UDC 548.3.546(65.21.22)

STRUCTURAL - CHEMICAL ASPECTS OF NEW PHASES FORMATION IN THE Ga_2S_3-Ln_2O_2S (Ln-La, Nd) SYSTEM

V.S. Mammadov

Acad. M. Nagiyev Institute of Catalysis and Inorganic Chemistry
National Academy of Sciences of Azerbaijan .
H. Javid Ave.113, Baku AZ 1143, e-mail: vilayetmemmedov1980@mail.ru

Received 12.03.2019

Abstract*:The paper explores questions of structural-chemical aspects of peritectic compounds formation in the Ga_2S_3-Ln_2O_2S (where Ln-La,Nd) system. It found that these reactions proceed due to inheriting structural peculiarities of the peritectic compound by the solid product of reaction. Specifically, the structure of peritectic compounds and solid products of their decomposition are interrelated by means of alternative, simple plans of reconstruction while the presence of a cooperative mechanism makes the kinetics of transition between them much easier. Note that the structures of all peritectic compounds of these reactions fall into the derivative or composite type.*

Keywords: *structural-chemical****,*** *inheriting, structural peculiarities, peritectic compounds.*
DOI: 10.32737/2221-8688-2019-2-246-251

Introduction

Effective luminophors, in particular, lanthanide oxysulfides and solid solutions obtained on their base are presently widely used in functional electronics devices, and in some cases they become an indispensable technical material in the production of appropriate photo-[1-3], cathode-[4-6], roentgen -[7-8] and some radio luminophors [9,10].

The paper [11-13] revealed that all sorts of lanthanide oxysulfides are formed by means of the peritectic reaction. In this paper, we cite examples of these reactions and consider structural and chemical aspects of their formation to mark new phases in the Ga_2S_3-Ln_2O_2S(where Ln-La,Nd) system.

Results and their discussion

It is known that three new complex oxysulfide compounds were obtained in Ga_2S_3-Ln_2O_2S systems (where Ln-La,Ce,Pr,Nd,Eu) due to the chemical interaction in the course of peritectic reactions ($L+LnOGaS_2 \leftrightarrow LnOGa_3S_5$; $L+(LnO)_4Ga_2S_5 \leftrightarrow LnOGaS_2$; $L+Ln_2O_2S \leftrightarrow (LnO)_4Ga_2S_5$ [11-13].

It was the presence of mono-crystal barrier that made it no possible to study the crystalline structures $LnOGa_3S_5$. Note that structures of two types of compounds like $LnOGaS_2$ and $(LnO)_4Ga_2S_5$(α-$LaOGaS_2$, β-$LaOGaS_2$, $(LaO)_4Ga_2S_5$, $(NdO)_4Ga_2S_5$ were examined in the works [14-17], accordingly.

Crystallographic parameters of initial components and synthesized compounds are displayed in Table 1.

To carry out a comparative crystallochemical analysis of the structures of peritectic compounds and formation of their solid phases we have chosen and built projects of their structures with the aim of putting up the problem.

The results of comparative crystallochemical analysis of the said structures, obtained peritectic compounds and initial components made it possible to infer that crystalline structures of new phases have been displayed by tetragon layers of ($Ga_4S_8)^{4-}$ composition in the projection perpendicular to the axis "a"(fig.1.c.) in the structure β-Ga_2S_3 and the layers formed from LnO_4 by means of tetrahedrs in the structures Ln_2O_2S.(Fig.1.a) [21].

Table 1. Crystallographic characteristics of polymorphous modifications of $LaOGaS_2$,$(LnO)_4Ga_2S_5$ and their initial components.

Compounds	Syngony	Space. groups.	Periods of grating,A^0				Z	V_1A^{03}
			a	b	c	β,degree		
α$LaOGaS_2$,	Rhombus[14]	P2ab	5.81	5.85	11.83	-	4	402,08
β $LaOGaS_2$,	Rhombus[15]	Pmca	5,54	5,767	11,443	-	4	365,72
$(LaO)_4Ga_2S_5$	Tetragony[16]	14/mm m	4.18	-	18.74	-	1	327.40
$(NdO)_4Ga_2S_5$	Rhombus[17]	Pbca	18.250	22.256	5.737	-	8	2370.33
La_2O_2S	Hexagony[18]	P3m1	4.049	-	6.935	-	1	97.83
Nd_2O_2S	Hexagony[19]	P3m1	3.953	-	6.784	-	1	91.17
Ga_2S_3	Monoclin[20]	Cc	11.140	6.411	7.038	β=121.22^0	4	424.38

