

New Solid–Gas Metathetical Synthesis of Binary Metal Polysulfides and Sulfides at Intermediate Temperatures: Utilization of Boron Sulfides

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Abstract: A new simple synthetic method for binary metal polysulfides and sulfides was developed by utilizing an in situ formation of boron sulfides and their subsequent reactions with metal-source oxides in a closed container at intermediate temperatures above 350 °C at which the boron sulfides react in a gaseous form. The versatility of the new method is demonstrated with oxides of various transition metals (Ti, V, Mn, Fe, Ni, Nb, Mo, Ru, and W) and rare-earth metals (Y, Ce, Nd, Sm, Eu, Tb, and Er) as starting materials that exhibit different chemical characteristics. Regardless of the oxidation states of metals in the starting materials, the sulfidation reactions occurred quantitatively with stoichiometric mixtures of boron and sulfur, and within 24 h the reactions yielded pure products of TiS_2 , TiS_3 , VS_4 , FeS_2 , NiS_2 , NbS_3 , MoS_2 , RuS_2 , WS_2 , Y_2S_3 , and RS_2 ($R = Ce, Nd, Sm, Eu, Tb, \text{ and } Er$) which were the thermodynamically stable phases under the reaction conditions. The scope and implications of the new sulfidation method are also discussed.

1. Introduction

Because of their wide range of semiconducting properties and unique structural characteristics, binary sulfides and polysulfides of transition metals and rare-earth metals are widely used in industrial applications such as catalysis, lubrications, battery fabrication, refractories, pigments, and optical and magnetic devices.¹ While metal sulfides can be prepared by employing various sulfidation methods, the synthesis of their polysulfide analogues has not been as straightforward because many polysulfides decompose at elevated temperatures and the source of the polyanions are relatively scarce. H_2S alone is not an efficient source of S^0 , and the thermodynamics of the thermal decomposition of H_2S is not favorable at low temperatures. For example, at temperatures below 550 °C, the equilibrium concentration of sulfur is less than 1%, and even at 900 °C it is only 13%.² Reactions with elemental sulfur often require a pressurized reaction container and/or a multistep procedure.³ More recently, solid-state metathesis and/or solution methods have been used for the preparation of disulfides of Fe, Co, Ni, La, and Pr by employing Na_2S_2 , K_2S_2 , or Na_2S_5 .⁴ FeS_2 and CoS_2

can be also prepared at higher temperatures by reacting H_2S with starting materials that contain the corresponding metal ions of high oxidation states, but the problem of incomplete reactions and/or of impurities still remains.⁵

Recently, we have found that boron sulfides, B_2S_3 , BS_2 , and their mixtures, could be versatile sources of sulfur that can operate at intermediate temperatures in their gaseous forms.⁶ B_2S_3 does not have a well-defined melting point, but begins to sublime at temperatures no higher than 300 °C, as found in the literature⁷ and from our experience. Although BS_2 melts congruently at 417 °C under atmospheric pressure, our experiences show that a significant amount of BS_2 evaporates even at 300 °C under vacuum. While all sulfur atoms in B_2S_3 have a formal oxidation state of -2 , the structure of crystalline BS_2 exhibits dimerized S^- ions in addition to S^{2-} .⁸ The gaseous boron sulfides are corrosive in nature, and indeed the preparation of boron sulfides, crystalline or vitreous (v), requires a heavy carbon-coating on silica reaction vessels over 800 °C.⁹ The composition and equilibrium behavior of the boron sulfide vapor are exceedingly complex because of the existence of polymeric species $S_n(g)$, $(BS_2)_n(g)$, and $(B_2S_3)_n(g)$.¹⁰ However, previous mass spectrometric studies have concluded that stoichiometric $B_2S_3(s)$ vaporizes congruently to give $B_2S_3(g)$ and its polymers,

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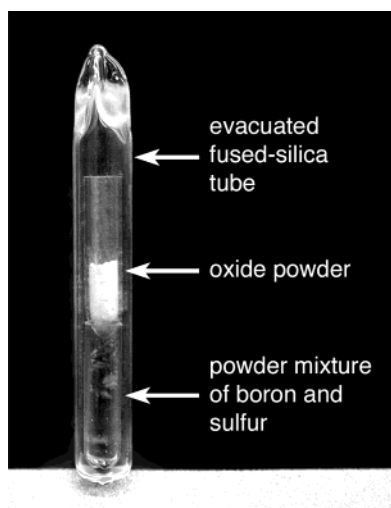


