

Synthesis of Rare-Earth Polychalcogenides by Moderate Temperature Solid-State Metathesis

John H. Chen and Peter K. Dorhout¹

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received August 28, 1994; in revised form January 9, 1995; accepted January 9, 1995

Alkali metal polychalcogenide salts of the form A_2Q_x (where $A = \text{Na, K}$; $Q = \text{S, Se, Te}$; $x = 1, 2, 3, 4$) have been used in moderate temperature solid-state metathesis reactions with lanthanoid halides, LnX_3 ($Ln = \text{La, Pr}$; $X = \text{Cl, Br}$), to prepare four phases of lanthanoid chalcogenides at temperatures below 400°C. For lanthanum, $\alpha\text{-LaS}_2$, $\beta\text{-LaS}_2$, LaSe_2 , and LaTe_3 were prepared and an irreversible phase transformation at 450°C between the metastable α - and thermodynamically stable $\beta\text{-LaS}_2$ was observed. For praseodymium, $\alpha\text{-PrS}_2$, PrSe_2 , and PrTe_3 were prepared and no phase transition from α - to $\beta\text{-PrS}_2$ was observed. © 1995 Academic Press, Inc.

INTRODUCTION

A recent review by Kumta and Risbud describes the family of rare-earth chalcogenides as an emerging class of optical materials (1). Traditional high-temperature synthetic methods used to synthesize these compounds often yield mixtures of phases or defect structures (2). A literature search revealed that a host of structures have been reported for the binary phases of lanthanoid (Ln) chalcogenides (Q) (2-4), including line-phase defects and superstructures (5-9) and alloys (10). The thermal degradation and reduction of binary LnQ_x phases have also been examined (11, 12).

Several unique synthetic methodologies have been employed in the synthesis of binary as well as ternary (and higher-order) lanthanoid chalcogenide systems. Wu and Ibers (13) and Sutorik and Kanatzidis (14) have utilized alkali metal chalcogenide fluxes to prepare several new lanthanoid sulfides and selenides. Recently, Parkin and Fitzmaurice dissolved europium in liquid ammonia and prepared polycrystalline EuS at low temperature (15).

The methods described by Wiley and Kaner for the rapid solid-state precursor synthesis using metathesis-type reactions between alkali metal chalcogenide salts (A_2Q , $A = \text{Na, K}$; $Q = \text{S}$) and transition metal halides

seemed to be a promising synthetic route to preparing known or perhaps new phases of lanthanoid chalcogenides (16). In order to isolate any metastable compounds that might be prepared at low temperatures, the rapid, highly exothermic reactions of Wiley and Kaner needed to be controlled. We have employed alkali metal polychalcogenide salts (A_2Q_x , $A = \text{Na, K}$; $Q = \text{S, Se, Te}$; $x = 2, 3, 4$) as reactants and mediators in the metathesis reactions with lanthanoid trihalides, LnX_3 . Unlike the high temperatures achieved in earlier metathesis reactions (16), the metathesis reactions reported here could be mediated to temperatures below 400°C, as evidenced by the isolation of a metastable phase of LaS_2 , which has been shown here to decompose irreversibly above 400°C.

EXPERIMENTAL

LnX_3 was prepared as described earlier by decomposition at 500-700°C of $(\text{NH}_4)_3\text{LnX}_6$ that was synthesized from the distilled lanthanoid metals (Ames laboratory, 99.999%) and the appropriate ammonium halide salt (17). The trihalide salts were then vacuum-sublimed before use. All alkali metal chalcogenide salts used (A_2Q_x , $A = \text{Na, K}$; $Q = \text{S, Se, Te}$; $x = 1, 2, 3, 4$) were prepared from the elements in liquid ammonia as described earlier (18, 19). The reactants (100-300 mg) were loaded into fused silica ampoules in an inert atmosphere glove box and sealed under vacuum ($<10^{-4}$ Torr) and heated for 24 to 120 hr at the temperatures described below.

The reaction products in their entirety were examined by powder X-ray diffraction before being washed with deionized water. From this, the relative ratios of starting materials to products could be realized. Powder diffraction data used for indexing were obtained from washed samples that contained no starting material or alkali metal halide salts.

