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Europium luminescence in $Eu_{1-x}Bi_xV_{1-y}As_yO_4$ materials of tetragonal form

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Abstract

An enhancement of the intensity of Eu^{3+} luminescence is observed when arsenic replaces vanadium in bismuth europium orthovanadates. This is connected to the progressive crystallographic modification induced by the cation substitution in the studied compounds. The optical spectroscopies of luminescence and Raman scattering bring out further information and improve X-ray diffraction results [1]. For the most efficient substitution, corresponding to the $Eu_{0.10}Bi_{0.90}V_{0.60}As_{0.40}O_4$ chemical formula, the energy level scheme is derived from the emission spectrum recorded at 77 K. A determination of the phenomenological crystal field parameters in a C_{2v} symmetry is performed with a good r.m.s. deviation of 4.3 cm^{-1}.

Keywords: Arsenovanadates; Europium; Bismuth; Luminescence; Raman scattering

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1. Introduction

$Eu_{1-x}Bi_xV_{1-y}As_yO_4$ bismuth and europium orthovanadates and orthoarsenovanadates are good luminophors when x and y give phases whose structure is derived from the $EuVO_4$ zircon stuctural variety [1,2]. The crystallographical description of the samples as a function of "x" and "y" has been previously reported [3]. In order to compare their emission efficiencies and to determine the optimal composition, we estimated the ratio of the line intensities of the $^5D_0 \rightarrow {}^7F_4$ electronic transition of the Eu^{3+} ion and of those corresponding to the X–O stretching vibrations of the tetrahedral XO_4^{3-} anions (X=V, As). These measurements have been corrected experimentally from the diffusion difference between vanadates and arsenates. The obtained curve can be correlated to the structural evolution in the chemical system.

2. Experimental

The studied compounds were obtained from a reaction in the solid state between the appropriate proportions of bismuth, europium, vanadium oxides and diammonium hydrogenoarsenate, according to the chemical equation:

$$(1-x)Eu_2O_3 + xBi_2O_3 + (1-y)V_2O_5 + 2y(NH_4)_2HAsO_4 \rightarrow 2Bi_xEu_{1-x}V_{1-y}As_yO_4 + 4yNH_3 + 3yH_2O.$$

The final products are obtained after several cycles of intimate grindings followed by heating, the temperature of the last annealing being 750°C. All phases have been checked by X-ray analysis. The Raman scattering and luminescence spectra were recorded on a computerized RT30 Dilor spectrometer; two excitation sources were used: Ar^+ and Kr^+ ion lasers (2025 Spectra Physics). The 77 K emission spectra were excited by a discrete blue line of a cw argon ion laser; the emission was analyzed through a 1 m Jarrell–Ash monochromator equipped by a Hamamatzu R374 photomultiplier in the 400–750 nm wavelength range.

3. Results

Fig. 1 shows the evolution of the $I(^5D_0 \rightarrow {}^7F_4)/I(\nu[X\text{–}O])$ ratio as a function of x, ratio of bismuth/europium substitution for different concentrations of arsenic (y) in the compounds. The areas of the luminescence and phonon peaks have been measured together in the same experimental setup by choosing a spectral range in which the Raman and luminescence bands do not overlap. For $Eu_{1-x}Bi_xVO_4$

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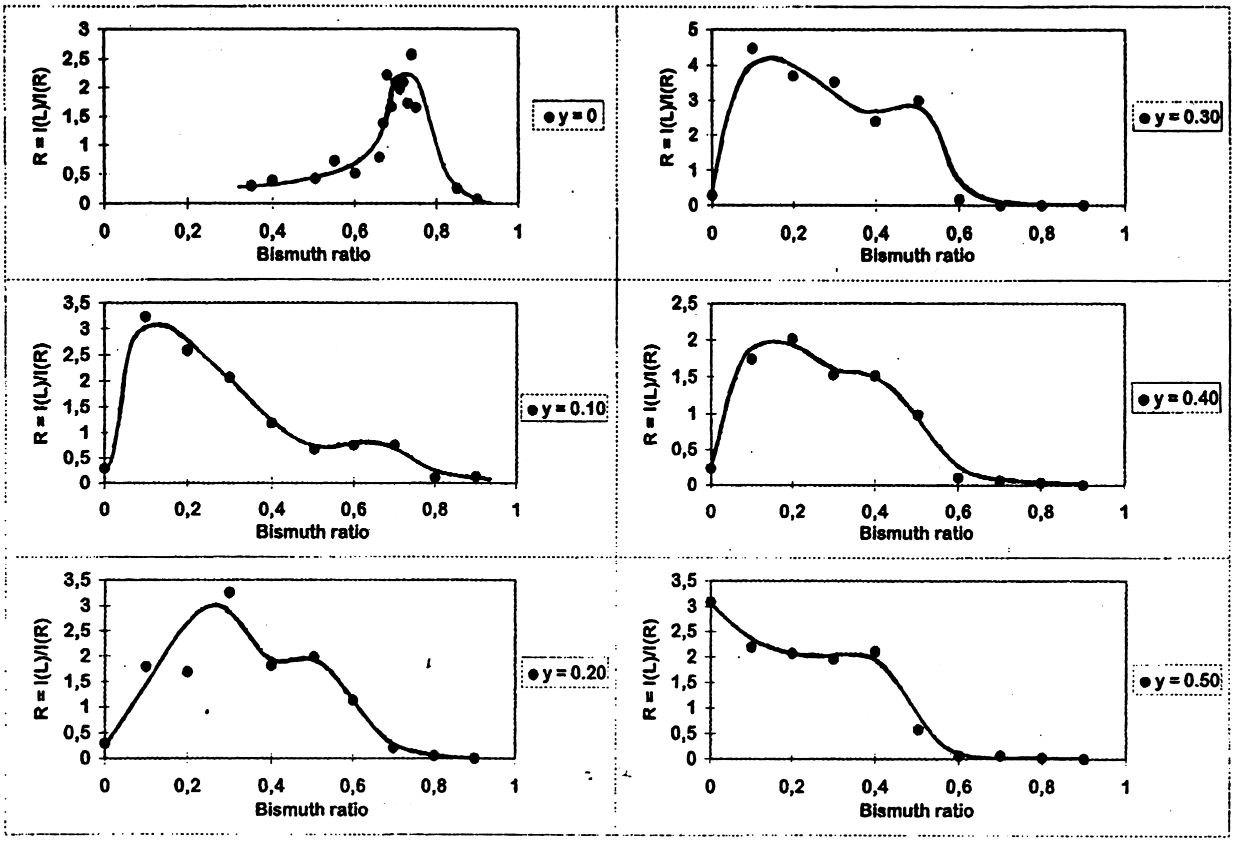

