Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 4142–4148

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Ordered ternary compounds of the rare earth sesquisulfides

P. Evan Dresel[1], William B. White*

Materials Research Institute, The Pennsylvania State University, Room 210 MRL Bldg., University Park, PA 16802, USA

Received 16 April 2004; received in revised form 12 August 2004; accepted 21 August 2004
Available online 7 October 2004

Abstract

Intermediate compositions were investigated in eight Ln_2S_3–$Ln_2'S_3$ systems and reaction products characterized by Raman spectroscopy. Raman spectra are reported for the ordered structures reported in earlier literature. Based on the Raman spectra, $LaLuS_3$ previously reported as isostructural with $LaDyS_3$ (the I-type structure) is actually a new ordered compound. It was indexed on an orthorhombic cell with $a = 7.304$, $b = 6.659$ and $c = 9.817$ Å. A second previously unreported compound, Dy_3ScS_6, was identified by its Raman spectrum. Sharp Raman lines with a unique arrangement for each structure-type indicate that the ternary rare earth sulfides are well-ordered structures.

Keywords: Rare earth sulfides; Lanthanide sulfides; Raman spectra; Phase equilibria

1. Introduction

The sesquisulfides of the rare earths form a sequence of structures known as the α, γ, δ, and ε varieties depending on temperature and rare earth radius [1]. These binary sulfides can be combined into ternary systems *Ln*–*Ln*′–S. A number of distinct ordered ternary compounds are formed when the combining rare earths are of substantially different ionic radius. When rare earth ionic radii are similar, continuous solid solutions of the various binary structure types are observed. Structures for four of the ternary compounds have been determined by Rodier and his colleagues [2]. These are listed in Table 1 along with cation coordination numbers and space group information. For brevity, the French researchers have designated the ordered compounds with capital letters as indicated in Table 1. This convention is retained in the present paper.

The monoclinic F-type structure exhibits an eight-fold site, a seven-fold site, and two six-fold cation coordination sites. The eight-coordinated prismatic sites are occupied by the lighter rare earths while the two octahedral sites are occupied by the heavy rare earths. The seven-coordinated sites, however, also may be occupied by the light rare earths giving the $LnLn'S_3$ composition or by the heavy rare earths forming $LnLn_3'S_6$. Disordered arrangements of both rare earths in the six-coordinated sites have only have been reported for the Er–Sc system [4]. F-type compounds have been previously reported at the $LnLn_3'S_6$ composition in the La–Lu, Pr–Lu, Nd–Lu, and Gd–Lu systems. $LnLn'S_3$ F-type compounds also have been reported in the Gd–Lu system.

The orthorhombic H-type compounds contain the light rare earths on prismatic eight-coordinated sites and the heavy rare earths on octahedral sites. $LnLn'S_3$ H-type compounds have been reported in the Pr–Lu and Nd–Lu systems. Although initial work by Tien and Khodadad [7] suggested that La–Lu forms an I-type compound at 1000 °C at the 1:1 composition, Rodier et al. [8] indicated that it forms an H-type compound at this temperature and forms an I-type compound at 1250 °C.

The orthorhombic I-type cell is reported to be similar to the H-type except that the eight-coordinated prismatic site is larger and can only be occupied by lanthanum in the reported La–Yb and La–Lu

---

*Corresponding author.
E-mail address: wbw2@psu.edu (W.B. White).
[1] Present address: Pacific Northwest National Laboratory, P.O. Box 999 Richland, WA 99352, USA. Fax: +1-814-865-2326.

0022-4596/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.08.029

Table 1
Structures of the ternary rare earth sulfides

Notation	Type compound	Space group	Z	Reference
F	$Ce^{VIII}Yb^{VII}Yb_2^{VI}S_6$	$P2_1/m$	2	[3,4]
G	$Ce_2^{VIII}Tm^{VII}Tm^{VI}S_6$	$P2_1/m$	4	[5]
H	$Nd^{VIII}Yb^{VI}S_3$	$B22_12$	4	[6]
I	$Y^{VIII}Sc^{VI}S_3$	$Pna2_1$	4	[9]

compounds. Where scandium occupies the octahedral sites, any of the lanthanides from La to Er may occupy the prismatic sites at the $LnLn'S_3$ composition. Two of the light rare earth-sulfur distances are much larger than the other six so that the prismatic site can be described as having either a six- or eight-fold coordination [9].