Powder X-ray diffraction photographs were taken on an Enraf-Nonius Guinier camera and indexed according to internal silicon standard lines using the program U-FIT (20).

¹ To whom correspondence should be addressed.

TABLE 1
Reaction Products and a Comparison with Literature Values

Phase	Crystal system	Cell parameters (Å °)	Reference
α -LaS ₂	Monoclinic	$a = 8.317(5)$, $b = 4.096(2)$ $c = 8.254(5)$, $\beta = 90.3(1)$	This work
α -LaS ₂	Monoclinic	$a = 8.18$, $b = 4.03$ $c = 8.13$, $\beta = 90$	(22)
α -PrS ₂	Monoclinic	$a = 8.119(4)$, $b = 4.043(2)$ $c = 7.930(1)$, $\beta = 88.8(1)$	This work
β -LaS ₂	Orthorhombic	$a = 8.142(3)$, $b = 16.365(6)$, $c = 4.140(1)$	This work
β -LaS ₂	Orthorhombic	$a = 8.131(5)$, $b = 16.34(1)$, $c = 4.142(2)$	(23)
LaSe ₂	Monoclinic	$a = 8.518(6)$, $b = 4.265(2)$ $c = 8.591(5)$, $\beta = 90.04(6)$	This work
LaSe ₂	Monoclinic	$a = 8.51(1)$, $b = 4.26(1)$ $c = 8.58(1)$, $\beta = 90.12(2)$	(36)
PrSe ₂	Monoclinic	$a = 8.397(3)$, $b = 4.192(2)$ $c = 8.452(3)$, $\beta = 89.82(3)$	This work
LaTe ₃	Orthorhombic	$a = 4.434(4)$, $b = 25.34(4)$, $c = 4.410(3)$	This work
LaTe ₃	Orthorhombic	$a = 4.422$, $b = 26.09$, $c = 4.422$	(2)
PrTe ₃	Orthorhombic	$a = 4.372(2)$, $b = 25.941(9)$, $c = 4.376(3)$	This work

RESULTS

The results of the temperature-dependent phase studies are summarized in Table 1. At low temperatures, the reactions produced dark, polycrystalline products that could be easily purified by washing away the starting materials and water soluble products with deionized water. At higher temperatures, alkali metal halide salts were observed to sublime to the cold end of the tube and orange-to-metallic-golden crystals of the phases of interest remained at the hot end of the tube. (The temperature gradient brought about by natural thermal gradients in a single-zone tube furnace over 5–10-cm tubes was about 30°C.) In all cases, nearly quantitative yields (>95% with respect to LnX_3) of the desired LnQ_x products could be obtained as determined by powder X-ray diffraction.

The most consistent results of this study were obtained from reactions of K_2Q_2 salts; sodium salts (Na_2Q_x) and salts with x greater than 2 gave the same products as A_2Q_2 . Reactions of high $Q:Ln$ ratios (generally greater than 3:1, using K_2Q_2) showed evidence of molten, unreacted K_2Q_x remaining with the products. Reactions with A_2Q salts as low $Q:Ln$ ratios gave little or no product, and starting materials remained unreacted; reactions with very high $Q:Ln$ ratios yielded starting materials and $KLnQ_2$ (21).

Polysulfides. Reactions of K_2S_2 with LaX_3 at temperatures as low as 300°C yielded exclusively the α -phase of LaS₂ as described earlier (22). This phase, when heated

above 400°C, transformed into the β -LaS₂ phase (22, 23). Heating the reactants directly to 450°C or above (to 850°C) yielded the β -phase exclusively. The β -phase was also observed at the higher temperatures when the source of polysulfide was changed to Na_2S_4 , indicating that the cation had little effect on the reaction. When one equivalent of K_2S was used, only starting materials and a minority phase attributed to $KLnS_2$ (21) could be seen in the product mixture. There appears to be no difference between using $X = Cl^-$ or Br^- in these reactions.

Reactions with PrX_3 and K_2S_2 at 400–600°C yielded only the α -PrS₂ phase (22). Reactions heated to 950°C did not yield the β -phase. No other reported phases for PrS_x were observed, including PrS and the cubic PrS_2 (24, 25). Heating above 950°C under vacuum yields a green phase. When the ratio of S:Pr exceeded 2:1, an unknown pale green phase was formed at temperatures as low as 600°C.