Figure 1. Reaction container (10 mm i.d.) for the sulfidation of metal oxides from in situ formation of boron sulfides (see text).

while a B–S system richer in sulfur than B_2S_3 evaporates incongruently into $(BS_2)_n(g)$ and $(B_2S_3)_n(g)$ and the composition of the vapor depends on the overall ratio of boron and sulfur.¹⁰ No other sulfur-richer species have been reported in the literature, and hence we suspect that any gaseous mixtures with a higher sulfur content ($S/B > 2$) should contain elemental sulfur vapor in addition to the $(BS_2)_n(g)$ and/or $(B_2S_3)_n(g)$ species.

The coexistence of S^- and S^{2-} ions in gaseous boron sulfide species provides a unique possibility for employing boron sulfides as a sulfiding agent that can provide both S^- and S^{2-} ions. Metathetical reactions of the boron sulfides are favored particularly when metal oxides are used as a metal source. The large formation energy of the coproduct B_2O_3 ($\Delta G_f^\circ(v-B_2O_3) = -1182.5$ kJ/mol),¹¹ as compared to those of boron sulfides ($\Delta G_f^\circ(v-B_2S_3) = -247.6$ kJ/mol; $\Delta G_f^\circ(v-BS_2) = -120$ kJ/mol),¹² may allow sulfidation of various metal oxides. In this paper, we report the synthesis of metal polysulfides and sulfides by utilizing an in situ formation of boron sulfides to convert a variety of metal oxides that contain transition metals (Ti, V, Mn, Fe, Ni, Nb, Mo, Ru, and W) or rare-earth metals oxides (Ce, Nd, Sm, Eu, Tb, and Er). It is emphasized that this work is intended for demonstration of the utility of the boron sulfide chemistry, rather than for exhaustive examination of all of the opportunities of the chemistry which will be carried out in due course.

2. Experimental Section

Amorphous boron powder (99.99%, 325 mesh), sulfur powder (99.999%), and metal oxides (99.9% or higher) were purchased from Alfa Aesar. The reaction materials were loaded in the scale of mmol in a glovebox or in air. In a general reaction scheme, a metal oxide in powder was placed in a short fused silica tube (Figure 1). Stoichiometric amounts of boron and sulfur powders were mixed and placed in a separate fused silica tube of the same size. The loaded ratios of the starting oxide:boron:sulfur are shown in Table 1, and they are indeed the reaction coefficients of the reactants in the individual balanced chemical equations for the oxides and target (poly)sulfides. The reactant ratios were chosen to provide the most sulfur-rich phases in the phase

diagrams at the designated reaction temperatures. To ensure a complete reaction of metal oxides, sulfur was loaded 10% more than the stoichiometric amounts. The two tubes were subsequently situated inside a larger silica tube container (10 mm i.d.), with the tube containing the metal oxide on top of the other (Figure 1). After the whole container was evacuated and flame-sealed, it was gradually heated at 50 °C/h to the designated reaction temperature, kept for 24 h, and subsequently cooled radiatively to room temperature. The reaction conditions and results are summarized in Table 1. After the reactions, the lower tube was empty, which indicated complete consumption of boron. The silica reaction tubes were intact, and there was no visible indication of corrosion on the inner surface of the tubes. The products were cleaned several times with CS_2 and deionized water (or methanol) to wash off unreacted sulfur, boron sulfides, and the byproduct B_2O_3 .¹³ The clean powder samples were found to be boron-free based on our atomic absorption spectrometric analysis within the detection limit (5 ppm) of the instrument (Varian SpectraAA-400 Flame). The phase identification was carried out from the powder X-ray diffraction patterns obtained by use of a Siemens X-ray diffractometer. The JADE program (version 6.1.3) was used for the unit cell refinements. The lattice parameters were matched with the values from the literature usually within much less than 0.2% for all of the sulfide products except for CeS_2 (0.5% for the b -axis). All of the products were X-ray pure without any impurities including the starting materials, as found from their powder patterns (Supporting Information). SEM/EDX analysis was conducted on a Hitachi S-4700-II high-resolution scanning electron microscope, and the obtained compositions were well in agreement with the previously reported data.

