JOURNAL OF MATERIALS SCIENCE **28** (1993) 3761–3763

Vibrational studies of the oxysulphide $(LaO)_4GaS_{4.5}$

S. BARNIER, M. PALAZZI, M. GUITTARD
Laboratoire de Chimie Minérale, associé au CNRS, UA200, Université René Descartes, 4 avenue de l'Observatoire, 75230 Paris Cedex 06, France

C. JULIEN
Laboratoire de Physique des Solides, associé au CNRS, UA154, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

Far-infrared and Raman spectra of the oxysulphide $(LaO)_4GaS_{4.5}$ single crystal were measured and analysed. The interpretation of the observed spectra is based on the existence of $(S–S)^{2-}$ disulphur groups which are responsible for the high-frequency features. Most of the frequencies are assigned in terms of internal and external vibrations of tetrahedral La_4O groups, GaS_4 units and $(S–S)^{2-}$ disulphur groups. Spectroscopy measurements are in good agreement with the recent structure determination.

1. Introduction

Rare-earth oxysulphides $(RO)_2S$ combine with different metal sulphides to form quaternary combinations of the general formula $(RO)_n(M_xS_y)$, with R = rare-earth, M = IB, IIIA, IVA or VA elements [1–5]. Of these oxysulphides compounds formed with two cations, the structures of $(CeO)_4Ga_2S_5$, $(NdO)_4Ga_2S_5$, $(LaO)_4Sn_2S_6$ and $(LaO)_4Ga_{1.33}S_4$ have been studied [4]. Although, these compounds crystallize in several different space groups, they all have sheet structures formed by alternation of an oxide sheet (RO) and a sulphide sheet (M_xS_y). The (RO) sheets have the same tetrahedral or pseudotetragonal array of R_4O tetrahedra, but the (M_xS_y) sheets have various structures, with 2, 3 or 4 layers of chalcogen atoms.

Two oxysulphide combinations have been observed in the $(LaO)_2S–Ga_2S_3$ system: $(LaO)_4Ga_{1.33}S_4$ and $LaGaS_2O$. The second compound does not exhibit a sheet structure; both metals are bonded simultaneously to the sulphur and to the oxygen atoms [2]. A third compound has been recently synthesized with the formula $(LaO)_4GaS_{4.5}$ [5]. This substance exhibits a sheet structure formed by the stacking of successive layers of La_4O tetrahedra, GaS_4 units and $(S–S)^{2-}$ layers.

This paper reports the studies of Raman and infrared spectra of $(LaO)_4GaS_{4.5}$. Comparison of the spectroscopic measurements may provide useful information on the structure, and in particular, on the presence of the disulphur group $(S–S)^{2-}$ in the crystal.

2. Experimental procedure

2.1. Crystal preparation

$(LaO)_4GaS_{4.5}$ single crystals were synthesized by direct fusion of a preparation heated at temperatures higher than 900 °C in a vacuum-sealed silica ampoule for 2 or 3 days, the interval necessary to obtain homogeneous products. The preparation consists of a mixture of $La_2O_2S_2$ (2 M concentration) and Ga_2S_3 (0.5 M concentration) with the addition of a large amount of KBr. After cooling by fast quenching, samples were washed in water. It should be noted that crystals of $(LaO)_4GaS_{4.5}$ are only grown in the presence of KBr. In the presence of iodine or potassium iodide, for instance, the crystalline phase was not formed.

2.2. Spectroscopy measurements

An unpolarized Raman spectrum was obtained with a Jobin–Yvon U1000 instrument equipped with holographic gratings and a photon counting system. The 647.1 nm line of a krypton ion laser was employed for sample excitation. A power excitation of 50 mW and spectral resolution of 2 cm^{-1} were used.

The powder far-infrared spectra were recorded between 50 and 650 cm^{-1} with a Bruker IFS113 vacuum fast-scan interferometer equipped with liquid helium-cooled bolometer and Mylar beam-splitter. Samples were mixed with Nujol and mounted between two polyethylene plates (TPX windows). Each spectrum is the average of 64 scans recorded with a spectral resolution of 2 cm^{-1}.

2.3. Structure and symmetry

$(LaO)_4GaS_{4.5}$ crystallizes in the quasi-tetragonal structure [5] in the centrosymmetric system. It belongs to the P4/*mmm* (D^1_{4h}) space group with one formula per elementary unit cell. The lattice parameters are $a = 0.416$ nm and $c = 1.586$ nm. Table I lists the position and site symmetry of the atoms in the unit cell. It may be noted that the sulphur atoms S(3)

---

* Author to whom all correspondence should be addressed.