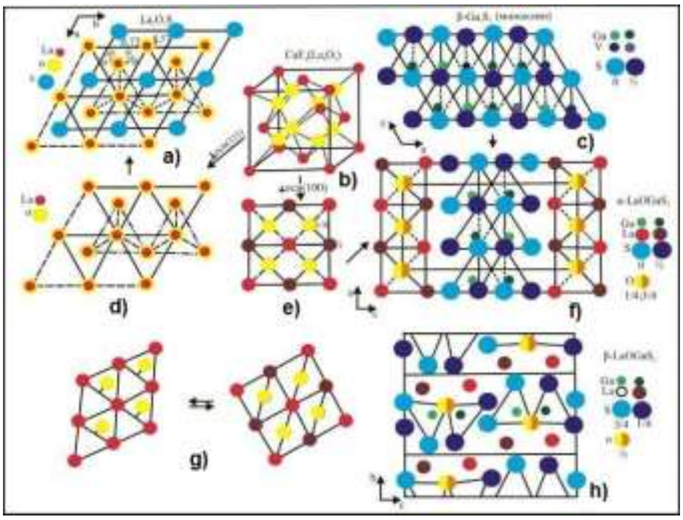

Fig.1. Projection of crystalline structure of $LaOGaS_2$, its components and a scheme of crystalline-chemical interactions.

Besides, as far as the reaction runs, the two-storied hexagon layer in La_2O_2S structure (Fig.1.b,d) changes into tetragon layer (Fig.1.e) in the scheme (Fig.1.g) which indicates to non-complementarity of hexagony layer as compared with tetragon layer ($Ga_4S_8)^{4-}$ and its ability to be in the structure alienated from these layers of mono, double and triple columns. In so doing, bands or fragments cannot be expelled that indicates to the possibility of repeated involvement in the latter layers to form the new ones.

Of particular interest is the comparison of structures α-and β-modifications of the compound $LaOGaS_2$.

At first sight, there are not any similarities (Fig.1.f and Fig.1.h)

From a structure displayed at Fig.2, it follows that between these modifications there is a certain similarity on hand (as visual aids in La_2Ga_2O tetrahedron inter-atom links have been indicated).

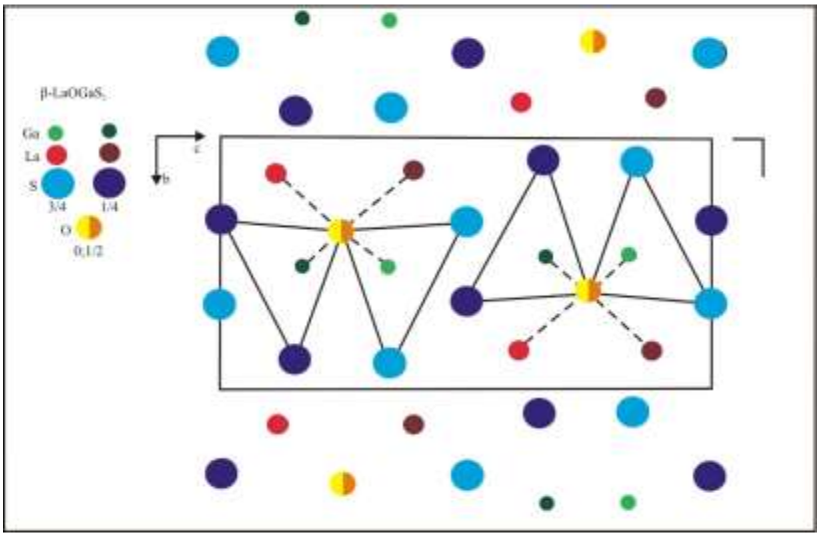

Fig. 2. Projection of β-$LaOGaS_2$. structure

If disregard all other atoms and imagine them in space, as displayed in Fig.3 schematically, it is easy to notice that after pinching out the atoms of gallium, they could join the well-known layers of tetrahedrs La_4O.