3. Results and Discussion

3.1. Transition Metal Polysulfides and Sulfides. The oxidation states of the transition metal ions in the starting materials range from +6 to +2, and the boron sulfides either reduce or oxidize the metal ions into the stable oxidation states in the corresponding polysulfides and sulfides (Table 1). The sulfidation reactions of TiO_2 at two different temperatures provided different phases, TiS_3 (at 400 °C)¹⁴ and TiS_2 (at 800 °C),¹⁵ both in a pure form. The lattice parameters of our TiS_2 product indicate that its S/Ti ratio is close to 1.94 due to a sulfur-deficiency in the structure. This nonstoichiometry is consistent with the previous studies in which the same amount of sulfur-deficiency was found in the most sulfur-rich product from the reactions between the elements at 800 °C.^{15,16}

The formation of VS_4 is interesting because its synthesis has not been very successful in previous efforts partly due to its decomposition above 400 °C.^{17–19} V_5S_8 appears to be the most sulfur-rich vanadium sulfide that can be prepared by reactions between the elements.¹⁷ V_2S_3 has been used to prepare crystalline VS_4 by the reaction with elemental sulfur at 400 °C, but the sulfidation was incomplete even after a 4-week reaction period.^{18,19} By utilization of the boron sulfide method in our experiments, however, V_2O_5 could be converted to pure VS_4 at 350 °C within 24 h, as found from the X-ray powder diffraction

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Table 1. Reaction Conditions and Results of the Metal Oxide Sulfidation^a