The purpose of the present investigation was to revisit selected members of this family of systems using Raman spectroscopy as a primary characterization tool. An objective was to determine the compositional ranges of selected compounds, and to look for possible phase changes or decomposition reactions. Because the rare earth sulfides are highly refractory, insulating compounds, they have some possible application as infrared optical materials.

2. Experimental methods

The compounds investigated were prepared from binary Ln_2S_3 sulfides by weighing the correct mole ratios and mixing by light grinding in an agate mortar. Approximately 0.5 g of each of the compositions were sealed under vacuum in silica glass tubes. The silica tubes were fired for 3–7 days at temperatures ranging from 1000 to 1300 °C and were then quenched in water. Synthesis of sulfides in evacuated silica tubes is prone to the introduction of oxygen as an impurity. To evaluate the silica tube synthesis, selected compounds were also synthesized in a graphite tube furnace in an atmosphere of flowing H_2S, a procedure that is very effective at stripping minor amounts of oxygen and water from the system. Results from the two procedures were essentially identical.

The phases in the run products were identified by X-ray diffraction and by Raman spectroscopy. Both Picker and Scintag PAD V diffractometers were used for the X-ray analysis. The X-ray patterns were measured using Cu$K\alpha$ radiation over the diffraction angles of 10–70°. Raman spectra were measured on an Instruments SA Ramanor U-1000 microfocus spectrometer using the 632.8 nm line of a He–Ne laser as the excitation source. Measurements were taken from 50 to 450 cm^{-1}.

3. Results and discussion

3.1. Synthesis and characterization of known compounds

A selection of compounds with established crystal structures were synthesized to act as reference materials. The identifications of these structures were confirmed by matching X-ray diffraction patterns with powder data from the literature.

The rare earth sulfide compounds are excellent Raman scatterers. It was possible to obtain high quality spectra using a He–Ne laser source with only 15 mW power. The red emission was close enough to the optical band gaps of the sulfides to produce resonance Raman enhancement of the intensities. In contrast, the green line of an argon ion laser simply destroyed the samples. The Raman spectra proved to be a more useful diagnostic tool than the X-ray diffraction patterns. Raman spectra of the reference compounds are shown in Figs. 1 and 2. These were used to identify the phases resulting from the other synthesis experiments. Raman spectra for the end member rare earth sesquisulfides were published earlier [10].

The F-type structure appears at both the $LnLn'S_3$ and $LnLn_3'S_6$ compositions. The Raman spectra for $GdLuS_3$ and $GdLu_3S_6$ are very similar (Fig. 2) as would be expected for compounds with the same structure. The Raman spectra of examples of the different structures, however, are quite distinct further supporting the idea of the spectra as specific structural signatures. As expected, all bands fall into the same general wavenumber range. The bands are sharp, indicating well-ordered structures. Other than to note that the high wavenumber bands, in the range of 250–300 cm^{-1} are associated with rare earth-sulfur stretching motions, detailed band assignments cannot readily be made.

3.2. The La_2S_3–Lu_2S_3 system

The La^{3+} and Lu^{3+} ions provide the maximum contrast in rare earth radii and so this was the most extensively studied of the systems. A summary of the results of 21 synthesis experiments are displayed in Fig. 3. Under the chosen experimental conditions, reactions were complete at all temperatures above 1000 °C. The 1000 °C runs sometimes contained unreacted starting materials or traces of phases that did not fit the overall phase relations.

The discussion begins with the 1:1 mol ratio phase. According to the structure listing by Rodier et al. [2] $LaLuS_3$ should take the I-type structure as should the adjacent $LaYbS_3$ compound. A later investigation [8] found that $LaYbS_3$ took the H-type structure at 1000 °C and found the I-structure at 1250 °C. In the present experiments based on both Raman spectra and X-ray diffraction patterns, the same 1:1 compound was formed

