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Abstract

Raman investigation of isostructural polycrystalline M^{II}Ga$_2$(S, Se)$_4$ compounds with M^{II} = Pb, Sr, Eu, Yb and Ca was performed. We observed that the effect of M^{II} atomic mass on the phonon frequencies is negligible and that the vibrations are essentially influenced by the sizes of the M^{II} cations. As the effects of cation substitution are small we concluded that the orthorhombic thiogallates M^{II}Ga$_2$S$_4$ exhibit nearly the same phonon energies: about 280 cm^{-1} ($\sim$35 meV) and 360 cm^{-1} ($\sim$45 meV) for the most intense vibration modes. The substitution of S atoms by heavier Se atoms causes the shift of the Raman spectrum to lower frequencies. The orthorhombic M^{II}Ga$_2$Se$_4$ compounds present phonon energy at about 185 cm^{-1} ($\sim$23 meV) for the most intense vibration mode. Results confirm that a molecular model is more adequate to describe the vibrations of these compounds than the factor-group analysis.

1. Introduction

Ternary compounds of general formula M^{II}M$_2^{III}$(S, Se)$_4$ (where M^{II} and M^{III} are respectively divalent and trivalent cations) form an extensive class of semiconductors and present luminescence properties when doped with rare earth elements. Photoluminescence and cathodoluminescence properties of thiogallate M^{II}Ga$_2$S$_4$ compounds doped with rare earth activators have been studied since the 1970s [1–3]. The Eu^{2+} and Ce^{3+} doped SrGa$_2$S$_4$ compounds are well known respectively as efficient green and blue phosphors with excellent colour coordinates [1]. They are used for full-colour thin-film electroluminescence (TFEL) displays [4, 5] and field emission display (FED) applications [6, 7]. Moreover, SrGa$_2$S$_4$:Eu

green phosphor is a promising candidate in phosphor converted light emitting diodes (pc-LED) for solid state lighting (SSL) [8].

We report here Raman investigation of the chalcogallate family $M^{II}Ga_2(S, Se)_4$ limited to compounds exhibiting the same orthorhombic structure with the space group D_{2h}^{24} ($Fddd$) [9]. We have studied $M^{II}Ga_2S_4$ with M^{II} = Pb, Sr, Eu, Yb and Ca and $M^{II}Ga_2Se_4$ with M^{II} = Pb and Ca. Raman spectra of $PbGa_2S_4$ [10], $EuGa_2S_4$ [11] and $CaGa_2S_4$ [12] have already been reported but the Raman vibrations of $SrGa_2S_4$, $YbGa_2S_4$ and $M^{II}Ga_2Se_4$ have not been reported up to now. For the first time Raman data of chalcogallate compounds extensively used for their luminescent properties are collected. The Raman spectra of the five different Sr, Eu, Pb, Yb and Ca thiogallates are discussed with respect to the mass and the ionic radius of the divalent cation. The effect of the change of sulfur atoms to selenium atoms in thiogallate compounds is studied with the Raman investigation of Pb and Ca selenide compounds. Selenide compounds are less extensively used than sulfides for industrial applications because of the toxicity of some Se compounds. Nevertheless the study of $M^{II}Ga_2Se_4$ compounds will help us in the assignment of the Raman vibrations in $M^{II}Ga_2S_4$ compounds.

The aim of this work is to clarify the origins of the vibration modes in the chalcogallate based phosphors in order to increase the knowledge about the lattice dynamical properties that influence the luminescence efficiency. Indeed, among the non-radiative transition mechanisms leading to a thermal relaxation of the luminescent centre, a multiphonon process is often observed between 4f excited levels of rare-earth ions. It involves mainly the high-energy optical phonons. The non-radiative multiphonon transition probability increases with increasing frequency of the high-energy phonons of the lattice. In the case of electroluminescent (EL) materials, the most frequent scattering event under high electric field is the emission of optical phonons and the cooling of 'hot electrons' is dominated by the coupling to the high-frequency modes. The scattering rate is lower for EL phosphors presenting low phonon energies. For cathodoluminescent (CL) materials the rate of phonon energy loss is controlled by the phonons with highest energy and the CL efficiency of the phosphors decreases with increasing phonon energy [13]. This work is also an opportunity to collect spectra of powders that will be used as references to study by Raman spectroscopy the quality of thin films prepared for device applications.