0022–2461

and S(4) have a fractional occupancy of 1/4 and 1/2, respectively.

Lanthanum and oxygen atoms form the (LaO) layers which consist of tetrahedra with one oxygen atom at the centre. The oxygen is bound exclusively to the rare-earth, and never to the second metal. Each tetrahedron is connected by edge-sharing with neighbouring tetrahedra in the layer. (LaO) layers are separated by (GaS_4) and (S–S) layers, as shown in Fig. 1. The GaS_4 unit is built by two pyramids with one gallium atom at the top. The pyramids are connected by their base which is formed by sulphur atoms. It may be remarked that sulphur atoms are bound to gallium and lanthanum atoms, and that gallium atoms are only bound to the sulphur.

Vibrational modes are obtained by the correlation method between site group and factor group; 39 fundamental modes are expected. The symmetries at the Brillouin zone-centre (at $q = 0$) are

$$\Gamma = 4A_{2u}(IR) + 3A_{1g}(R) + 1B_{1g}(R) + 9E_u(IR) + 6E_g(R) + B_{2u}(IN) \qquad (1)$$

where (IR), (R) indicate infrared and Raman activity, respectively, and (IN) corresponds to the inactive optical modes.

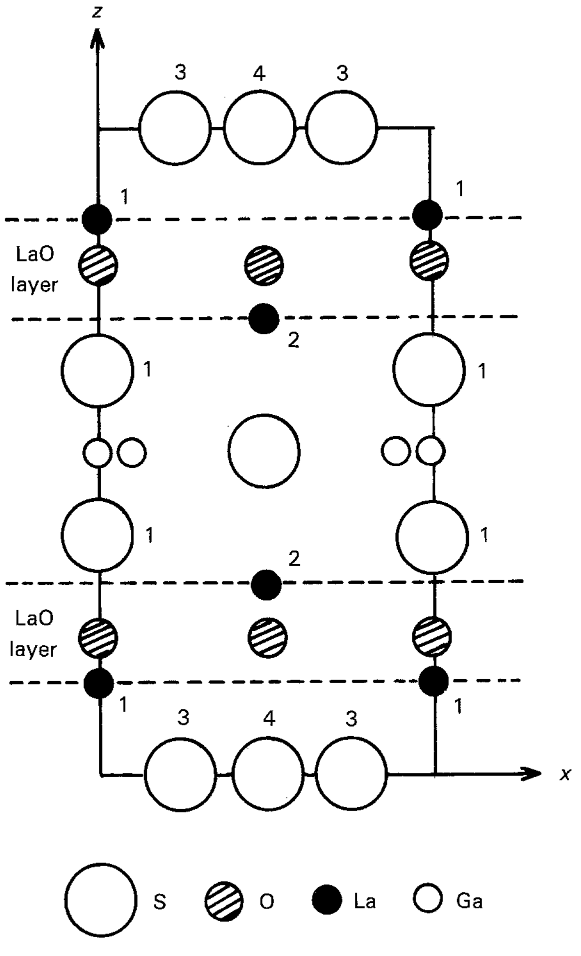

Figure 1 The structure of $(LaO)_4GaS_{4.5}$. The successive sheets of the crystal are shown in the *xz* plane.

TABLE I Atomic position and site symmetry of the $(LaO)_4GaS_{4.5}$ unit cell

Atom		Position	Symmetry
La(1)	(2g)	(0, 0, 0.14)	$C_{4v}(4mm)$
La(2)	(2h)	(1/2, 1/2, 0.292)	$C_{4v}(4mm)$
O	(4i)	(0, 1/2, 0.21)	$C_{2v}(mm)$
Ga	(4m)	(0.2, 0, 1/2)	$C_{2v}(mm)$
S(1)	(2g)	(0, 0, 0.37)	$C_{4v}(4mm)$
S(2)	(1d)	(1/2, 1/2, 1/2)	$D_{4h}(4/mmm)$
S(3)	(4n)	(1/4, 1/2, 0)	$C_{2v}(mm)$
S(4)	(1c)	(1/2, 1/2, 0)	$D_{4h}(4/mmm)$

3. Results and discussion

Fig. 2 shows the Raman spectrum of $(LaO)_4GaS_{4.5}$ recorded at room temperature. This spectrum displays two strong peaks at 318 and 448 cm^{-1}, bands with medium intensity at 365, 398, 408 and 458 cm^{-1},