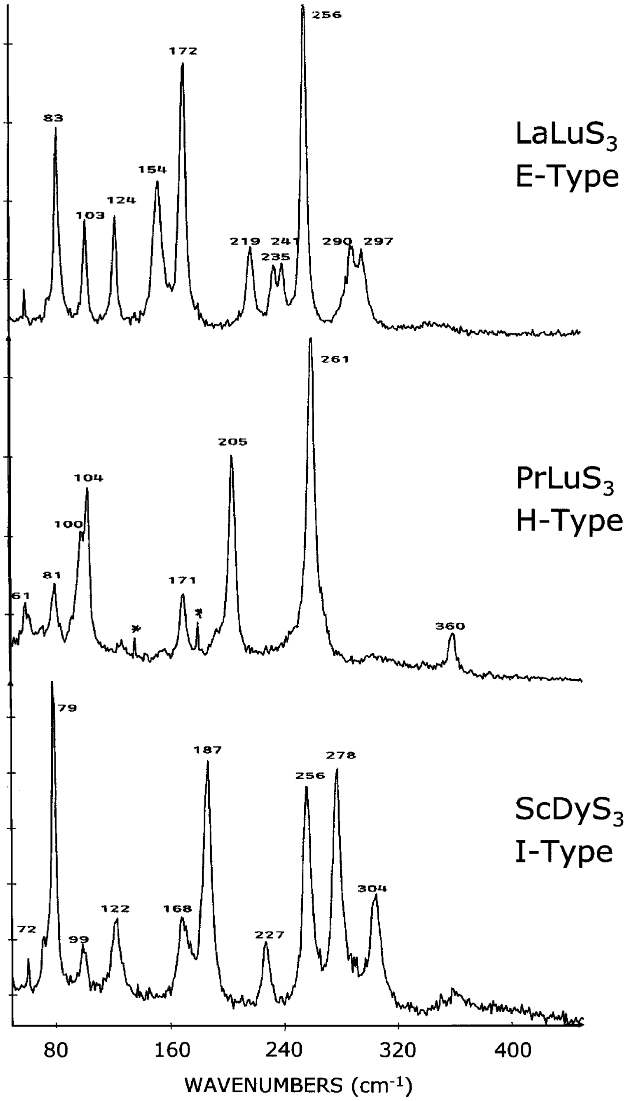

Fig. 1. Reference Raman spectra for $LaLuS_3$, reference for the E-structure phase, $PrLuS_3$, reference for the H-structure phase, and $ScDyS_3$, reference for the I-structure phase.

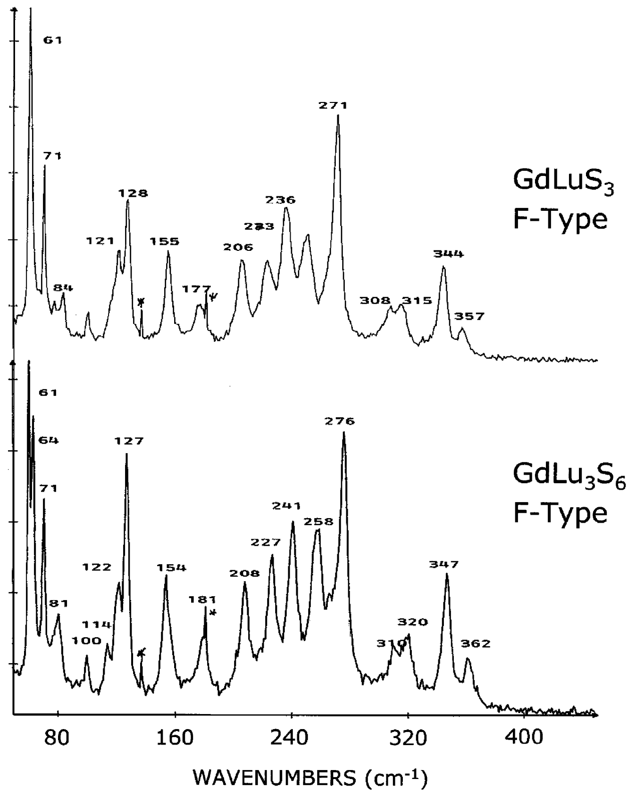

Fig. 2. Reference Raman spectra for $GdLuS_3$ and $GdLu_3S_6$ as reference spectra for the F-type structure.

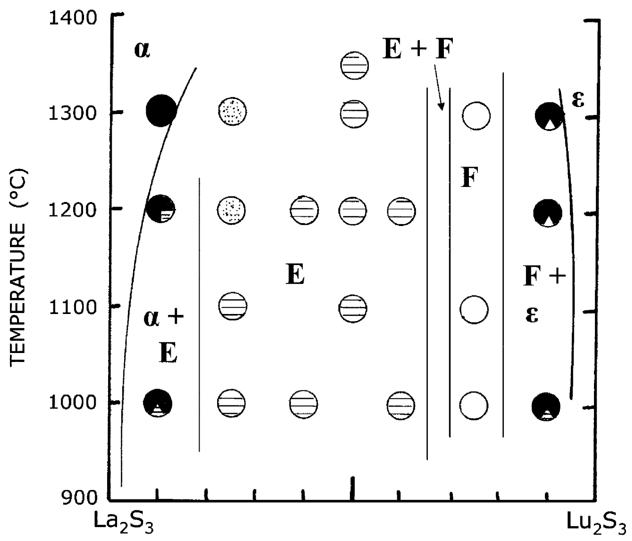

Fig. 3. Experimental runs and phase relations for the system La_2S_3–Lu_2S_3. Circles with dotted pattern indicate highly disordered products not further identified.