starting oxide	loaded ratio (oxide:B:S)	reaction temp (°C)	product (space group)	lattice parameters	lattice parameters in the literature	color of the product	ref
TiO ₂	3:4:9	400	TiS ₃ (<i>P2₁/m</i>)	$a = 4.957(5) \text{ \AA}$ $b = 3.397(4) \text{ \AA}$ $c = 8.788(8) \text{ \AA}$ $\beta = 97.23(5)^\circ$	$a = 4.958(2) \text{ \AA}$ $b = 3.401(2) \text{ \AA}$ $c = 8.778(4) \text{ \AA}$ $\beta = 97.32(4)^\circ$	grey	14
TiO ₂	3:4:9	800	TiS ₂ (<i>P3̄m1</i>)	$a = b = 3.407(1) \text{ \AA}$ $c = 5.703(1) \text{ \AA}$	$a = b = 3.407(1) \text{ \AA}$ $c = 5.695(1) \text{ \AA}$	black	15
V ₂ O ₅	3:10:24	350	VS ₄ (<i>I2/c</i>)	$a = 6.782(3) \text{ \AA}$ $b = 10.421(4) \text{ \AA}$ $c = 12.101(5) \text{ \AA}$ $\beta = 100.71(5)^\circ$	$a = 6.775(5) \text{ \AA}$ $b = 10.42(1) \text{ \AA}$ $c = 12.11(1) \text{ \AA}$ $\beta = 100.8(2)^\circ$	black	20
MnO ₂	3:4:6	550	MnS (<i>Fm3̄m</i>)	$a = b = c = 5.221(1) \text{ \AA}$	$a = b = c = 5.22(1) \text{ \AA}$	black	30
Fe ₂ O ₃	1:2:4	550	FeS ₂ (<i>Pa3̄</i>)	$a = b = c = 5.426(1) \text{ \AA}$	$a = b = c = 5.428(1) \text{ \AA}$	black	25
Fe ₃ O ₄	3:8:18	550	FeS ₂ (<i>Pa3̄</i>)	$a = b = c = 5.421(1) \text{ \AA}$	$a = b = c = 5.428(1) \text{ \AA}$	black	25
NiO	3:2:6	550	NiS ₂ (<i>Pa3̄</i>)	$a = b = c = 5.683(1) \text{ \AA}$	$a = b = c = 5.677(1) \text{ \AA}$	black	26
NbO	3:2:9	550	NbS ₃ (<i>P1̄</i>)	$a = 4.961(6) \text{ \AA}$ $b = 6.732(9) \text{ \AA}$ $c = 9.15(1) \text{ \AA}$ $\beta = 97.3(1)^\circ$	$a = 4.963(2) \text{ \AA}$ $b = 6.730(2) \text{ \AA}$ $c = 9.144(4) \text{ \AA}$ $\beta = 97.17(1)^\circ$	black	32
Nb ₂ O ₅	3:10:18	550	NbS ₃ (<i>P1̄</i>)	$a = 4.963(5) \text{ \AA}$ $b = 6.728(6) \text{ \AA}$ $c = 9.144(9) \text{ \AA}$ $\beta = 97.2(1)^\circ$	$a = 4.963(2) \text{ \AA}$ $b = 6.730(2) \text{ \AA}$ $c = 9.144(4) \text{ \AA}$ $\beta = 97.17(1)^\circ$	black	32
MoO ₂	3:4:6	800	MoS ₂ (<i>P6₃/mmc</i>)	$a = b = 3.162(3) \text{ \AA}$ $c = 12.281(8) \text{ \AA}$	$a = b = 3.160(1) \text{ \AA}$ $c = 12.294(4) \text{ \AA}$	black	36
MoO ₃	1:2:2	550	MoS ₂ (<i>P6₃/mmc</i>)	$a = b = 3.159(4) \text{ \AA}$ $c = 12.284(1) \text{ \AA}$	$a = b = 3.160(1) \text{ \AA}$ $c = 12.294(4) \text{ \AA}$	black	36
RuO ₂	3:4:6	550	RuS ₂ (<i>Pa3̄</i>)	$a = b = c = 5.611(2) \text{ \AA}$	$a = b = c = 5.610(1) \text{ \AA}$	black	27
WO ₃	1:2:2	550	WS ₂ (<i>P6₃/mmc</i>)	$a = b = 3.154(4) \text{ \AA}$ $c = 12.33(1) \text{ \AA}$	$a = b = 3.153(1) \text{ \AA}$ $c = 12.323(5) \text{ \AA}$	grey	37
Y ₂ O ₃	1:2:3	800	Y ₂ S ₃ (<i>P2₁/m</i>)	$a = 17.50(1) \text{ \AA}$ $b = 4.007(2) \text{ \AA}$ $c = 10.183(4) \text{ \AA}$ $\beta = 98.62(4)^\circ$	$a = 17.523(1) \text{ \AA}$ $b = 4.011(1) \text{ \AA}$ $c = 10.174(1) \text{ \AA}$ $\beta = 98.60(1)^\circ$	light yellow	42
Ce ₂ O ₃	1:2:4	550	CeS ₂ (<i>P2₁/c</i>)	$a = 8.101(4) \text{ \AA}$ $b = 4.054(3) \text{ \AA}$ $c = 8.081(5) \text{ \AA}$ $\beta = 89.86(7)^\circ$	$a = 8.107 \text{ \AA}$ $b = 4.075 \text{ \AA}$ $c = 8.084 \text{ \AA}$ $\beta = 89.80^\circ$	grayish yellow	38
Nd ₂ O ₃	1:2:4	550	NdS ₂ (<i>P2₁/c</i>)	$a = 8.028(5) \text{ \AA}$ $b = 4.002(2) \text{ \AA}$ $c = 8.001(5) \text{ \AA}$ $\beta = 90.00(1)^\circ$	$a = 8.015 \text{ \AA}$ $b = 4.012 \text{ \AA}$ $c = 7.988 \text{ \AA}$ $\beta = 90.0^\circ$	grayish yellow	38
Sm ₂ O ₃	1:2:4	550	SmS ₂ (<i>P4₂/n</i>)	$a = b = 8.781(5) \text{ \AA}$ $c = 15.84(1) \text{ \AA}$	$a = b = 8.796 \text{ \AA}$ $c = 15.889 \text{ \AA}$	grayish yellow	38
Eu ₂ O ₃	1:2:4	550	EuS ₂ (<i>P4/nmm</i>)	$a = b = 7.842(7) \text{ \AA}$ $c = 8.066(8) \text{ \AA}$	$a = b = 7.871 \text{ \AA}$ $c = 8.040 \text{ \AA}$	grayish yellow	43
Tb ₄ O ₇	3:14:24	550	TbS ₂ (<i>P2₁/m</i>)	$a = 3.871(2) \text{ \AA}$ $b = 3.865(2) \text{ \AA}$ $c = 7.880(4) \text{ \AA}$ $\beta = 90.05(5)^\circ$	$a = 3.872(1) \text{ \AA}$ $b = 3.860(1) \text{ \AA}$ $c = 7.887(1) \text{ \AA}$ $\beta = 90.1(1)^\circ$	grayish yellow	44
Er ₂ O ₃	1:2:4	550	ErS ₂ (<i>P4/nmm</i>)	$a = b = 7.649(5) \text{ \AA}$ $c = 7.827(7) \text{ \AA}$	$a = b = 7.636(1) \text{ \AA}$ $c = 7.811(6) \text{ \AA}$	grayish yellow	39

^a The JADE program was employed for X-ray powder diffraction pattern analysis and unit cell refinement.

