1.223	1.212	1.212	1.206	1.205
5 5 2		5 5 2	*w*			1.223	1.222				1.204
		7 1 2					1.222				1.204
		7 2 1	*w*			1.221	1.221			1.202	1.203
		4 2 6	*w*			1.206	1.206			1.186	1.186
6 4 2	*w*	6 2 4		1.209	1.209		1.202	1.190	1.190		1.184
		6 4 2	*w*			1.201	1.200			1.183	1.182
7 3 2	*vw*			1.149	1.149			1.131	1.131		
6 5 1											
6 5 3	*vvw*			1.082	1.082						
8 2 2											
6 6 0	*vw*			1.067	1.066						
8 3 1											
7 5 0	*w*			1.052	1.052						

TABLE II

	La_3S_4	La_3Se_4	Pr_3S_4	Pr_3Se_4	Eu_3S_4 (*2*)
a (cubic), Å	8.720(2)	9.0481(4)	8.569(2)	8.9038(4)	8.532
a (tet), Å	8.648(2)	8.971(2)	8.539(3)	8.844(3)	8.505
c (tet), Å	8.730(2)	9.055(2)	8.552(3)	8.890(3)	8.539
c/*a*	1.010	1.009	1.002	1.005	1.004
T_{tr} (°K)	90	60	40	40	168

unique and strong enough to yield accurate tetragonal lattice parameters at various temperatures upon warming through the transition. For most experiments these were the (116), (611), (206), and (620) among others. At all temperatures the observed 2θ angles were corrected by calibration with the internal silicon standard reflections adjusted for thermal expansion. Least-squares lattice parameter refinements were carried out at 298 and 4.2°K. At the latter temperature, the number of reflections was restricted to ~12 well resolved medium intensity lines.

Results

An example of the X-ray powder diffraction data is given in Table I where the observed and calculated interplanar *d*-spacings are reported for La_3Se_4 and Pr_3Se_4 at 298 and 4.2°K. Table II shows the lattice parameters and c/a for all the sulfides and selenides studied at 298 and 4.2°K and compares them with Eu_3S_4 at 298 and 168°K and lists the transition temperatures. The cubic to tetragonal distortion as a function of temperature is shown in Fig. 1 for La_3Se_4 and Pr_3Se_4. The small discontinuous decrease in volume at the transition is typical of all the La and Pr chalcogenides and is conclusive evidence for a first-order transition. The order parameter $(c/a - 1)^2$ is plotted against temperature for La_3S_4 in Fig. 2. Note the mean field behavior over a range of temperature from 20°K to the transition region at 90°K. This behavior suggests that although the transition from cubic symmetry to tetragonal is definitely first order, the gradual change in c/a with further lowering of temperature shows strong second-order character. Finally in Fig. 3 the lattice parameters at 298°K of the rare earth sulfides with the Th_3P_4 structure are plotted against atomic number and compared with the transition temperatures where known. The lattice parameters of Sm_3S_4 (*8*) and Eu_3S_4 (*2*) are anomalously large and do not fall on the trend line for normal lanthanide contraction. This strongly indicates a mixed valence state for these cations. The transition temperatures for these compounds are also anomalously high.

X-ray powder diffraction experiments were also carried out on the compounds La_3Te_4, Pr_3Te_4, and $La_{2.94}Se_4$. No cubic to tetragonal distortion was observed for the isostructural tellurides down to 4.2°K but some line broadening was observed for the cation deficient selenide at ~50°K. (In fact, this line-broadening was used as a qualitative test for small deviations in stoichiometry since all samples that were deliberately grown off-stoichiometry either showed this effect or did

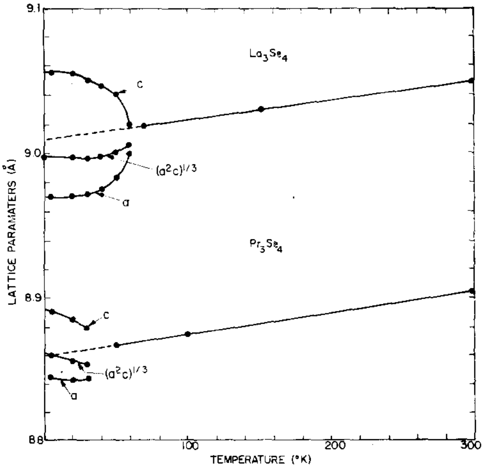

FIG. 1. Lattice parameters and reduced volume of La_3Se_4 and Pr_3Se_4 are plotted against temperature.