2. Samples and experimental details

Polycrystalline $M^{II}Ga_2(S, Se)_4$ compounds were synthesized from $M^{II}S(Se)$ and $Ga_2S(Se)_3$ compounds mixed in stoichiometric composition in sealed quartz tubes and annealed at $1200\,°C$ for 4 h in a single-zone furnace, then re-annealed in a $900\,°C$ heat-treatment for 12 h. The good crystalline properties of the powders were shown by XRD measurements.

Stokes and anti-Stokes spectra were recorded between -500 and $+500$ cm^{-1} in order to distinguish Raman lines from luminescence or satellite lines and to obtain more precision on the vibration energies. Line positions are determined by calculating the arithmetic average of both Stokes and anti-Stokes values. Raman scattering spectra of $SrGa_2S_4$ and $CaGa_2S_4$ were measured by a Jobin–Yvon U1000 double monochromator with a S20 photomultiplier at room temperature in back-scattering configuration. The 676.4 nm line of a Kr Spectra Physics laser was used as the excitation source at a power level of 140 mW. With a beam spot diameter of about 100 μm the power density on the samples was about 500 W cm^{-2}. The spectral resolution of the spectrometer is about 1 cm^{-1}. Raman spectra of the other compounds were recorded by a Dilor XY spectrometer, with a Kr laser and a CCD detector. Measurements were performed at room temperature in microscopic and back-scattering configuration. The 647.1 nm line of a Kr Spectra Physics laser was used as the excitation source at a power level
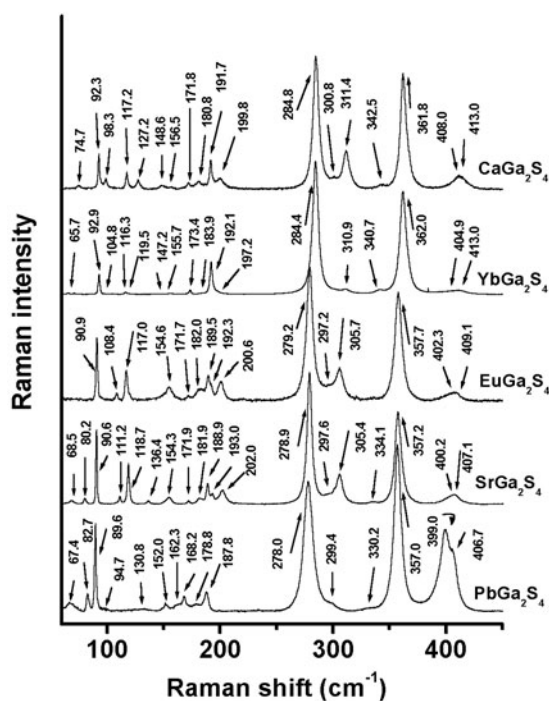
Figure 1. Raman spectra of polycrystalline Pb, Sr, Eu, Yb and $CaGa_2S_4$ measured at 300 K. Spectra of Sr and $CaGa_2S_4$ compounds were recorded using the 676.4 nm Kr laser line and those of Pb, Eu, $YbGa_2S_4$ using the 647.1 nm Kr laser line. The vibration frequencies are given in cm^{-1}.

of 6 mW. With a beam spot diameter of about 5 μm the power density on the samples was about 10 kW cm^{-2}. Some measurements were performed at lower power density (down to 200 W cm^{-2}) in order to evaluate the influence of the laser power on the Raman spectra. We do not observe significant changes in the position of the Raman lines but the heating induced by high power density (10 kW cm^{-2}) results in a broadening of Raman lines of about 20–30% compared to a power density of 200 W cm^{-2}. The spectral resolution of the spectrometer is about 2 cm^{-1}.