at all temperatures between 1000 and 1350 °C as shown in Fig. 3. The Raman bands are sharp and intense. However, the Raman spectrum of $LaLuS_3$ is distinctly different from the Raman spectra of either H-type or I-type compounds formed with the heavier rare earths although the X-ray pattern is rather similar to that of $LaYbS_3$ (ICPDS card no. 36-1260). Indeed, the Raman spectrum (Fig. 1) does not match any of the known ternary phases. It seems possible that $LaLuS_3$ is a previously unrecognized ternary compound in the rare earth sulfide systems. For ease of discussion, this compound is designated the E-type phase. The Raman spectrum for $LaLuS_3$ shown in Fig. 1 is taken as the signature for this compound.

X-ray powder data for the E-phase are listed in Table 2. Because of the similarity of the pattern to that of $LaYbS_3$, an attempt was made to index the powder pattern on an orthorhombic cell with similar cell dimensions to the H-type structure but no combination of cell edges could be found that fit the powder pattern to within experimental error. Better success was

Table 2
X-ray powder diffraction data for $LaLuS_3$

h k l	*d*-Observed	*d*-Calculated	$I/I_{max} \times 100$
1 1 1	4.392	4.399	13
2 0 0	3.646	3.652	20
1 1 2	3.470	3.475	100
2 0 1	3.421	3.423	6
0 2 0	3.329	3.329	26
2 0 2	2.932	2.930	5
1 2 1	2.894	2.895	9
1 1 3	2.723	2.725	12
2 1 2	2.681	2.682	6
1 2 2	2.579	2.578	7
0 0 4	2.455	2.454	23
2 2 1	2.387	2.387	10
3 1 1	2.227	2.227	12
1 3 0	2.123	2.124	3
3 1 2	2.073	2.073	9
2 0 4	2.037	2.037	13
0 2 4	1.975	1.975	28
3 1 3	1.876	1.874	5
2 2 4	1.738	1.738	10
1 1 6	1.552	1.553	10
4 2 2	1.523	1.522	7
2 0 6	1.493	1.493	3
3 1 5	1.490	1.490	2
5 1 0	1.426	1.427	2

Indexing by Appleman Program based on orthorhombic cell with $a = 7.304$, $b = 6.659$, and $c = 9.817$ Å.

obtained using the orthorhombic cell established for the I-structure. The indices listed in Table 2 and the calculated *d*-spacings are based on an orthorhombic cell with dimensions $a = 7.304$, $b = 6.659$ and $c = 9.817$ Å. These cell parameters are very close to those reported by Rodier et al. [8] for $LaYbS_3$ with the I-type structure. It is the distinctly different Raman spectrum that leads us to suggest the possibility of a new structure.

The compound designated the E-phase appears at all temperatures from 1000 to 1200 °C at the 3:2 and 2:3 compositions, indicating a substantial range of solid solution. The E-phase appears at 1000 and 1100 °C at the 3:1 composition but at higher temperatures the structure becomes completely disordered. The Raman spectra of the 1200 and 1300 °C preparations are very weak compared with the spectra of the crystalline compounds (Fig. 4). The dominant feature in the spectra is a clump of broadbands in the range of 220–240 cm^{-1}. This feature also appears in the 1100 °C preparation indicating that the disorder process is already underway. At the 9:1 ratio, a two-phase field occurs between the α-La_2S_3 end member and the E-type compound. There is also evidence for β-La_2S_3 in the high temperature runs. This is the stable temperature range for β-La_2S_3 and also a small amount of oxygen tends to stabilize the β-phase [11].

A distinctly different compound forms at all temperatures at the 1:3 composition. The Raman spectra of these products match closely the reference spectra of the monoclinic F-type compounds shown in Fig. 2. In contrast to the E phase, the F phase has a very narrow composition range in this system. Between the 2:3 composition and 1:3 composition must exist a two-phase region of co-existing E and F structures. Another two-phase field region was found between the F-type structure and ε-Lu_2S_3 at the 1:9 ratio.

