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Joint experimental and theoretical study of $PbGa_2S_4$ under compression†

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The effect of pressure on the structural, vibrational, and optical properties of lead thiogallate, $PbGa_2S_4$, crystallizing under room conditions in the orthorhombic $EuGa_2S_4$-type structure (space group *Fddd*), is investigated. The results from X-ray diffraction, Raman scattering, and optical-absorption measurements at a high pressure beyond 20 GPa are reported and compared not only to *ab initio* calculations, but also to the related compounds α'-Ga_2S_3, $CdGa_2S_4$, and $HgGa_2S_4$. Evidence of a partially reversible pressure-induced decomposition of $PbGa_2S_4$ into a mixture of $Pb_6Ga_{10}S_{21}$ and Ga_2S_3 above 15 GPa is reported. Thus, our measurements and calculations show a route for the high-pressure synthesis of $Pb_6Ga_{10}S_{21}$, which is isostructural to the stable $Pb_6In_{10}S_{21}$ compound at room pressure.

1 Introduction

Ternary metal chalcogenides of the $A^{II}B_2^{III}X_4^{VI}$ family (X = S, Se, Te) can be basically divided into three subfamilies. The first one is constituted by compounds with both A and B cations showing a fourfold coordination. These compounds usually crystallize in the defect chalcopyrite, defect stannite (or defect famatinite), pseudo-cubic, and related structures that are derived from the zinc blende or wurtzite structures. Examples of those compounds are $(Zn,Cd,Hg)(Al,Ga)_2(S,Se)_4$ compounds. The second subfamily is constituted by compounds in which there is a mixture of cations with fourfold and sixfold coordination. These compounds crystallize mainly in the spinel ($MgAl_2O_4$) or in related structures, such as $(Mg,Zn,Cd,Mn)In_2(S,Se)_4$, and show similar structural characteristics to many oxospinels. The third subfamily, and the less studied one, is composed of A cations featuring a coordination much larger than six. Examples of these compounds are those crystallizing in the orthorhombic $EuGa_2S_4$-type and related structures, such as $(Ca,Sr,Pb,Eu,Sm,Yb)(Al,Ga,In)_2(S,Se,Te)_4$.[1]

The studies in the last subfamily of $EuGa_2S_4$-type compounds have come from the interest in the development first of phosphors,[2] and later of mid-infrared (35 μm) solid-state lasers,[3–5] due to the large band gap, low-phonon energy, and chemical and thermal stability of these ternary sulphides. In particular, mid-infrared (mid-IR) laser radiation in $PbGa_2S_4$ has been consistently reported.[6–10] This fact has resulted in recent studies to improve the crystal quality of this mid-IR laser material.[11,12]

Several works have reported the structural, vibrational, and optical properties of $PbGa_2S_4$ under room conditions. From the structural point of view, $PbGa_2S_4$ is a layered material that crystallizes in the orthorhombic $EuGa_2S_4$-type structure (space group No. 70, D_{2h}^{24}–*Fddd*).[2,13–15] The crystal structure (see Fig. 1 and Fig. S1 and S2 in the ESI†) is built on a framework of GaS_4 tetrahedral units and square antiprismatic PbS_8 polyhedra. The GaS_4 tetrahedra are located in layers stacked along the *c*-axis, where such layers are constructed from edge-shared Ga_2S_6 dimers connected to three other dimers *via* sharing corners. By contrast, the PbS_8 polyhedra are linked to two other

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15.3 GPa (shown in Fig. S7 in the ESI†) and those already described for $PbGa_2S_4$.

4 Conclusions

We have reported the effect of pressure on the structural, vibrational, and optical properties of lead thiogallate by means of powder HP-XRD, HP-RS, and HP-OA measurements beyond 20 GPa. Those measurements have been complemented with *ab initio* calculations at HP. First of all, we have checked that $PbGa_2S_4$ crystallizes at room conditions in the $EuGa_2S_4$-type orthorhombic (space group *Fddd*) structure by means of single-crystal XRD measurements. Then, we have shown by means of powder HP-XRD measurements that $PbGa_2S_4$ is an anisotropic material, as expected from its layered-like structure. Its axial and bulk moduli are of the same order as those of monoclinic α'-Ga_2S_3 and tetragonal $CdGa_2S_4$ and $HgGa_2S_4$; *i.e.* semiconductors with similar GaS_4 tetrahedra.

After checking the complex vibrational pattern of $PbGa_2S_4$ by means of polarized RS measurements at room conditions, we have shown that the vibrational modes of $PbGa_2S_4$ show phonon spectra that show a considerable similarity to those of α'-Ga_2S_3, $CdGa_2S_4$, and $HgGa_2S_4$. In fact, we have shown that the pressure dependence of the Raman-active modes in $PbGa_2S_4$ is similar to those of the mentioned semiconductors and have made a tentative assignment of the symmetry of the Raman-active modes experimentally observed.

Finally, we have measured the pressure dependence of the optical bandgap of $PbGa_2S_4$ by means of HP-OA measurements. We have confirmed that $PbGa_2S_4$ is an indirect bandgap semiconductor, whose bandgap decreases as pressure increases, unlike what happens in α'-Ga_2S_3, $CdGa_2S_4$, and $HgGa_2S_4$. The different behavior is explained by the contribution of the 6s lone electron pair of Pb to the topmost valence band and the strong decrease of the Pb–S bond distance upon compression that leads to a strong increase of the energy of the topmost valence band under pressure.

To finish, we want to stress that all our measurements have shown evidence of a partially reversible pressure-induced decomposition of $PbGa_2S_4$ into a mixture of $Pb_6Ga_{10}S_{21}$ and β'-Ga_2S_3 above 16 GPa. This decomposition is supported by enthalpy *vs.* pressure calculations of the three compounds and makes sense because both compounds show sixfold-coordinated Ga atoms in comparison with the fourfold-coordinated Ga atoms in $PbGa_2S_4$. The structure of the new compound $Pb_6Ga_{10}S_{21}$ at HP, which is isostructural to already known $Pb_6In_{10}S_{21}$ at RP, is reported at 23.5 GPa since it seems not to be stable at RP. Moreover, we have determined its Raman-active phonons and optical bandgap above 16 GPa. In summary, this work shows the first HP study of a compound with $EuGa_2S_4$-type (orthorhombic *Fddd*) structure and the route for the synthesis of $Pb_6Ga_{10}S_{21}$. Therefore, this work will be of interest for the study of the $EuGa_2S_4$-type subfamily of $A^{II}B^{III}_2X^{VI}_4$ compounds, in which the effect of pressure is far from being understood.

Author contributions

Tania Garcia-Sanchez: investigation, formal analysis, discussion, writing, review and editing Samuel Gallego-Parra: investigation, formal analysis Akun Liang: investigation, formal analysis José Luis Rodrigo-Ramon: investigation, formal analysis Alfonso Muñoz: investigation, formal analysis Plácida Rodriguez-Hernandez: investigation, formal analysis Javier Gonzalez-Platas: investigation, formal analysis Juan Ángel Sans: investigation Vanesa Paula Cuenca-Gotor: investigation Hussien H. Osman: investigation Catalin Popescu: investigation Veaceslav Ursaki: investigation Ion M. Tiginyanu: investigation Daniel Errandonea: formal analysis, validation, funding acquisition, writing, review, and editing Francisco Javier Manjón: conceptualization, investigation, formal analysis, validation, writing, review, and editing, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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