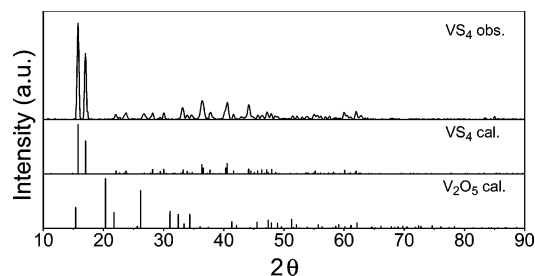


Figure 2. X-ray powder diffraction pattern of the product from the reaction of V₂O₅. The pattern matches well with the calculated powder pattern of VS₄ and does not exhibit any Bragg reflection peaks of the starting V₂O₅.

pattern of the product in Figure 2, which matches well with the previous data.²⁰ The starting oxide powder needed to be well dispersed on the surface of the reaction container; otherwise

the initial formation of a thin layer of a black melt at the top of the oxide sample prohibited a complete sulfidation of the material underneath.

Numerous synthetic methods have been proposed for pyrite, FeS₂, because of its importance particularly in recent thermal battery and lithium primary battery applications.²¹ FeS₂ starts to lose sulfur above 550 °C and decomposes at 743 °C.²² In addition, it transforms into a marcasite structure below 445 °C.²³

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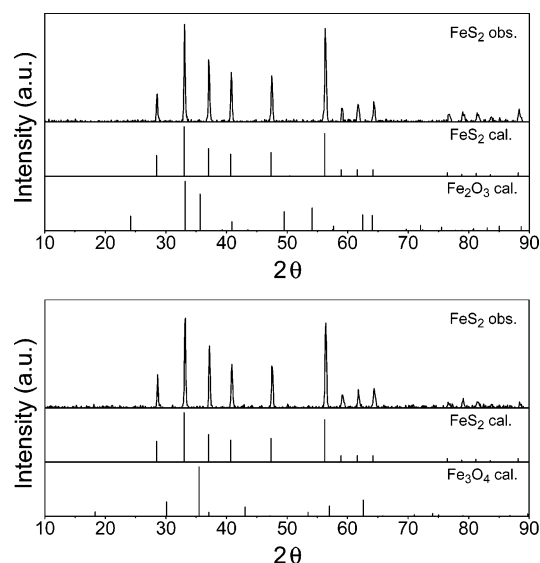


Figure 3. X-ray powder diffraction patterns of the products from the reactions of Fe_2O_3 (top) and Fe_3O_4 (bottom). The patterns match well with the calculated powder pattern of FeS_2 and do not exhibit any Bragg reflection peaks of the starting oxides.

The reaction between the elements has not been successful.²⁴ The reactions of FeCl_2 or Fe_2O_3 with H_2S are not complete for the temperature region where the pyrite structure is stable.^{5b} Low-temperature solution synthesis in previous studies often resulted in amorphous products and/or the marcasite phase as an impurity.^{21d} Figure 3 shows the X-ray powder diffraction patterns of the products from the reactions of Fe_2O_3 and Fe_3O_4 with appropriate amounts of boron and sulfur that were carried out at 550 °C. Both of the patterns match well with that of the previously known stoichiometric pyrite,²⁵ and no impurities were observed. The sulfidation of NiO and RuO_2 also provided pure NiS_2 and RuS_2 of the pyrite-type structure under the same reaction condition for the FeS_2 . The calculated unit cell parameters are in agreement with those of the known stoichiometric compounds.^{26,27} An isotopic compound, MnS_2 , is not stable under our reaction conditions and decomposes into $\alpha\text{-MnS}$ (rock-salt structure) around 260 °C.²⁸ Two other polymorphic forms (β , zinc blend; γ , wurtzite) are known, but only $\alpha\text{-MnS}$ is thermodynamically stable.^{28a} It is reasonable, therefore, that our sulfidation of MnO at 550 °C provided pure $\alpha\text{-MnS}$ as the product, and the refined unit cell parameters match well with the known values.²⁹ Interestingly, the RuS_2 product was found to consist of nanosized particles (<15 nm), as indicated from our SEM and TEM studies (Figure 4). The Bragg reflection peaks in the X-ray powder diffraction pattern of the product (Figure 5) were very broad, and the estimated average particle size was 13 nm, which is consistent with the findings in our electron microscopy studies. The starting RuO_2 particles were very small as well, with an average diameter of 26 nm as estimated from our powder diffraction.³⁰ It is suspected that the high melting point of RuS_2 (>1200 °C) does not allow a

significant fusion of the sulfide particles once they were formed initially and hence afforded the sulfide product particles much smaller than the original oxide particles. The particle size of our RuS_2 product is in fact much smaller than the particle sizes (<50 nm) in a previous report in which crystalline RuS_2 nanoparticles were obtained after annealing of the amorphous product from the aqueous reaction of RuCl_3 and H_2S .³¹