3. Results

Stokes spectra of the polycrystalline thiogallates are given in figure 1. The Pb, Sr, Eu, Yb and Ca thiogallate compounds present very similar Raman spectra with respectively 16, 19, 15, 17 and 18 clearly identified vibration lines (listed in table 1). In all spectra the Raman vibration lines are divided into two groups separated by a domain without Raman frequencies between 200 and 270 cm^{-1}. Below the silent Raman frequency domain, the full widths at half maximum (FWHMs) of the more intense vibration lines are lower than 2 cm^{-1} whereas the vibration lines at higher frequencies beyond the silent Raman frequency domain have FWHMs higher than 5 cm^{-1}. Two intense vibration lines dominate the spectra respectively for Pb, Sr, Eu, Yb and Ca thiogallates at 278.0–357.0, 278.9–357.2, 279.2–357.7, 284.4–362.0 and 284.8–361.8 cm^{-1}.

Raman spectra of $PbGa_2Se_4$ and $CaGa_2Se_4$ exhibit an intense vibration line at respectively 182.7 and 185.3 cm^{-1} (figure 2). The Raman vibration lines are also divided into two groups

Table 1. Raman frequencies (cm^{-1}) of Pb-, Sr-, Eu-, Yb- and $CaGa_2S_4$ polycrystals. The horizontal line separates the two frequency domains on both sides of the silent Raman frequency domain.

|	$PbGa_2S_4$	$SrGa_2S_4$	$EuGa_2S_4$	$YbGa_2S_4$	$CaGa_2S_4$
1	67.4	68.5		65.7	74.7
2	82.7	80.2			
3	89.6	90.6	90.9	92.9	92.3
4	94.7				98.3
5		111.2	108.4	104.8	
6		118.7	117.0	116.3	117.2
7				119.5	127.2
8	130.8	136.4			
9	152.0	154.3	154.6	147.2	148.6
10	162.3			155.7	156.5
11	168.2	171.9	171.7	173.4	171.8
12	178.8	181.9	182.0	183.9	180.8
13	187.8	188.9	189.5	192.1	191.7
14		193.0	192.3		
15		202.0	200.6	197.2	199.8
16	278.0	278.9	279.2	284.4	284.8
17		297.6	297.2		300.8
18	299.4	305.4	305.7	310.9	311.4
19	330.2	334.1		340.7	342.5
20	357.0	357.2	357.7	362.0	361.8
21	399.0	400.2	402.3	404.9	408.0
22	406.7	407.1	409.1	413.0	413.0

separated by a domain without Raman frequencies between 140 and 180 cm^{-1}. 12 and 17 vibration lines (listed in table 2) are observed respectively in the $PbGa_2Se_4$ and $CaGa_2Se_4$ spectra. The FWHMs of Raman lines in the $CaGa_2Se_4$ spectrum are between 2 and 5 cm^{-1}. The low number of identified Raman lines and the high peak FWHM (higher than 4 cm^{-1}) in $PbGa_2Se_4$ spectrum can be explained by the lower crystalline quality of the sample. The band at about 155 cm^{-1} present in the $PbGa_2Se_4$ Raman spectrum may correspond to the Ga_2Se_3 compound [14, 15].