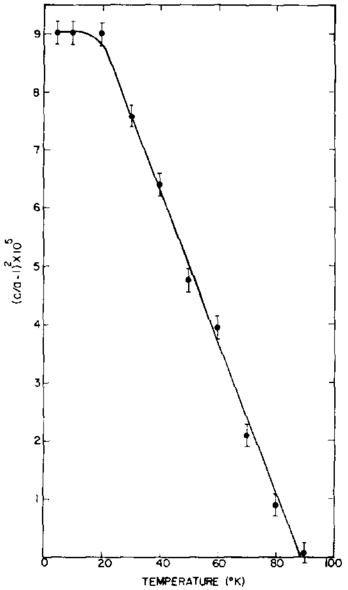

FIG. 2. The order parameter $(c/a-1)^2$ for La_3S_4 in the tetragonal phase is plotted against temperature.

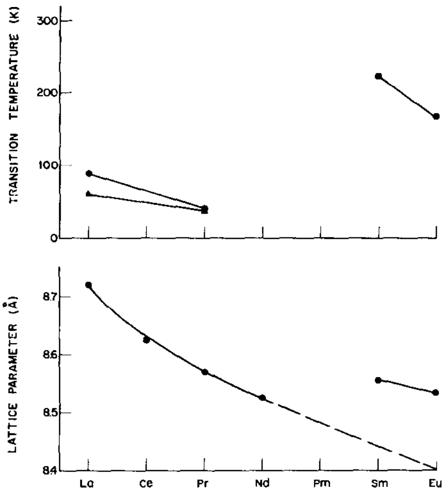

FIG. 3. Lattice parameters of the cubic Th_3P_4 type sulfides of La, Ce, Pr, Nd, Sm, and Eu at 298°K are plotted against atomic number and compared with the known transition temperatures. The triangular points represent the transition temperatures for the respective selenides.

not transform at all.) The lattice parameter for $La_{2.94}Se_4$ at 298°K was 9.0487(5) Å. The lattice parameters at 298 and 4.2°K for the La and Pr tellurides were 9.6247(8)–9.5910(6) Å and 9.487(1)–9.447(2) Å, respectively.

Discussion

The cubic (Th_3P_4) to tetragonal phase transitions in La_3S_4, Pr_3S_4, La_3Se_4, and Pr_3Se_4 appear to be structurally related to that observed in Eu_3S_4 (*2*). The most probable tetragonal space group is $I\,\bar{4}2d$ with four cations entering the $4b$ sites, $(0,0,\frac{1}{2})$, and the remaining eight cations entering the $8d$ sites $(x,\frac{1}{4},\frac{1}{8})$. The 16 Se anions in position (x,x,x) in the cubic cell $I\,\bar{4}3d$ would transform to the general position $16e$ (x,y,z) (*1*). However, for the proper generation of transformed coordinates, a shift in the origin to $(0,-\frac{1}{4},\frac{1}{8})$ and an interchange of x and y axes is required. The transition does not require a doubling of cell edges and the number of formulas per unit cell remains constant at four. The coordination number for the rare earth ions is 8 while that for selenium is 6.

In the case of Sm_3S_4 (*5*) and Eu_3S_4 (*3*), Mössbauer experiments agree well with a "charge hopping" model in which the cations in equivalent sites in the cubic high-temperature phase can be alternately divalent or trivalent. At low temperatures charge ordering has been proposed (*3*) with a 2:1 ratio of trivalent $8d$ sites, to divalent $4b$ sites in the $I\,\bar{4}2d$ cell. However, this model is in direct conflict with the case of La_3S_4, La_3Se_4, Pr_3S_4, or Pr_3Se_4. Although it is conceivable that charge fluctuations may occur at high temperatures, static charge ordering involving La^{2+}/La^{3+} or Pr^{2+}/Pr^{3+} ions at low temperatures is highly unlikely. In fact, La_3Se_4 is superconducting (*6*), $Tc = 8.6$°K, in the very regime where charge ordering is proposed.

Another difficulty involves the magnitude of the c/a ratio and the estimated displacements in atomic positional parameters. Since in general no major shifts in relative intensities of reflections occur across the transition, it would seem that the tetragonal distortion is predominantly reflected in the c/a ratio rather than internal shifts in atomic displacements. For La_3S_4 the largest value of c/a is only 1.010 ($c/a = 1.004$ for Eu_3S_4) which yields nearly identical average La–S bond lengths at 4.2°K for the two different cation sites. If complete charge ordering were to occur the average bond lengths should differ by approximately 17%. A model involving charge ordering does not seem compatible with experimental evidence in this case.

One possibility that is compatible with experimental results would involve a softening in certain lattice modes (7) analogous to that associated with structural transitions in perovskite compounds. However, more experimental work is needed to understand the subtle nature of the transition and the systematics in this series and we expect to continue to explore them in the near future.

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