It is emphasized that the sulfidation reactions were efficient regardless of the initial oxidation states of the metal atoms in the starting materials. For instance, both Fe_2O_3 and Fe_3O_4 provided FeS_2 , with proper amounts of boron and sulfur to react with. Such flexibility in selection of starting materials is demonstrated more dramatically in our preparation of NbS_3 . In addition to Nb_2O_5 , the sulfidation was also carried out by employing NbO (Nb^{2+}) as a testing example because of the extensive Nb–Nb bonds in its structure which is in contrast to Nb_2O_5 in which Nb atoms are in a fully oxidized state (Nb^{5+}). Under exactly the same reaction temperature, nevertheless, both of the oxides provided pure NbS_3 (Nb^{4+}) as indicated from the X-ray powder diffraction analysis (Table 1).³² In other words, by controlling the loading ratios of boron and sulfur, the Nb atoms could be oxidized or reduced during the sulfidation processes. The nanoscopic structural nature of the NbS_3 product is worth mentioning. The reaction products from both NbO and Nb_2O_5 exhibit a fiberlike morphology, and some of the products were found on the surface of the silica jacket outside of the container in which the original oxide was located, while most the product remained in the container. More detailed work is in progress.

MoS_2 and WS_2 do not exhibit sulfur–sulfur bonds and yet are the most sulfur-rich crystalline phases in their binary phase diagrams.³³ Solution reaction routes have provided sulfur-richer WS_5 and MoS_x ($x = 5\text{--}6$) in an amorphous state.³⁴ Figure 6 shows the X-ray powder diffraction patterns of the products from MoO_2 and WO_3 obtained from the boron sulfide reactions at 550 °C. The MoS_2 product from MoO_3 showed a similar powder pattern (see Supporting Information). The Bragg reflection peaks are broad, comparable to previous studies based on various reaction routes,³⁵ and yet the relatively sharp (002) reflection peaks ($2\theta \approx 14^\circ$) imply that the disulfide layers are well stacked. There are no impurities found in the powder patterns.^{36,37} Although not shown here, the products from the reactions at 800 °C essentially show the same type of broad peaks in the X-ray powder patterns, yet with sharper (002) reflection peaks.

3.2. Rare-Earth Metal Disulfides and Sulfides. All of the rare-earth metal elements are known to form a disulfide as the most sulfur-rich phase in their binary system, although the stability and compositional range of the disulfides can vary with different metal elements.³⁸ In particular, YS_2 can be prepared

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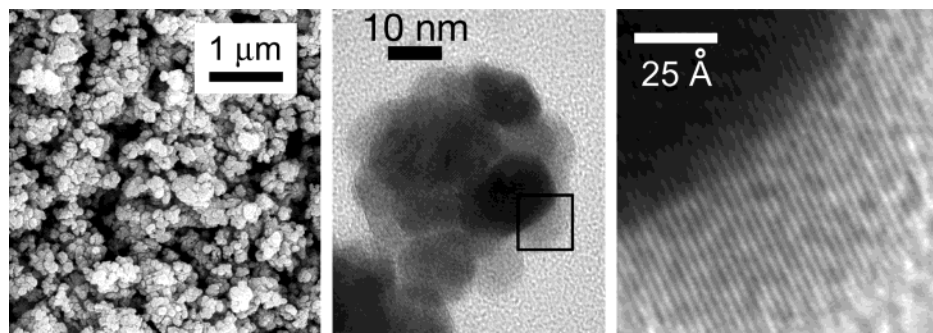


Figure 4. Left: A representative SEM image of the RuS₂ product. Center: A representative TEM image of the RuS₂ product in which the RuS₂ particles of <20 nm diameter are aggregated. Right: A zoomed image of the square box shown in the image at the center. The well arranged lattice fringes indicate a good crystallinity of the RuS₂ nanoparticles.