4. Discussion

4.1. Factor-group analysis

The chalcogallate compounds of the type $M^{II}Ga_2(S, Se)_4$ (where M^{II} = Pb, Sr, Eu, Ca, Yb) belong to the orthorhombic crystal class with the space group D_{2h}^{24} ($Fddd$). There are 32 formula-mass units per unit cell ($z = 32$) and therefore 56 atoms in a primitive cell: 8 M^{II}, 16 Ga, 32 S or Se. According to XRD data [9] the M^{II} atoms occupy square anti-prismatic sites formed by eight sulfur or selenium atoms (symmetry group D_{4d}) forming $M^{II}(S, Se)_8$ units. They are situated in three slightly different sites, 8a, 8b and 16e, whose multiplicity is not equal and exhibits a 1:1:2 relative ratio dictated by symmetry. Gallium atoms are tetrahedrally coordinated to four sulfur or selenium atoms forming $Ga(S, Se)_4$ units (symmetry group T_d) and the sulfur (or selenium) atoms are at the centre of deformed $M_2^{II}Ga_2$ tetrahedrons forming $(S, Se)M_2^{II}Ga_2$ units. The assembly of the $M^{II}(S, Se)_8$ anti-prismatic units with common edges forms chains parallel to the a axis of the unit cell. Each chain is linked to four chains by corner sharing. Gallium atoms are located between two consecutive chains. The unit cell consists of four layers along the c axis. Figure 3 illustrates the symmetry of the Ga and M^{II} environments.
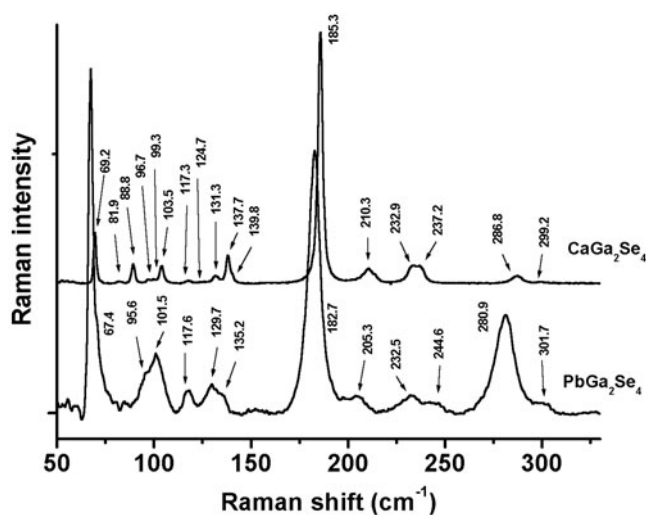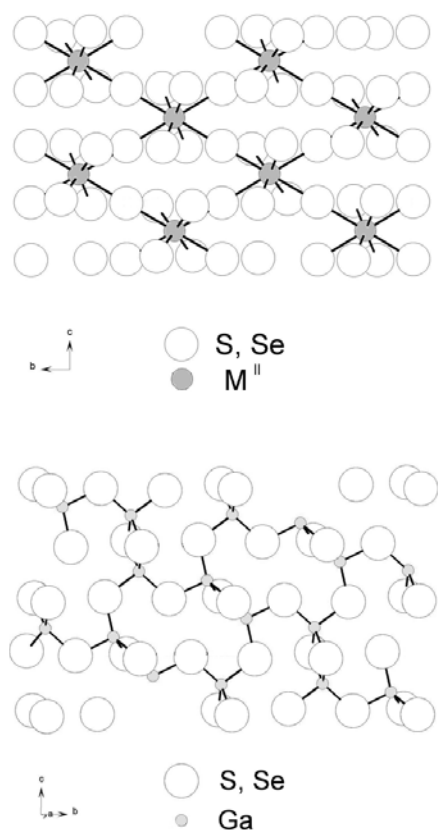
Figure 2. Raman spectra of polycrystalline $PbGa_2Se_4$ and $CaGa_2Se_4$ measured at 300 K using the 647.1 nm Kr laser line. The vibration frequencies are given in cm^{-1}.

Table 2. Raman frequencies (cm^{-1}) of $PbGa_2Se_4$ and $CaGa_2Se_4$ polycrystals. The horizontal line separates the two frequency domains on both sides of the silent Raman frequency domain.