Polyselenides. Reactions of K_2Se_2 with LaX_3 or PrX_3 yielded the $CeSe_2$ type (26) or the "B-form" (27) of LaSe₂ and $PrSe_2$. These phases were stable at temperatures from 400 to 850°C, and the crystallinity of the samples increased with increasing temperature. At high selenium to lanthanide ratios, an unidentified phase was observed.

Polytellurides. Reactions of K_2Te_2 with LaX_3 or PrX_3 yielded a different stoichiometric phase than for the LnS_2 or $LnSe_2$ phases. EDS confirmed a 1:3 ratio for LaTe₃ and PrTe₃. These phases match the reported NdTe₃ phase (2). At high tellurium to lanthanide concentrations, an unidentified phase was also observed.

DISCUSSION

Previous to our study, polychalcogenides of the rare-earth elements had been prepared from the action of H_2Q ($Q = S, Se$) on Ln_2O_3 , from direct combination of the elements at high temperatures, from reactions at high pressure, or from the action of thiocyanate on rare-earth carbonates (4). Moderate-temperature metathesis-type reactions of polychalcogenides directly with rare-earth halides had not been pursued. Our results indicate the formation of four different phases of polychalcogenides under moderate synthetic conditions (Table 1).

Polysulfides. The reactions of LaX_3 with K_2S_2 yielded two phases of LaS₂ that had been previously reported as having been prepared at temperatures in excess of 700°C (22–25, 28). The low-temperature metathesis route we have employed yielded an identifiable phase at temperatures below 300°C. This phase was the α -LaS₂ phase. Upon being heated to 450°C, this phase irreversibly transformed into the β -LaS₂ phase, a transition reported previously to occur at 750°C and which was reversible (22). A second reaction of LaX_3 with K_2S_2 at 600°C exclusively yielded the β -phase. As described before (22), the relationship between the α - and β -phases can be viewed as

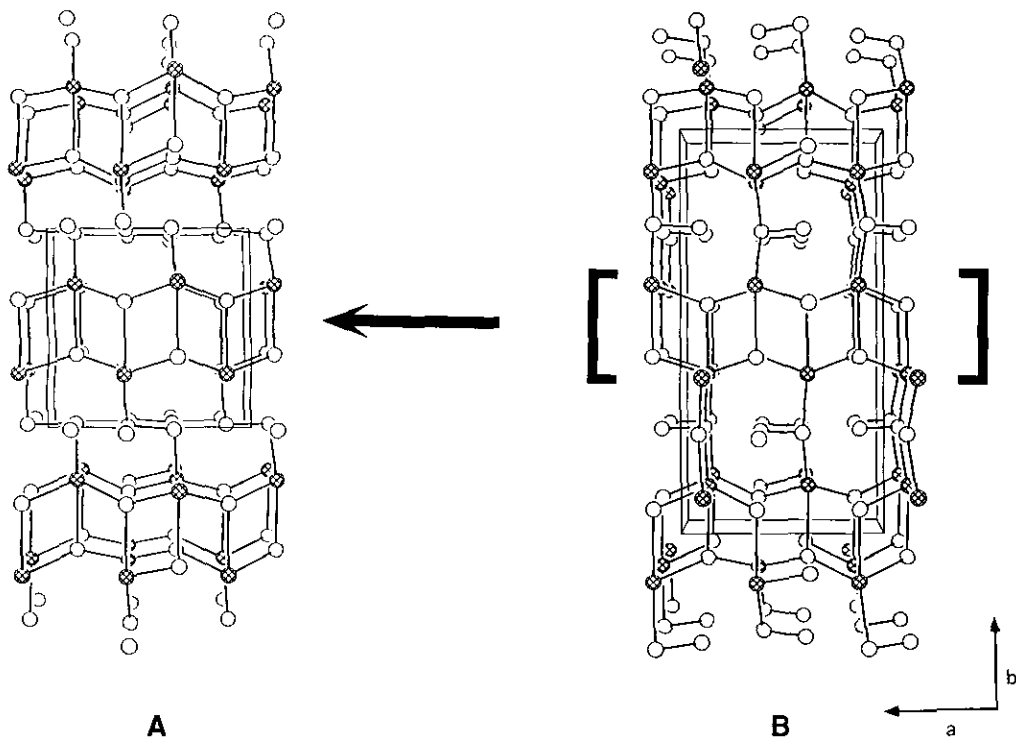


FIG. 1. A view of α - LaS_2 (A) and β - LaS_2 (B) down [001] showing the transformation (glide of one layer) relating the α and β phases. Sulfur atoms are open circles; lanthanum atoms are crossed circles.