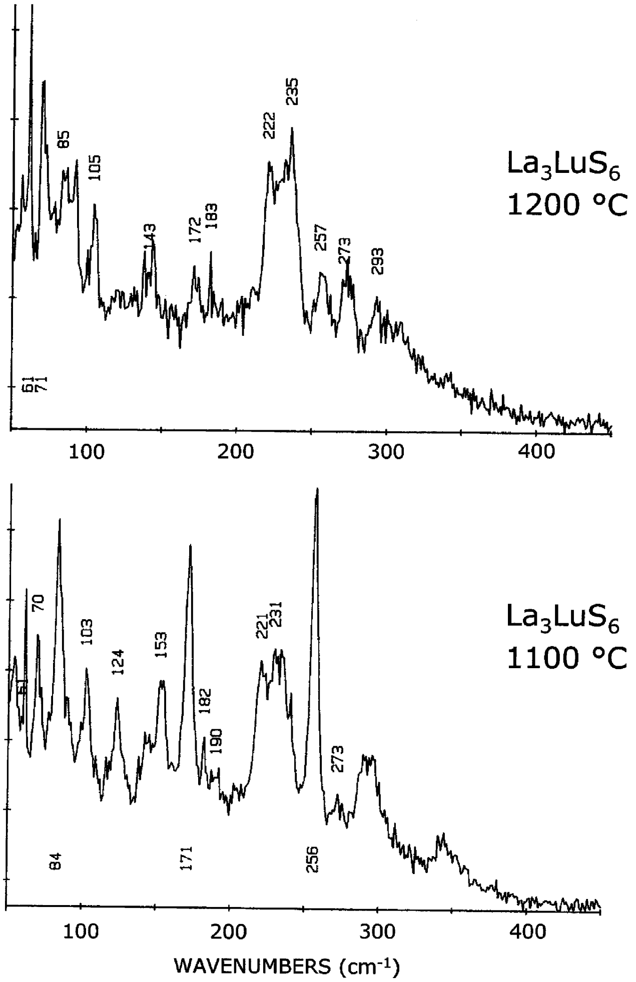

Fig. 4. Raman spectra of the disordered structure that appears at high temperatures at the composition La_3LuS_6. At 1100 °C the 221–231 cm^{-1} band cluster appears amidst sharp Raman lines of the E-type structure. At 1200 °C the spectrum is dominated by the 222–235 cm^{-1} band cluster.

3.3. The Pr_2S_3–Lu_2S_3 system

The results of nine synthesis experiments are summarized in Fig. 5. The compounds with a Pr:Lu ratio of 1:1 exhibit the orthorhombic H-type structure over the range of 1000–1350 °C. Rodier et al. [2] found that the 1:1 compound dissociated into a two-phase assemblage F + γ at 1350 °C. No evidence for this dissociation was observed in the present results perhaps because our

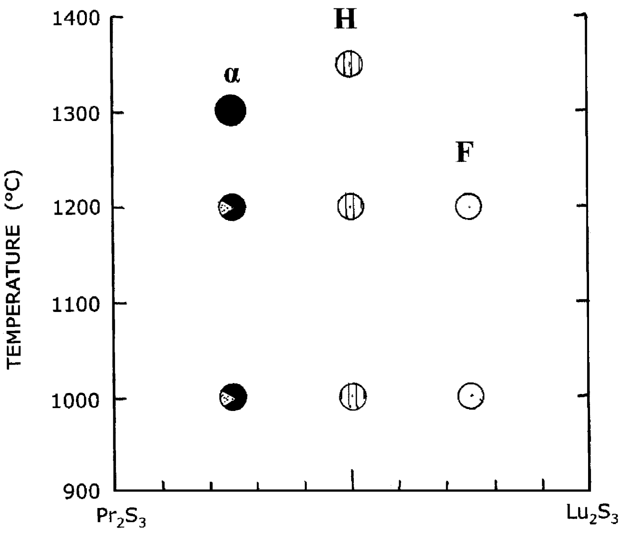

Fig. 5. Experimental runs and phase relations for the system Pr_2S_3–Lu_2S_3.

highest temperature experiment was at 1350 °C. Both Raman spectra and X-ray patterns are very clean so that the Raman spectrum of the 1200 °C preparation was selected as the type spectrum for the H structure (Fig. 1). At the 1:3 ratio, a single phase with the F-type structure appears at all temperatures up to 1300 °C. This agrees with Rodier et al.'s results. At a Pr:Lu ratio of 3:1, there appears a poorly crystallized mixture of a predominant maroon-colored phase and a smaller amount of a bright green compound. Both Raman and X-ray identify the maroon phase as α-La_2S_3. The high temperature γ-La_2S_3 appears in the high temperature runs. The green phase was not identified.