	$PbGa_2Se_4$	$CaGa_2Se_4$
1	67.4	69.2
2		81.9
3		88.8
4	95.6	96.7
5		99.3
6	101.5	103.5
7	117.6	117.3
8		124.7
9	129.7	131.3
10	135.2	137.7
11		139.8
12	182.7	185.3
13	205.3	210.3
14	232.5	232.9
15	244.6	237.2
16	280.9	286.8
17	301.7	299.2

    The site symmetry of each atom can be obtained from the correlation tables [16]. The factor-group analysis [17] shows that vibration modes can be classified as $\Gamma_v = 19A_g + 21B_{1g} + 22B_{2g} + 22B_{3g} + 19A_u + 20B_{1u} + 21B_{2u} + 21B_{3u}$. According to the symmetry rules, the A_g, B_{1g}, B_{2g} and B_{3g} modes are Raman active and the B_{1u}, B_{2u} and B_{3u} modes are IR active while the phonons of A_u symmetry are forbidden in both IR and Raman scattering. Thus the factor-group method predicts that the total number of Raman-active phonons is 84 for this structure.

Figure 3. Symmetry of the Ga and M^{II} environments in orthorhombic $M^{II}Ga_2(S, Se)_4$.

4.2. Raman vibrations of thiogallate compounds

Since the polycrystalline $M^{II}Ga_2S_4$ (M^{II} = Pb, Sr, Eu, Yb and Ca) compounds present very similar Raman spectra the correlation between most lines is possible without ambiguity. The change of M^{II} cation leads to a slight translation in frequency of the overall spectrum. The frequency shifts are too small ($<10\,cm^{-1}$) to be ascribed to mass effects. Since the mass of M^{II} affects very slightly the vibration frequencies we suppose that no vibration involving directly the divalent cation is present in the Raman spectra. We suggest that the vibration frequencies are influenced by the size of the divalent cation. The change of M^{II} by divalent cations having different size induces modifications in binding lengths and in cell parameters and consequently in vibration frequencies (table 3). Two groups of compounds can be distinguished: the first one is composed of $PbGa_2S_4$, $SrGa_2S_4$ and $EuGa_2S_4$ and the second one of $YbGa_2S_4$ and $CaGa_2S_4$. Compounds of the same group present vibration lines at about the same positions due to the nearly similar ionic radius for M^{II} (table 3). Most phonon frequencies ν increase in the order of decreasing M^{II} ionic radius, i.e. in the following order: $\nu_{Pb} \approx \nu_{Sr} \approx \nu_{Eu} < \nu_{Yb} \approx \nu_{Ca}$.

Fewer than 19 phonon modes for the studied chalcogallates are observed while the factor-group analysis predicts 84 Raman-active phonons. The reduced numbers of modes in the Raman spectra are in favour of a molecular model to describe the vibrations of these compounds [12, 22]. Furthermore spectra present a silent Raman frequency domain which is widely spread in a molecular crystal [12]. According to XRD data different structural units can

Table 3. Physical and crystal constants of $PbGa_2S_4$, $SrGa_2S_4$, $EuGa_2S_4$, $YbGa_2S_4$ and $CaGa_2S_4$ compounds. Compounds are presented in the order of decreasing size of the divalent cation.

Compounds $M^{II}Ga_2S_4$	Atomic mass of M^{II} [18]	Ionic radius of M^{II} [19] [a] (Å)	Lattice parameters (Å)	Mean interatomic lengths (Å)
$PbGa_2S_4$	207.24	1.29	$a = 20.706$ $b = 20.380$ $c = 12.156$[1]	$Pb–S \approx r(Pb^{2+})$ $+ r(S^{2-}) = 3.13$[b]
$SrGa_2S_4$	87.62	1.26	$a = 20.840$ $b = 20.495$ $c = 12.21$ [1]	Ga–S 2.29 Sr–S 3.12 [9]
$EuGa_2S_4$	151.96	1.25	$a = 20.716$ $b = 20.404$ $c = 12.2$ [1]	Ga–S 2.29 Eu–S 3.10 [20]
$YbGa_2S_4$	173.04	1.14	$a = 20.112$ $b = 20.082$ $c = 12.132$ [2]	Ga–S 2.26 Yb–S 3.02 [21]
$CaGa_2S_4$	40.08	1.12	$a = 20.087$ $b = 20.087$ $c = 12.12$ [1]	Ga–S 2.28 Ca–S 3.00 [9]

[a] The ionic radii taken from [19] are the result of calculations from interatomic distances in halides and chalcogenides.