a glide of one-quarter of the unit cell along [100] as seen in Fig. 1. Both phases contain the "herringbone" pattern of disulfides parallel to the (010) plane (Fig. 2). In addition to these observations, no evidence for the formation of LaS cubic phases was seen (the result of direct reaction of La and S metals at moderate to high temperatures (25, 29)).

The chemistry of PrX_3 is not identical to that of lanthanum. The low-temperature phase α - PrS_2 (isotypic with α - LaS_2) is stable up to its decomposition point above 850°C,

at which point it is converted to a green phase that is not the sesquisulfide Pr_2S_3 (3, 4, 24). No transition to the unknown β - PrS_2 phase (22) or the known cubic PrS_2 phase (24) was observed. The stability of the α -phase over the β -phase may be attributed, in part, to the coordination spheres around Ln in both phases. In the α -phase, the ninefold coordination of Ln , shown in Fig. 3, is close to a capped square-antiprismatic with a distortion of Ln out of the center of the sulfide prism along [010]. In the β -phase, the Ln-S layers are shifted along [100] by half the unit cell and the sulfide layers are also shifted slightly

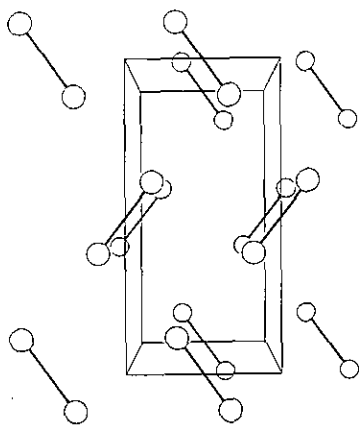


FIG. 2. A view down [010] illustrating the "dumbbell" dimers of S_2 in the sulfur layers of α - LaS_2 .

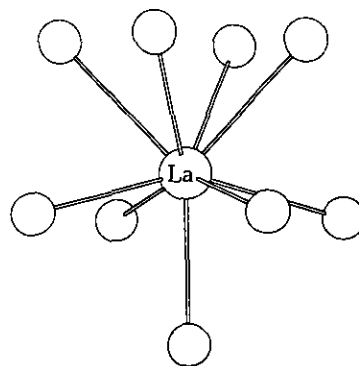


FIG. 3. The coordination sphere around La in α - LaS_2 .

along [100], allowing closer contacts of other sulfides to the lanthanoid. In fact, the radius of the hole created by the sulfides is larger by 0.034 Å in the β -phase. Such a configuration should be favored for larger cations seeking a larger coordination sphere. This would favor the formation of the β -phase for lanthanum, $r_{La} = 1.865$ Å and the α -phase for the smaller praseodymium, $r_{Pr} = 1.838$ Å (30).

It should also be noted that the d -spacings for α -PrS₂ could be solved in the tetragonal NdS₂ structure type (31) as well as the monoclinic α -LaS₂ type. The monoclinic solution yielded lower errors and gave better agreement between observed and calculated d -spacings. Single crystals of PrS₂, mounted on a 4-circle goniometer, did not display any fourfold axis of symmetry.

Polyselenides. Unlike the sulfides, reactions of LaX₃ and PrX₃ with polyselenide salts at low temperatures yielded single, isotypic phases of LnSe₂ that are isostructural with CeSe₂ (26) and the α -phase of LaS₂ (22). The LnSe₂ phases we observed are consistent with the distorted orthorhombic phases predicted to be most stable by Lee and Foran (9). In the case of LaSe₂, heating to 850°C does not yield a β -type phase as was found for the sulfide. Continued heating to 950°C under vacuum caused some decomposition of the phase but no La₂Se₃ or La₃Se₇ were observed (2–4). Heating of PrSe₂ yielded similar results.