3.4. The Nd_2S_3–Lu_2S_3 system

The results of 12 synthesis experiments are summarized in Fig. 6. The compounds that form at the 1:1 Nd:Lu ratio have Raman spectra that appear similar to the reference spectrum for the H-type structure. However, the bands are not as intense or as well defined as in the reference spectrum. The spectral bands of the H-structure are superimposed on a broadband in the 125–225 cm^{-1} range. The X-ray patterns match the expected pattern of the H-type structure but with a possible second phase.

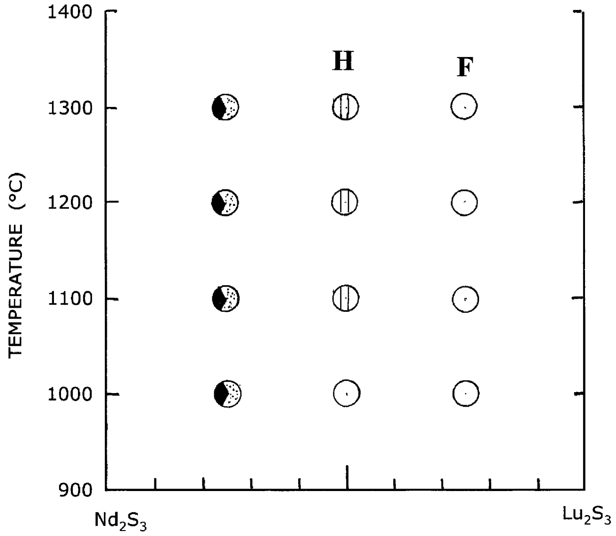

Fig. 6. Experimental runs and phase relations in the system Nd_2S_3–Lu_2S_3.

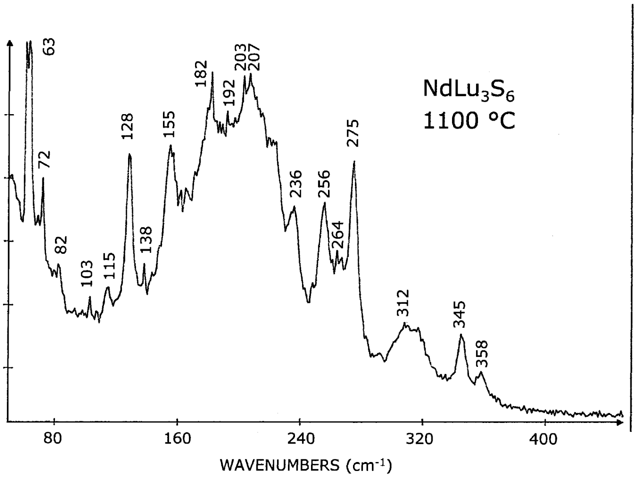

Fig. 7. Raman spectrum of $NdLu_3S_6$ prepared at 1100 °C showing the sharp lines of the F-type structure superimposed on a broader feature, presumably a Nd^{3+} luminescence band at an equivalent Raman shift of 200 cm^{-1} (15,600 cm^{-1} absolute).

Reactions at the 3:1 composition produce mixtures of phases. At 1000 °C the H phase appears coexisting with α-La_2S_3. At higher temperatures the spectra become weak and poorly resolved possibly due to conversion to the defect γ-La_2S_3 structure. Reaction products with the 1:3 ratio form F-type structure compounds at all temperatures. The Raman lines for the F-structure are superimposed on a broadband centered at about 200 cm^{-1} (Fig. 7). This band appears in reaction products from all temperatures and is similar to the band that appears in the 1:1 composition. It appears to be a fluorescence band of the Nd^{3+} ion. The $^2H_{11/2}$ states of Nd^{3+} occurs very close to the wavelength of the He–Ne laser and can be pumped by the 632.8 nm laser line [12].