[b] To our knowledge the values of interatomic distances for $PbGa_2S_4$ are not available in the literature. For the Pb–S length we give the sum of the ionic radii of Pb^{2+} and S^{2-} ions (the validity of this calculation was checked for the other M^{II}–S bonds).

generate the vibration spectrum: the tetrahedrons GaS_4, the deformed tetrahedrons $SGa_2M_2^{II}$ or the square antiprisms $M^{II}S_8$. The interpretation of the spectra in terms of vibrations of isolated groups seems to provide an adequate first approximation because the binding energy of the bonds M^{II}–S and Ga–S is significantly different (because of different ionic character). The analysis of the Raman vibrations will help us to propose some vibrating units responsible for the spectra.

First the interpretation of the Raman spectra with the model of the $SGa_2M_2^{II}$ vibrating units can be excluded because we have observed that the M^{II} mass has very little influence on the Raman vibrations. If the vibrations of S around M^{II} are described with $M^{II}S_8$ molecular units there is no contradiction with the fact that no motion involving directly the M^{II} cation is observed: in the D_{4d} group the Raman-active modes have the A_1, E_2 and E_3 symmetry and their frequencies are independent of the M^{II} mass [23]. At this point of the discussion considering the structure as isolated GaS_4 and $M^{II}S_8$ vibrating units is in agreement with the observations made from the Raman spectra. The vibrations of the S anions in the vibrating $M^{II}S_8$ units are expected at lower frequencies than those in the GaS_4 units because the interatomic distances M^{II}–S are larger than Ga–S and because the number of vibrating S atoms in $M^{II}S_8$ (8 S) units is larger than in GaS_4 units (4 S).

We propose to investigate the Raman vibrations of Ga–S bindings in respect with the Ga_2S_3 Raman spectrum because the vibrations of Ga_2S_3 have been also described in the GaS_4 molecular model in the T_d symmetry [14]. The spectrum was analysed both in terms of GaS_4 internal vibrations and in terms of external modes. In the Ga_2S_3 Raman spectrum the peaks located between 200 and 450 cm^{-1} are ascribed to bond-stretching vibrations in the tetrahedral GaS_4 units associated with the A_1 and F_2 modes in the T_d symmetry group. The lines below 200 cm^{-1} are ascribed to bond-bending vibrations of GaS_4 tetrahedral units

(E and F_2 modes) and to external vibrations (rotational F_1 modes and translation F_2 modes in T_d symmetry). The most intense line near 230 cm^{-1} is ascribed to the breathing mode issued from the A_1 mode in the GaS$_4$ model and corresponds to the vibrations of the S anions around vacant sites along the anion–vacancy bond direction [24]. By analogy with the assignment of the Ga$_2$S$_3$ vibrations, some vibration lines above 270 cm^{-1} in thiogallate spectra can be assigned to stretching vibrations in the tetrahedral GaS$_4$ units. Among those located at frequencies lower than 200 cm^{-1} some lines may be due to bending vibrations of the GaS$_4$ tetrahedral units and others may correspond to external vibration modes issued from rotational and translation vibrations of molecular GaS$_4$ subunits [10, 11]. As in the case of the Ga$_2$S$_3$ Raman spectrum, stretching modes can be distinguished from bending modes by considering the FWHM: bending vibration lines below 200 cm^{-1} have FWHM equal or inferior to about 2 cm^{-1} whereas stretching vibration lines above 270 cm^{-1} are broader and have FWHM superior to 5 cm^{-1}.