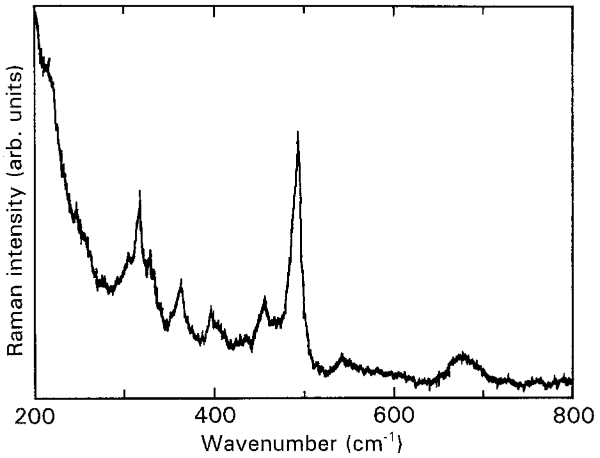

Figure 2 Room-temperature Raman scattering spectrum of $(LaO)_4GaS_{4.5}$ recorded with the 647.1 nm line of a Kr^+ laser..

TABLE II Infrared absorption and Raman bands in the region 50–650 cm^{-1} of $(LaO)_4GaS_{4.5}$

Infrared (cm^{-1})		Raman (cm^{-1})		Assignment
75	s			δ-GaS_4
109	s			T′-GaS_4
156	s			δ-GaS_4
185	m			T′-GaS_4
194	sh			
		210	sh	
237	sh			
		248	sh	ν-La_4S
272	vs			
314	vs	318	s	
330	sh	332	sh	ν-GaS_4
360	sh	358	sh	
		365	s	
		370	sh	
		398	m	ν-La_4O
		408	m	
		420	w	
437	s			ν-La_4O
450	sh			
		458	m	
490	w	490	sh	
		498	vs	ν-$(S–S)^{2-}$
515	sh			
		540	w	
600	m			
		680	m	

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

and broad bands in the high-frequency region. Fig. 3 shows the infrared absorption spectrum of $(LaO)_4GaS_{4.5}$. We observe that the predominant bands are located at 75, 109, 156, 272, 314 and 437 cm^{-1}. The frequency and intensity of the Raman and infrared bands are listed in Table II. It may be noted that a small number of coincidences (Table II), which would be expected for a structure containing an inversion centre, are observed.

The structure of $(LaO)_4GaS_{2.5}$ $(S–S)^{2-}$ has no isomorphic structure, such as the structure with Pr^{3+} or Nd^{3+} cations, and it is difficult to give a proper assignment for the vibrational modes. However, each structural unit can be considered separately. The lanthanum La(1) atom has nearest neighbours consisting of a layer of oxygen atoms and a double-layer of sulphur S(3) atoms located along the z-axis (see Fig. 1). This La(1) atom vibrates between four oxygen atoms situated below it and four sulphur atoms located above it. Vibrational modes of the La–S bonds are expected at 180–280 cm^{-1} [6] and those due to the La–O bonds are expected at 364–487 cm^{-1} [7].

In a first approximation, the assignment of the Raman and IR band may be as follows: (i) bands in the range 185–272 cm^{-1} are due to the La–S bending modes, and (ii) bands in the range 358–437 cm^{-1} are attributed to the La–O bending modes. The reality is more complex, because La(2) atoms are connected to the gallium atoms through the sulphur S(1) and S(2) atoms. If one considers that the Ga–S bonds are sufficiently strong to lay down their own vibrational modes, the La(2)–S(1) or La(2)–S(2) bonds are not taken into consideration, and the La–O bonds only are considered.

The bending mode of the GaS_4 tetrahedral group has an average frequency of 309 cm^{-1} [8]. Consequently, the origin of the bands observed in the range 300–358 cm^{-1} is mainly attributed to the GaS_4 group [9]. The low-frequency bands at 75 and 156 cm^{-1} are assigned to the deformation mode of the GaS_4 tetrahedral group. The external modes of the GaS_4 with T′ and R′ symmetries are observed at 109 and 185 cm^{-1}.