3.5. The Gd_2S_3–Lu_2S_3 system

The results of 12 synthesis experiments are summarized in Fig. 8. The spectra of the run products at both 1:1 and 1:3 compositions are sharp and well defined for experiments at all temperatures from 1000 to 1300 °C. Gadolinium lutecium sulfides form the F-type structure at both the 1:1 and 1:3 ratios so that the spectra of these compounds become the reference for the F-structure

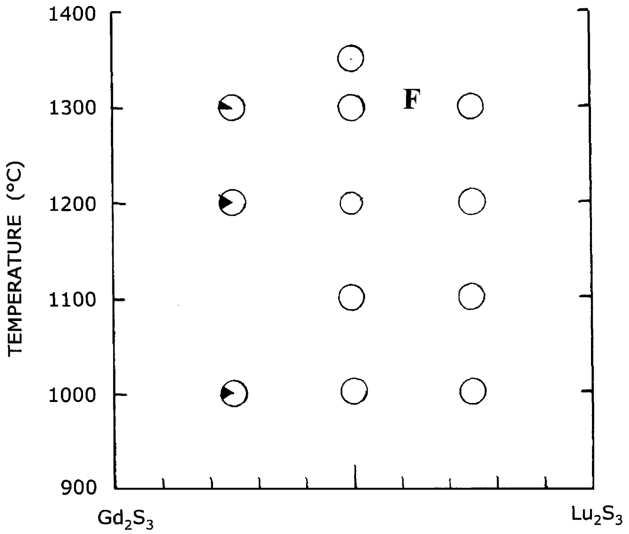

Fig. 8. Experimental runs and phase relations in the system Gd_2S_3–Lu_2S_3.

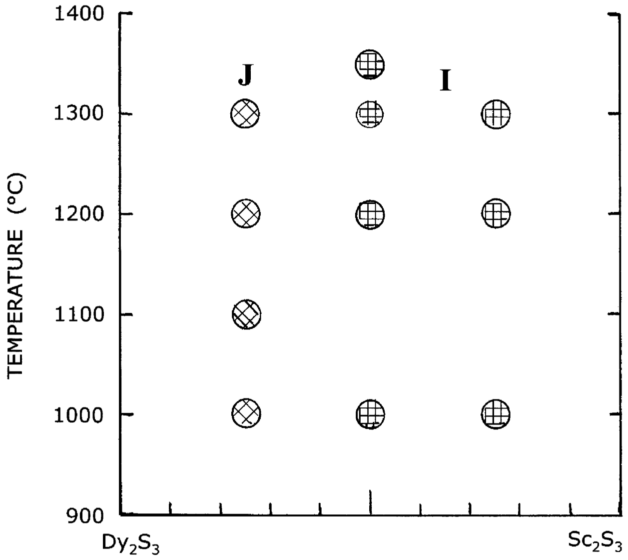

Fig. 9. Experimental runs and phase relations in the system Dy_2S_3–Sc_2S_3.

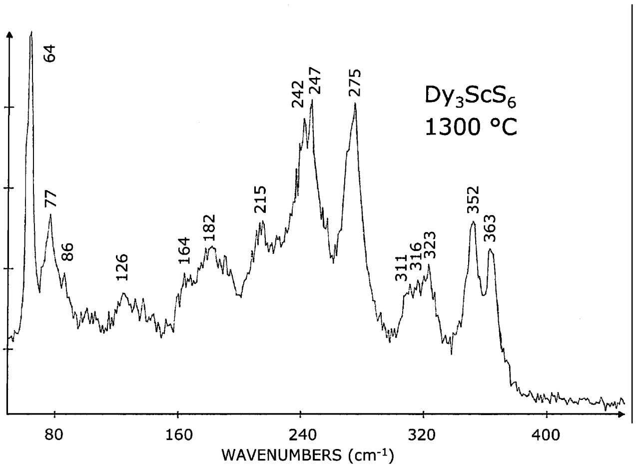

Fig. 10. Raman spectrum of Dy_3ScS_6 showing broadbands of what appears to be a distinct but somewhat disordered phase.

(Fig. 2). The only difference in the spectra of $GdLuS_3$ and $GdLu_3S_6$ is in the relative intensity of the bands and a small wavenumber shift of up to 8 cm^{-1}. Compositions with a 3:1 mol ratio of Gd to Lu produce X-ray patterns and Raman spectra of F-type structures but with much lower band intensities and broader bands. The 3:1 composition is a two-phase region with the F-type $GdLuS_3$ coexisting with α-La_2S_3.