No phase having the Ln₁₀Se₁₉ structure was observed during our studies. The twinned phase reported by Benazeth to have a monoclinic cell 8.52 × 8.58 × 8.52 Å did not index well to our data (32). Phases isostructural with defect structures of DySe_{1.85} or LaSe_{1.9} were not observed (6, 7).

Polytellurides. The LnTe₃ structure type has been described as a double layered LnQ₂ type, similar to the α -LnS₂ phase, with a van der Waals gap between chalcogenide layers, as in Fig. 4 (2). Attempts to find LnTe₂ (33) or Ln₂Te₅ by altering the stoichiometry and the chalcogenide salt (K₂Te₃ or K₂Te₂) were unsuccessful as only the LnTe₃ phases were observed. Reactions at high temperature (950°C) show decomposition of LaTe₃ to a pale yellow unknown phase but no decomposition of PrTe₃ to Pr₃Te₇ or Pr₄Te₁₁ (2). Pr₃Te₇ or Pr₄Te₁₁ have alternately layered $mLnTe_2 \cdot nLnTe_3$ orthorhombic structures and are reported to be metastable at room temperature; we had hoped to "trap" these using the metathesis reactions, but none were observed. Finally, at high Te : Ln loadings, an unknown phase was observed but not indexed.

CONCLUSIONS

Alkali metal polychalcogenide salts have been used in the preparation of polychalcogenides of the rare-earth elements lanthanum and praseodymium from rare-earth halide salts in moderate temperature metathesis-type re-

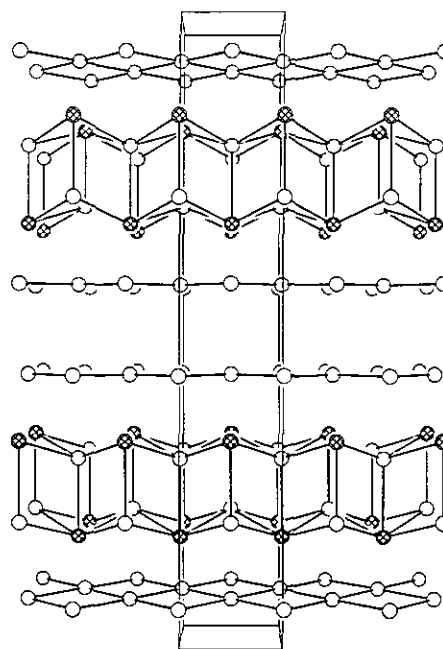


FIG. 4. A view along [100] of LaTe₃. Tellurium atoms are open circles; lanthanum atoms are crossed circles.

actions. The investigation of the sulfides revealed a low-temperature α -LaS₂ phase that irreversibly converts to the β -LaS₂ phase at 450°C, 300°C lower in temperature than previously reported. This strongly suggests that the metathesis reactions reported here are being mediated by the presence of the polysulfide salts. The selenide chemistry yielded a single CeSe₂-type phase for both La and Pr that, when heated, decomposes to several unknown phases. The telluride chemistry favors the NdTe₃-type double-layered cell with a van der Waals gap between layers of Te. The chalcogenide-halide metathesis reactions described here have proven useful for the preparation of pure phases of LnQ_x at moderate temperatures.

Further investigations with uranium (IV) chloride and polychalcogenides also illustrate the utility of the mediated metathesis route to materials. We have been able to identify US₃, USE_x, and β -UTe₃ in redox-metathesis reactions at temperatures of 400°C or less (34). The results of this study will be presented in a forthcoming paper (35).

ACKNOWLEDGMENTS

Financial support from Colorado State University Faculty Research Grants and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. P.K.D. wishes to thank the Research Corporation Cottrell Scholar Foundation for additional support.

REFERENCES

1. P. N. Kumta and S. H. Risbud, *J. Mater. Sci.* **29**, 1135 (1994).
2. E. I. Yarembash, A. A. Eliseev, E. S. Vigileva, and L. I. Antonova *Inorg. Mater.* **3**, 2184 (1967).