IR absorption and Raman spectra show intense bands in the spectral range 400–550 cm^{-1} for which the analysis is further supported by consideration of the modes derived from the $(S–S)^{2-}$ groups. The existence of chain-like sulphur species (S_n, $n = 2–4$) cannot be excluded, because it has been reported that homo-nuclear vibration of S–S bonds in various inorganic compounds containing sulphur chains give rises to peaks in the range 470–500 cm^{-1} [10–14]. It has been shown that the $(S–S)^-$ anions dispersed in potassium iodide exhibit an intense Raman spectrum with bands at 582 and 598 cm^{-1} [15]. Recently, LeRolland *et al.* [13] assigned the band at 400–550 cm^{-1} in their vibrational studies of rare-earth polysulphides to the S–S stretching within the $(S–S)^{2-}$ groups. These modes have also been observed in arsenic-based glasses at 468–475 cm^{-1} [12] and in the spectrum of $La_2O_2S_2$ single crystals at 487–500 cm^{-1} [14]. The spectrum of $(LaO)_4GaS_{4.5}$ exhibits the same type of features attributed to the $(S–S)^{2-}$ group and the existence of a disulphur group in the crystal seems a correct hypothesis.

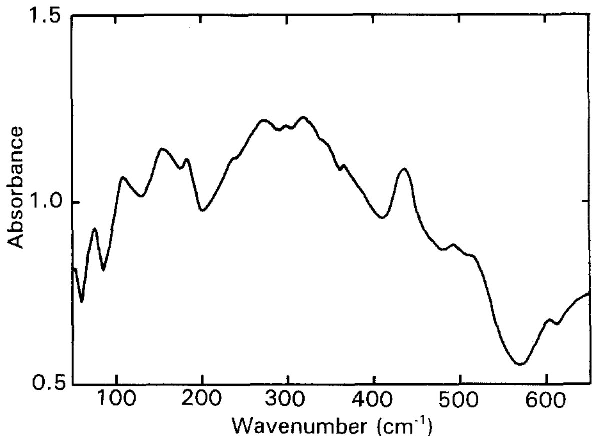

Figure 3 Far-infrared absorption spectrum of $(LaO)_4GaS_{4.5}$.

4. Conclusion

The lattice vibrations of $(LaO)_4GaS_{4.5}$ single crystal were investigated by Raman scattering and far-infrared techniques. Most of the frequencies are assigned in terms of internal and external vibrations of tetrahedral La_4O units and GaS_4 groups. Spectroscopy measurements give information on the structure of the sheet-formed crystal and show the existence of $(S–S)^{2-}$ disulphur groups which are responsible for the high-frequency features.

Acknowledgements

The authors thank Dr M. Massot for technical assistance and Dr J. Deppe for comments on the manuscript.

References

1. J. DUGUE and M. GUITTARD, *Acta Crystallogr.* **B 38** (1982) 2368.
2. S. JAULMES, *ibid.* **B 34** (1978) 2610.
3. A. MAZURIER, M. GUITTARD and S. JAULMES, *ibid.* **B 38** (1982) 379.
4. M. GUITTARD, S. BENAZETH, J. DUGUE, S. JAULMES, M. PALAZZI, P. LARUELLE and J. FLAHAUT, *J. Solid State Chem.* **51** (1984) 227.
5. S. JAULMES, M. PALAZZI and M. GUITTARD, personal communication (1991).
6. S. BARNIER and G. LUCAZEAU, *J. Chim. Phys.* **73** (1976) 580.
7. S. BARNIER, C. JULIEN and M. GUITTARD, *Spectrochim. Acta* **A 44** (1988) 707.
8. E. FINKMAN, J. TAUC, R. KERSHAW and A. WOLD, *Phys. Rev.* **B 11** (1975) 3785.
9. G. LUCAZEAU and J. LEROY, *Spectrochim. Acta* **A 34** (1978) 29.
10. S. BARNIER, M. GUITTARD and J. FLAHAUT, *Mater. Res. Bull.* **14** (1979) 973.
11. M. PISARCIK and L. KOUDELKA, *Mater. Chem.* **7** (1982) 499.
12. H. H. ERYSEL and S. SUNDER, *Inorg. Chem.* **18** (1979) 2626.
13. B. LeROLLAND, P. McMILLAN and P. COLOMBET, *C. R. Acad. Sci. Paris* **312** (1991) 217.
14. J. DUGUE, Thesis, Université Descartes, Paris (1978) unpublished.
15. W. HOLZER, W. F. MURPHY and H. J. BERNSTEIN, *J. Molec. Spectrosc.* **32** (1969) 13.

Received 24 January
and accepted 20 November 1992