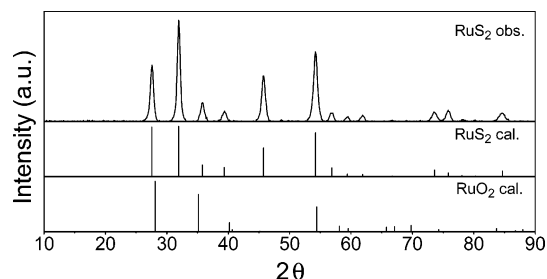


Figure 5. X-ray powder diffraction pattern of the product from the reaction of RuO₂. The pattern matches well with the calculated powder pattern of RuS₂ and does not exhibit any Bragg reflection peaks of the starting RuO₂. The Bragg reflection peaks are broad with an estimated particle size of 13 nm.

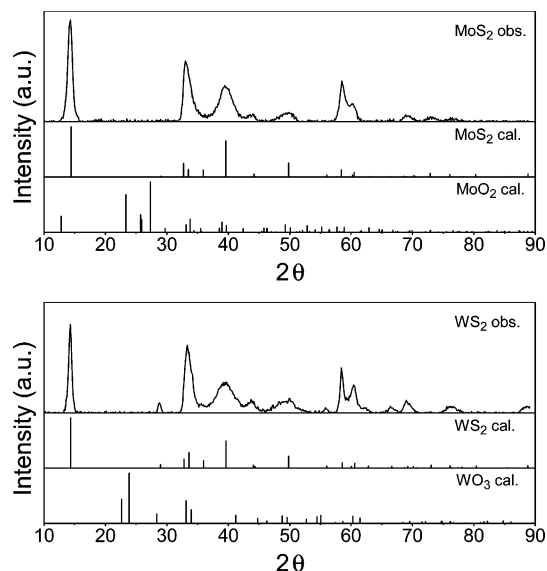


Figure 6. X-ray powder diffraction patterns of the products from the reactions of MoO₂ (top) and WO₃ (bottom). The patterns match well with the calculated powder patterns of hexagonal (shown here) or rhombohedral MoS₂ and WS₂ and do not exhibit any Bragg reflection peaks of the starting oxides.

only under a high-pressure condition (> 35 kbar) over 500 °C,^{39a} and the disulfides of heavy rare-earth metals (Eu–Yb) exhibit significant sulfur-deficiencies (5–15%).³⁸ The reaction of La and Nd oxides with H₂S begins only at 700 °C,^{39b} and the reaction temperature could be lowered only to 500 °C under a high-pressure condition.⁴⁰ In the previous studies of others, crystals of the rare-earth disulfides could form when the

corresponding sesquisulfides were treated with elemental sulfur over 600 °C, but still in a low yield.⁴¹ LaS₂ and PrS₂ have been prepared from the reactions of the corresponding chlorides and bromides with K₂S₂ at temperatures as low as 300 °C after which the unreacted starting materials were washed away.^{4b}

In our experiments (Table 1), the sulfidation reactions of R₂O₃ (R = Y, Ce, Nd, Sm, Eu, and Er) and Tb₄O₇ with boron sulfides resulted in pure products of their corresponding disulfides at 550 °C, with the exception of the Y₂O₃. The reaction of Y₂O₃ at 550 °C provided Y₂S₃ with a large amount of unreacted starting material after a 24-h reaction period. The same reaction condition at 800 °C resulted in pure Y₂S₃. The powder X-ray diffraction patterns matched well with those from the literature for all of the rare-earth disulfides and sulfide.^{38,42–44} The compositions obtained from the EDX studies are also in good agreement with the literature,³⁷ in that the light rare-earth disulfides (R = Ce and Nd) are stoichiometric (within ±0.2%), while significant amounts of sulfur-deficiency were found in the samples of the heavy rare-earth disulfides (SmS_{1.93}, EuS_{1.91}, TbS_{1.88}, and ErS_{1.87}). The values correspond to the lower limits found in the samples reported previously in the literature.³⁸ The refined unit cell parameters also match well with the literature values with a maximum deviation of 0.5% and typically with deviations below 0.2% (Table 1).^{38,42–44} The lattice parameters in the literature are rather scattered because of the synthetic problems as well as the structural changes by nonstoichiometries and synthetic conditions.³⁸ More detailed studies are in progress on the relationships among the lattice parameters, compositions, and reaction temperatures of the rare-earth disulfides based on this new boron-sulfide metathesis method.