3. F. Hulliger, "Structural Chemistry of Layer-Type Phases." Reidel, Dordrecht, 1976.
4. M. Guittard and J. Flahaut, in "Synthesis of Lanthanide and Actinide Compounds" (G. Meyer and L. R. Morss, Eds.), Kluwer, Dordrecht, 1991.
5. R. A. Tamazyan, V. N. Molchanov, G. M. Kuz'micheva, and I. G. Vasil'eva, *Russ. J. Inorg. Chem.* **39**, 397 (1994).
6. M. Grupe and W. Umland, *J. Less-Common Met.* **170**, 271 (1991).
7. B. Foran, S. Lee, and M. C. Aronson, *Chem. Mater.* **5**, 974 (1993).
8. G. M. Kuz'micheva, *Russ. J. Inorg. Chem.* **39**, 393 (1994).
9. S. Lee and B. Foran, *J. Am. Chem. Soc.* **116**, 154 (1994).
10. T. Takeshita, K. A. Gschneidner, Jr., and B. J. Beaudry, *J. Appl. Phys.* **57**, 4633 (1985).
11. T. Amano, B. J. Beaudry, and K. A. Gschneidner, Jr., *J. Appl. Phys.* **59**, 3437 (1986).
12. G. M. Kuz'micheva and S. Y. Khlyustova, *Russ. J. Inorg. Chem.* **35**, 1344 (1990).
13. P. Wu and J. A. Ibers, *J. Solid State Chem.* **107**, 347 (1993).
14. A. C. Sutorik and M. G. Kanatzidis, *Angew. Chem. Int. Ed. Eng.* **31**, 1594 (1992).
15. I. P. Parkin and J. C. Fitzmaurice, *Polyhedron* **12**, 1569 (1993).
16. J. B. Wiley and R. B. Kaner, *Science* **255**, 1093 (1992).
17. G. Meyer, S. Doetsch, and T. Staffel, *J. Less-Common Met.* **127**, 155 (1987).
18. J.-H. Liao and M. G. Kanatzidis, *J. Am. Chem. Soc.* **112**, 7400 (1990).
19. I. Schewe-Miller, "Metallreiche Hauptgruppenmetall-Chalkogenverbindungen: Synthese, Strukturen und Eigenschaften." Universität Stuttgart, 1990.
20. M. Evain, "U-FIT: A Cell Parameter Refinement Program" IMN, Nantes, France, 1992.
21. J. P. Cotter, J. C. Fitzmaurice, and I. P. Parkin, *J. Mater. Chem.* **4**, 1603 (1994).
22. S. Benazeth, M. Guittard, and J. Flahaut, *J. Solid State Chem.* **37**, 44 (1981).
23. J. Dugue, D. Carré, and M. Guittard, *Acta Crystallogr. Sect. B* **34**, 403 (1978).
24. O. V. Andreev, N. N. Parshukov, and V. M. Andreeva, *Russ. J. Inorg. Chem.* **39**, 4 (1994).
25. A. Iandelli, *Gazz. Chim. Ital.* **85**, 881 (1955).
26. J. P. Marcon and R. Pascard, *C.R. Seances Acad. Sci. Ser. C* **266**, 270 (1968).
27. S. Benazeth, D. Carré, and P. Laruelle, *Acta Crystallogr. Sect. B* **38**, 33 (1982).
28. S. A. Ring and M. Tecotzky, *Inorg. Chem.* **3**, 182 (1964).
29. A. V. Golubkov, A. V. Prokofev, and V. M. Sergeeva, *Inorg. Mater.* **24**, 1779 (1988).
30. L. Pauling and B. Kamb, *Proc. Nat. Acad. Sci.* **83**, 3569 (1986).
31. A. A. Eliseev, S. I. Uspenskaya, and A. A. Fedorov, *Z. Neorg. Khim.* **16**, 1485 (1971).
32. S. Benazeth, D. Carré, and P. Laruelle, *Acta. Crystallogr. Sect. B* **38**, 37 (1982).
33. R. Wang, H. Steinfink, and W. F. Bradley, *Inorg. Chem.* **5**, 142 (1966).
34. J. C. Fitzmaurice and I. P. Parkin, *New J. Chem.* **18**, 825 (1994).
35. J. H. Chen and P. K. Dorhout, in preparation.
36. G. Venturini, B. Malaman, J. Steinmetz, and B. Roques, *Mater. Res. Bull.* **16**, 715 (1981).