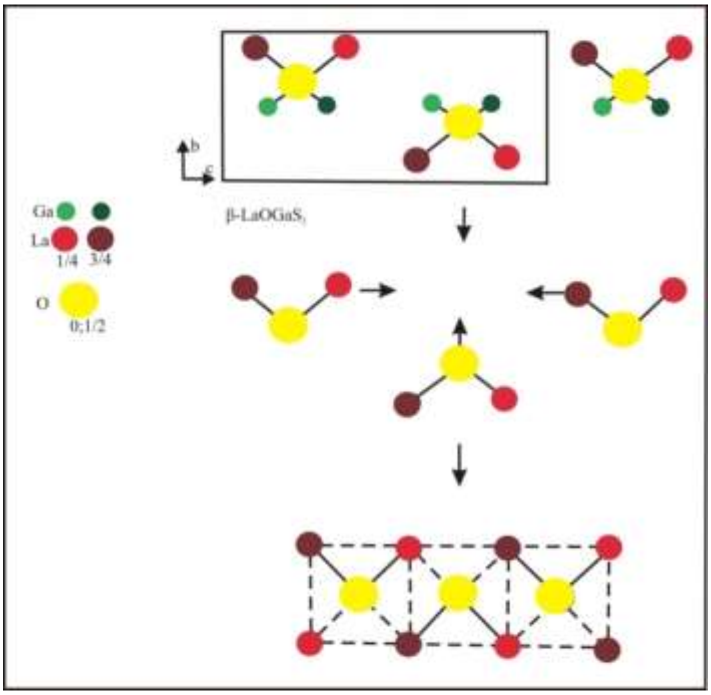

Fig.3. Possible scheme of tetragon layers formation out of La_4O tetrahedrs in the reaction.

The $(LnO)_4Ga_2S_5$ structures are crystallized in two types: La, Ce, Pr in tetragon, and Nd, Eu – in rhombus syngony (Fig. 4 and Fig. 5).

The presence of typical layers $(Ln_2O_2)^{2+}$ in both structures doesn't lead to the formation of isostructural compounds, as is the case with nonisostructure of $(LnO)_4Ga_2S_5$ and $(NdO)_4Ga_2S_5$, so it requires a separate investigation.

From the mentioned above it follows that the compounds with the structural type of wurtzite (CdS, ZnS, HgS and oth.) with layers $(Me_4S_8)^{4-}$ in interaction with Ln_2O_2S theoretically can form the mentioned above compounds.