4.3. Raman vibrations of selenium chalcogallate compounds

Raman investigation was performed on selenide compounds in order to confirm the vibration mode assignment in thiogallate compounds. Physical properties of PbGa$_2$Se$_4$ and CaGa$_2$Se$_4$ compounds are presented in table 4. As in the thiogallate compounds the change of M^{II} cation has very little influence on Raman frequencies and the phonon energies increase with decreasing M^{II} size. The substitution of S atoms by Se atoms leads to a shift of the vibration lines to weaker energies. The frequency shift is mainly due to the difference in mass between S and the heavier Se atoms. For most homologue lines above the silent Raman frequency domain the ratios of the frequencies ν_S/ν_{Se} are close to the ratio $\sqrt{m_{Se}}/\sqrt{m_S} \approx 1.57$ (table 5). The fact that these frequencies depend mainly on the sulfur or selenium mass suggests that the contribution of Ga or M^{II} atoms is weak. This confirms that among the lines located above the silent Raman frequency domain some lines are due to bond-stretching vibrations in the tetrahedral Ga(S, Se)$_4$ units. We can also assign some of these lines to bond-stretching vibrations in the M^{II}(S, Se)$_8$ units. The highest ratio is obtained for the most intense lines at $\sim$280 cm^{-1} in sulfide spectra and at $\sim$180 cm^{-1} in selenide spectra. For example the most intense line in the PbGa$_2$Se$_4$ spectrum at 182.7 cm^{-1} and the most intense line in the PbGa$_2$S$_4$ spectrum at 278 cm^{-1} present a frequency ratio equal to 1.52. Likewise the most intense line in the CaGa$_2$Se$_4$ spectrum at 185.5 cm^{-1} and the most intense line in the CaGa$_2$S$_4$ spectrum at 284.5 cm^{-1} present a frequency ratio equal to 1.53. These vibrations corresponding to the most intense lines may be associated with modes issuing from the totally symmetrical mode where the S or Se anions move together in the cation–anion direction (in Ga(S, Se)$_4$ or in M^{II}(S, Se)$_8$ units). These observations show also that the variation of strength constants due to the substitution of S atoms by Se atoms is weak. These observations are similar to those resulting from the comparison between Ga$_2$S$_3$ and Ga$_2$Se$_3$ [14, 15] Raman spectra. The most intense Raman lines dominating respectively the Ga$_2$S$_3$ and Ga$_2$Se$_3$ spectra exhibit a ratio of 1.50.

The vibration lines situated below the silent Raman frequency domain present a weaker ratio ν_S/ν_{Se} between 1.29 and 1.42 (table 5). Some of them present the corresponding ratio close to $\sqrt{m_{GaSe_4}}/\sqrt{m_{GaS_4}} \approx 1.396$ and so may be assigned to vibrations issuing from the translation and rotation motions of the tetrahedral GaS(Se)$_4$ units. No vibration mode presenting a ratio ν_S/ν_{Se} close to $\sqrt{m_{Se}}/\sqrt{m_S} \approx 1.57$ is observed below the silent Raman frequency domain, which suggests that no internal vibration in M^{II}(S, Se)$_8$ units, i.e. vibration of S(Se) anions around M^{II}, occurs in this frequency domain.

In conclusion, the comparison between sulfide and selenide chalcogallates confirms that the vibrations above the silent Raman frequency domain are due to bond-stretching modes in

Table 4. Physical and crystal constants of $PbGa_2Se_4$ and $CaGa_2Se_4$ compounds. Compounds are presented in order of decreasing size of the divalent cation.

Compounds $M^{II}Ga_2Se_4$	Atomic mass of M^{II} [18]	Ionic radius of M^{II} [19] (Å)	Lattice parameters (Å)	Mean interatomic lengths (Å)
$PbGa_2Se_4$	207.24	1.29	$a = 21.54$ $b = 21.28$ $c = 12.718$ [25]	Ga–Se 2.43 Pb–Se 3.21 [26]
$CaGa_2Se_4$	40.08	1.12	$a = 21.324$ $b = 21.012$ $c = 13.638$ [2]	Ca–Se $\approx r(Ca^{2+})$ $+ r(Se^{2-}) = 3.10^a$

[a] To our knowledge the values of interatomic distances for $CaGa_2Se_4$ were not available in literature. For the Ca–Se length we give the sum of the ionic radii of Ca^{2+} and Se^{2-} (the validity of this calculation was checked for the other M^{II}–Se bonds).