3.6. The Dy_2S_3–Sc_2S_3 system

The results of 12 synthesis experiments are summarized in Fig. 9. At the 1:1 Dy:Sc ratio, a single compound, $DyScS_3$ was formed at all temperatures from 1000 to 1350 °C. X-ray diffraction patterns identified the I-type structure. Raman spectra of reaction products at all temperature were essentially identical. The product of the 1300 °C run was selected as a reference spectrum (Fig. 1). Reaction products at the 1:3 Dy:Sc ratio exhibited the same I-type structure as evidenced by both X-ray diffraction patterns and the Raman spectra. This suggests that the smaller Sc^{3+}-ion substitutes readily into the prismatic Dy^{3+} sites. The 3:1 Dy:Sc compositions have distinct X-ray patterns and Raman spectra, suggesting a new, and at present unidentified phase (for lack of a better name called “J” in Fig. 9). The Raman spectrum (Fig. 10) consists of broad lines that indicate a disordered structure. The spectrum has some similarities with the spectrum of the defect structure γ-La_2S_3 but the position of the bands is quite different.

3.7. The La_2S_3–Dy_2S_3 system

Some efforts were made to investigate the G phase by firing 1:1 mixtures of La_2S_3 and Dy_2S_3. The results were inconclusive. Good quality Raman spectra that might characterize the G phase were not obtained.

3.8. The La_2S_3–Gd_2S_3 system

Compositions were prepared at 0.1 mol fraction intervals and fired for 24 h at 1400 °C. The results showed a complete solid solution series with the orthorhombic α-Ln_2S_3 structure. Raman spectra were similar for all compositions. There were small shifts in band position as well as a continuous variation of linewidth with the maximum width at about 0.6 mol fraction of the heavy rare earth. A detailed description of the Raman variations in line width with composition are given elsewhere [13].

3.9. The Dy_2S_3–Er_2S_3 system

Compositions were prepared at 0.1 mol fraction intervals and fired for 20 h at 1200 °C. The results showed a complete solid solution series with the monoclinic δ-Ln_2S_3 structure. The Raman spectra of all compositions were very similar with band shifts of only a few wavenumbers. Again, there was a line broadening for intermediate compositions but a much smaller effect than observed in the La_2S_3–Gd_2S_3 system [13].

4. Conclusions

Phase stability regions in eight of the 90 possible Ln_2S_3–$Ln_2'S_3$ systems were examined using Raman spectroscopy as a primary characterization tool. Reference spectra were obtained for the phases designated F, H, and I by previous investigators. Raman lines are sharp indicating that the intermediate rare earth sulfides are well ordered structures. Two previously unrecognized phases, $LaLuS_3$, designated E and Dy_3ScS_6 designated J were identified by their Raman spectra. The orthorhombic unit cell for the E-phase has parameters very similar to those of $YbScS_3$ with the known I-type structure but the Raman spectra are quite different. The J-phase was recognized only from its Raman spectrum which indicated a distinct but disordered structure. Raman spectra provide useful signatures of all of the individual structure types.

Acknowledgments

This work was supported by the Office of Naval Research under Contract No. N00014-85-K-0219.

References

[1] J. Flahaut, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of the Rare Earths, vol. 4, North-Holland, Amsterdam, 1979, pp. 1–88 Chapter 31.
[2] N. Rodier, V. Tien, M. Guittard, Mater. Res. Bull. 11 (1976) 1209–1218.
[3] N. Rodier, V. Tien, Comp. Rend. Acad. Sci. Paris 279 (1974) 817–820.
[4] N. Rodier, P. Laruelle, Bull. Soc. Fr. Mineral. Cryst. 96 (1973) 30–36.
[5] N. Rodier, Bull. Soc. Fr. Mineral. Cryst. 96 (1973) 350–355.
[6] D. Carre, P. Laruelle, Acta Crystallogr. B 30 (1974) 952–954.
[7] V. Tien, P. Khodadad, Bull. Soc. Chim. France 1971 (1971) 3454–3458.
[8] N. Rodier, R. Julien, V. Tien, Acta Crystallogr C 39 (1983) 670–673.
[9] N. Rodier, P. Laruelle, Comp. Rend. Acad. Sci. Paris 270 (1970) 2127–2130.
[10] D.S. Knight, W.B. White, Spectrochim. Acta 46A (1990) 381–387.
[11] C.M. Vaughan, W.B. White, Mater. Res. Soc. Symp. Proc. 97 (1987) 397–402.
[12] M. Faucher, D. Garcia, E. Antic-Fidancev, M. Lemaitre-Blaise, J. Phys. Chem. Solids 50 (1989) 1227–1230.
[13] D.S. Knight, W.B. White, J. Am. Ceram. Soc. 79 (1996) 1394–1396.