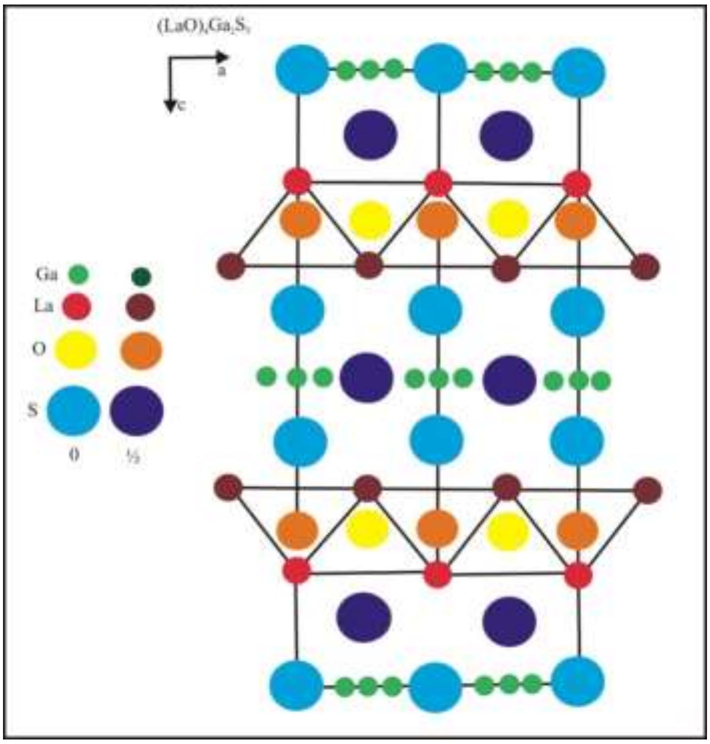

Fig.4. Projection of $(LaO)_4Ga_2S_5$. Structure

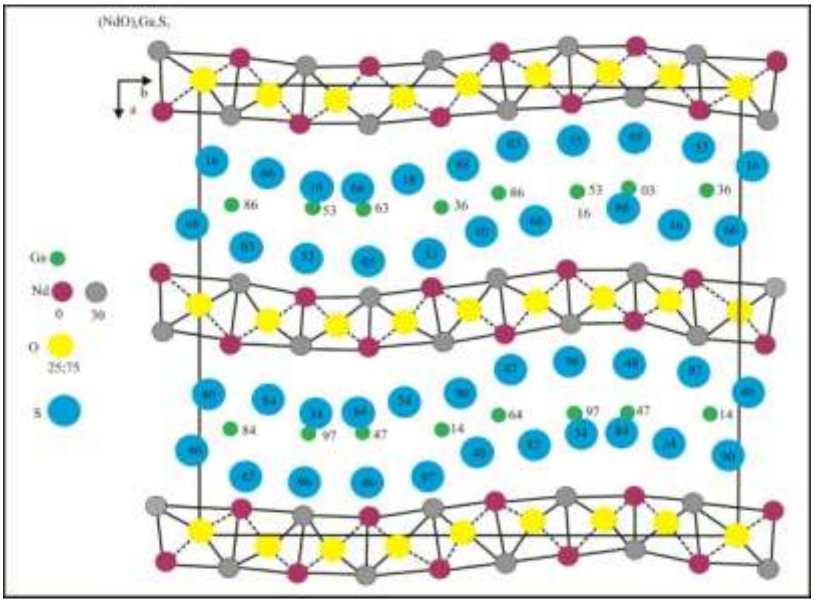

Fig.5. Projection of $(NdO)_4Ga_2S_5$ structure

For example, for $LaOGaS_2$ accordingly:

$$(Ln_4O_4)^{4+}+(Ga_4S_8)^{4-}\rightarrow Ln_4O_4Ga_4S_8\rightarrow LnOGaS_2\ ;$$
$$(Ln_4O_4)^{4+}+(Zn_2S_4)^{4-}\rightarrow Ln_4O_4Zn_2S_4\rightarrow Ln_2O_2ZnS_2;$$
$$(Ln_4O_4)^{4+}+(Gd_2S_4)^{4-}\rightarrow Ln_4O_4Gd_2S_4\rightarrow Ln_2O_2GdS_2;$$
$$(Ln_4O_4)^{4+}+(Hg_2S_4)^{4-}\rightarrow Ln_4O_4Hg_2S_4\rightarrow Ln_2O_2HgS_2.$$

It is possible geometrically to create the structures with multistoried or mixed layers, but the created electroneutral structures must be high-ordered, as well as with gallium or oxygen insufficiency. The obtained effect can reduce the possibility of complex structures formation.

This work supported by the Science Development Foundation under the President of the Azerbaijani Republic. ***Grant № EİF/MQM/Elm-Tehsil-1-2016-1(26)-71/15/1***

References

1. Zhang P., Huang Q., Cheng H., Fan X., Wang X., Qian G., Wang M. Influence of flux on the luminescent properties of Y2O2S : Ti long aftergloLi phosphors. *Journal of the Chinese Ceramic Society*. 2005, vol. 33, no.2, pp. 140-144.
2. Nagasaki S., Otake S. Red phosphor and fluorescent lamp using the same. Japan patent 2004182907, 2004.
3. Murakami Y., Arai K. Red light emitting long afterglow photoluminescence phosphor and afterglow lamp thereof. US patent, 2001043042, 2001.
4. Yamaguchi K., Inoue K., Ito T., Matsuura S. Phospor for display and field- emission display. US patent, 2003132699, 2003.
5.WakasukiT., Tadayashi Y. Red- light-emitting phosphor and color display using the same. Japan patent 2003160786, 2003.
6. Igarashi T., Kusunori T., Kusunoki T., Ohno K. Method for manufacturing luminescent material, luminescent material manufactured by the same manufacturing method, and display substrate and display apparatus having the same luminescent material. US patent, 2002074536, 2002.
7. Oyaisu E., Okamura M. Phosphor sheet for radiation detector employing it and equipment for detecting radiation. EU Pat. 1550885, 2005.
8. Masi F., Tecotzky M. X-ray conversion screen utilizing yttrium oxysulfide phosphor. Canada patent, 963183, 1975г.
9. Fukuta Y., Oota H.. Ceramic scintillator, and radiation detector and radiographic examination apparatus using same. MP Patent 2005028591, 2005.
10. Maekawa T., Sumita A. α/β radiation detector using wavelength and delayed fluorescence discrimination. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment.* 2002, vol. 480, issues 2-3. pp. 626-635.
11. Bakhtiyarov I.B., Rustamov P.G. System La_2S_3-La_2O_3-Ga_2S_3. Russian Journal of Inorqanic Chemistry. 1987, vol. 32, no. 4, pp. 1016-1021.
12. Bakhtiyarov I.B., Rustamov P.G., Nakhmetov S.M. et.al. The Ga_2S_3-Eu_2O_2S system. *Z.Anorq. Allg. Chem*. 1986, vol. 533, no. 2, pp.186-190.
13. Bakhtiyarov I.B., Abbasov M.M. Phase diagram of the system Pr_2S_3-Pr_2O_3-Ga_2S_3. *Z. Anorg. Allg. Chem*. 1990, vol. 582, no. 3, pp. 217-223.
14. Guittard M., Jaulmes S., Loireau-Lozac`h A.M. et al . Etude du systeme La_2S_2-La_2O_3-Ga_2O_3-Ga_2S_3. Despcription structurale des pases quaternalres et appreche du diagramme de phase. *J.solid.state chem.* 1985, vol. 58, no.3, pp. 276-281.
15. Jaulmes S. Oxysulfure de gallium et de lanthane $LaOGaS_2$. *Acta cryst*. 1978, B34, p. 2610.
16. Jaulmens S., Godlewski E., Pallazi M. et al. Deux structure isotypes a sites anioniques et lacunaires;$(CeO)_4Ga_2S_5$ et $(LaO)_4$ As_2S_5. *Acta cryst*.1982, B38 , pp. 1707-1717.
17. Dugue J., Guittard M. Structure de l`oxysulfure de neodyme et de gallium $(NdO)_4Ga_2S_5$. *Acta Cryst.* 1982, B38, p. 2368.
18. Morosin B., Newman D.J. La_2O_2S structure refinement and crystal field. *Acta cryst*. 1973, B29, p. 2647.
19. Eliseev A.A., Grisik A.A. Rare earth oxyhalides: Rare earth semiconductors., L.Science. 1977, pp.178-201.
20. Goodyear I., Stiegmann G.A. The crystal structure of α-Ga_2S_3. *Acta Cryst.*,1963, vol. 16, no. 10, pp. 946-949.
21. Bakhtiyarov I.B. Structural aspects of formation Ln_2O_2S. *Russian Journal of Inorqanic Chemistry*.1996, vol. 41, no.8, pp.1259-1261.