Table 5. Phonon frequency (cm^{-1}) ratios of $M^{II}Ga_2S_4$ and $M^{II}Ga_2Se_4$ vibrations.

$PbGa_2S_4$	$PbGa_2Se_4$	Ratio ν_S/ν_{Se}
89.6	67.4	1.33
162.3	117.6	1.29
168.2	129.7	1.30
187.8	135.2	1.39
278.0	182.7	1.52
299.4	205.3	1.46
357.0	244.6	1.46
399.0	280.9	1.42

$CaGa_2S_4$	$CaGa_2Se_4$	Ratio ν_S/ν_{Se}
92.3	69.2	1.33
117.2	88.8	1.31
148.5	103.5	1.43
156.5	117.3	1.33
171.8	124.7	1.37
180.8	131.3	1.37
191.7	137.7	1.39
199.8	139.8	1.42
284.8	185.3	1.53
311.4	210.3	1.48
342.5	232.9	1.47
361.8	237.2	1.52
408.0	286.8	1.42

$GaS(Se)_4$ units and in $M^{II}(S, Se)_8$ units and that among the vibration modes occurring below the silent Raman frequency domain some are due to vibrations issuing from the translation and rotation motions of tetrahedral $GaS(Se)_4$ units.

5. Conclusion

The Raman study of polycrystalline $M^{II}Ga_2S_4$ compounds with $M^{II} = Pb$, Sr, Eu, Yb and Ca was performed to clarify the origins of the Raman vibrations. We observe that no vibration involving directly the divalent cation M^{II} is present in the Raman spectra since the mass of the M^{II} cation has very little influence on the vibration frequencies. The Raman vibrations

depend essentially on the M^{II} cation size. Since the effect of the M^{II} cation on the $M^{II}Ga_2S_4$ Raman spectra is very slight we conclude that the orthorhombic thiogallates present nearly the same phonon energies whatever the M^{II} cation. Raman spectra of polycrystalline $M^{II}Ga_2Se_4$ compounds with $M^{II} = Pb$ and Ca were also measured. The substitution of S atoms by heavier Se atoms causes the shift of the Raman spectrum to lower frequencies.

Results confirm that a molecular model is more adequate to describe the vibrations of these compounds than the factor-group analysis. We proposed to assign the vibration lines above $270\ cm^{-1}$ in the thiogallate spectra to stretching modes of Ga–S in tetrahedral GaS_4 units and to stretching modes of M^{II}–S in $M^{II}S_8$ units. Some vibration lines below $200\ cm^{-1}$ were ascribed to bending vibrations in GaS_4 units and to external vibrations between tetrahedral GaS_4 units. Further studies and in particular IR measurements are necessary to determine with accuracy the vibrating molecular units.

Concerning luminescence properties perturbed by dynamical properties several conclusions can be drawn from Raman spectra of chalcogallate based phosphors. The optical phonons influencing the luminescence efficiency of thiogallate based phosphors correspond to the two vibration modes dominating the high-frequency spectra. The first one is situated at about $280\ cm^{-1}$ (~35 meV) and the second one at about $360\ cm^{-1}$ (~45 meV). The selenide compounds exhibit lower phonon energies ($185\ cm^{-1}$ (~23 meV) for $M^{II}Ga_2Se_4$ compounds) than sulfides. We can compare these phonon energies with those of other phosphor host matrixes: the oxide compounds exhibit higher phonon energies than selenides and sulfides, for example $Y_3Al_5O_{12}$ and Zn_2SiO_4 present phonon energy at respectively $847\ cm^{-1}$ (105 meV [13]) and $1050\ cm^{-1}$ (130 meV [13]). The phonon energies of thiogallate ternary compounds are comparable to those of binary sulfides: SrS and CaS present phonon energy at respectively $300\ cm^{-1}$ (37 meV [27]) and $380\ cm^{-1}$ (47 meV [13]).

Acknowledgments

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