3.3. Scope of the Method. As shown in the previous sections, the new sulfidation method was found to be efficient for various metal oxide compounds that contain transition metals or rare-earth metals in different oxidation states. Although not described here, our other experiments indicated that the reaction temperatures could be varied without much difference in the results. In another set of experiments for polysulfide synthesis, reactions were repeated with the amounts of sulfur less than required for the stoichiometric reactions. The results were the incomplete

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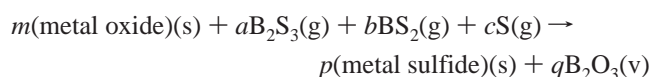
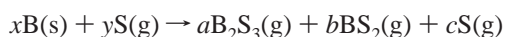
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sulfidation that still provided polysulfides and left some amount of oxides unreacted, rather than the formation of the corresponding sulfides with less sulfur content. Regardless of the chemical nature of the metal oxides, therefore, the reaction products were indeed the most sulfur-rich compounds that are expected thermodynamically at the reaction temperatures. In a simplified picture, the reaction procedures can be broken down into two subsequent reactions described by the following equations, and yet it is noted that the formation of boron sulfides in the first step is not necessarily complete before the second step proceeds:



While the new sulfidation method utilizes solid–gas reactions between the metal source and gaseous boron sulfides, there is a striking difference between the new method and the traditional solid–gas synthesis based on the sulfiding gases, H_2S and CS_2 ; the reactions are loaded with all solid-state materials (metal source, boron, and sulfur) in a closed container. Given a target sulfide, the starting materials are mixed at an appropriate ratio, and the reaction proceeds to its completeness until the starting materials are all consumed. There is no need for a continuous, and sometimes prolonged, flow of a sulfiding gas for a complete reaction, and the risk of harmful gases can be minimized. In this regard, the new method has a great resemblance to the sulfidation reaction between elements, that is, metal and sulfur. Differently from sulfur, however, boron sulfides can act as either a reducing or an oxidizing agent, depending on the oxidation states of the metal ions in the starting materials and the loaded ratios of boron and sulfur. This also contrasts the new boron sulfide method with the recently proposed sulfidation method that employs “gaseous” Y_2S_3 in which the oxidation state of sulfur is fixed.⁴⁵ In addition, the in situ preparation of boron sulfides is greatly advantageous over the expensive Y_2S_3 method in industrial applications; that is, the boron powder may not even need a high purity. When the impurities, mostly magnesium in industrial boron powder, react with sulfur, the resulting sulfides are expected to remain in the original container because of their typically high boiling point, while only boron sulfides evaporate to react with the metal source compounds in a separate container.

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The precise role of boron in the reaction mechanism is not clear yet and will require a thorough examination of the reactions both experimentally and theoretically. As mentioned earlier, the obvious benefit of boron is that the coproduct of the reactions, $\text{B}_2\text{O}_3(\text{v})$, is strongly favored thermodynamically. This reminds us of the well-established alkali sulfide solid-state metathesis method which is primarily based on the simple exchanges of ions during the reaction processes driven by the large enthalpy of formation of alkali halides, the coproduct.⁴⁶ However, the reaction mechanism in the boron sulfide metathesis could be more complicated because the boron sulfides react in a form of gaseous molecules as H_2S does in its much studied sulfidation processes.⁴⁷ This argument is supported by the large difference in the bond enthalpies between B–O and B–S (228 kJ/mol).¹³ Accordingly, we suspect that understanding the reactions at the molecular level could be important.

4. Concluding Remarks

As demonstrated in our experiments, the newly found use of boron sulfides offers a convenient route for synthesizing a broad range of crystalline metal polysulfides and sulfides in a pure form at intermediate temperatures. We believe that the mild reaction condition also can play an important role in preparation of nanostructured materials of such compounds, as indicated by our recent work on preparation of NdS_2 nanoparticles.⁶ We are currently extending our work to other various metal-source materials that contain different ligands, with preliminary success. It will not be impossible to apply the same preparative technique for polyselenides and selenides as well, because boron selenides are similar to boron sulfides in their characteristics.

Acknowledgment. D.-K.S. is grateful for financial support from the National Science Foundation through his CAREER Award (DMR – Contract No. 0239837). The authors thank Dr. Lynda Williams for her help in using SEM/EDX.

Supporting Information Available: X-ray powder diffraction patterns of the products listed in Table 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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