СТРУКТУРНО-ХИМИЧЕСКИЕ АСПЕКТЫ ОБРАЗОВАНИЯ НОВЫХ ФАЗ В СИСТЕМЕ Ga_2S_3- Ln_2O_2S (Ln-La, Nd)

В.С. Мамедов

Институт Катализа и Неорганической химии им. акад. М. Нагиева
Национальной АН Азербайджана
AZ 1143 Баку, пр. Г.Джавида, 113; e-mail:vilayetmemmedov1980@mail.ru

В настоящей работе обсуждаются структурно-химические аспекты образования перитектических соединений в системе Ga_2S_3- Ln_2O_2S (где,Ln-La,Nd). Установлено, что эти реакции протекают унаследованием структурных особенностей перитектического соединения твердым продуктом реакций. А именно, структура перитектических соединений и твердых продуктов их распада связаны между собой альтернативными, простыми планами реконструкции и наличие кооперативного механизма облегчает кинетику перехода между ними. Структуры всех перитектических соединений этих реакций относятся к производному или составному типу.

Ключевые слова: *структурно-химический аспект, унаследование, структурные особенности, перитектические соединения, компоненты*

Ga_2S_3-Ln_2O_2S (Ln-La,Nd) SİSTEMİNDƏ ƏMƏLƏ GƏLƏN YENİ FAZALARIN QURULUŞ-KİMYƏVİ ASPEKTLƏRİ

V.S. Məmmədov

AMEA-nın akad.M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu
Bakı, AZ 1143, H.Cavid pr.113, e-mail vilayetmemmedov1980@mail.ru

Bu işdə Ga_2S_3-Ln_2O_2S(Ln-La,Nd) sistemdə aşkar olunan peritektik birləşmələrin quruluş aspektləri müzakirə olunur.Müəyyən olunmuşdur ki, peritektik reaksiyalarla əmələ gələn birləşmələrin quruluşu ilə onu əmələ gətirən bərk fazaların quruluşu arasında irsilik prinsipi ödənilir.Başqa sözlə nonvariant reaksiyalar zamanı peritektik birləşmələrin quruluşunda sadə planlı rekonstruksiya prosesi baş verir və atomların kollektiv cüzi şürüşməsi ilə peritektik birləşmə onu əmələ gətirən bərk fazaya çevrilir. Bu bağlılıq peritektik birləşmələrlər və bərk məhlullar arasında bir quruluş oxşarlığı olduğunu göstərir.

Açar sözlər*:quruluş-kimyəvi,irsilik, quruluş xüsusiyyətləri, peritektik birləşmələr, komponentlər*