Fig. 1. Evolution of the $I(^5D_0 \rightarrow {}^7F_4)/I$(stretching vibrations) as a function of bismuth concentration for different "y" compositions in arsenovanadates.

samples a single maximum is observed, located at the limit of the existence of the tetragonal phase ($x = 0.73$). In the case of the arsenovanadate compounds two maxima are obtained if the arsenic concentration is comprised between 10 to 40%; for arsenic concentration greater than 40% only one maximum is found ($x = 0.40$ and $y = 0.50$). It is also shown that for $y \geq 0.20$, only one maximum shifts if the arsenic content increases. The second can be assigned to the distorted scheelite phase detected in the $Eu_{1-x}Bi_xV_{1-y}As_yO_4$ system.

These observations can be correlated to the Raman spectra presented in Fig. 2, obtained under excitation at 647.1 nm; Raman mode assignments have been previously presented in Refs. [4,5]. In the low frequency range only external modes owing to the crystalline lattice appear and significant modifications are observed as a function of the arsenic concentration. It is noteworthy that the $^5D_0 \rightarrow {}^7F_3$ transitions located in the excited line region are too weak to be observed and do not disturb the Raman spectra. For $y = 0.00$ only four principal bands at 125, 154, 236 and 254 cm^{-1} are found, characterizing the zircon structure. For $y = 0.10$, the Raman spectrum suggests a beginning of transformation, because among the four previous lines, only the two higher frequencies are obtained and several weak bands take the place of the two others. These modifications appear to be well confirmed for $y = 0.20$.

On the anti-Stokes side, the same spectral feature is observed whatever the concentrations. The maximum shift of the luminescence yield can signify that during the arsenic/vanadium substitution: (i) the same site is occupied and the Eu^{3+} ion is only under the influence of the bismuth, or (ii) the arsenic is located at a site slightly shifted from the original crystallographic position and consequently, the europium luminescence must show the perturbation of the oxygen environment. The luminescence of Eu^{3+} is principally observed with a very weak $^5D_0 \rightarrow {}^7F_0$ line at -1760 cm^{-1}, for the $0 \leq y \leq 0.50$ domain. It is due to the form deviated from the zircon structure; the few bands resulting from the scheelite variety can be hidden by the strong intensity of the previous ones as can be seen in the luminescence of $Na_5Eu(MoO_4)_4$, which belongs to the scheelite structure [6,7].

4. Crystal field calculations

The analysis of the fluorescence lines observed on the Raman spectrum as well as from the classical laser excitation (Fig. 3) permits the connection of the observed electronic transitions to the symmetry of the point site occupied by the rare earth and presents the difference between these two structure types: the $^5D_0 \rightarrow {}^7F_2$ transition exhibits two main lines at 16 254 and 16 157 cm^{-1} for the

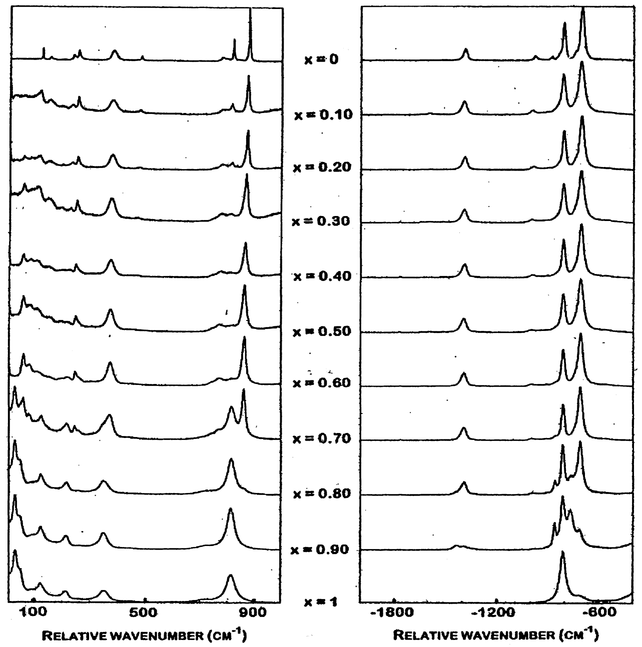

Fig. 2. Stokes and anti-Stokes Raman spectra as a function of x in $Eu_{1-x}Bi_xV_{0.80}As_{0.20}O_4$, ($\lambda_{exc.}=647.1$ nm) The anti-Stokes side shows Eu^{3+} fluorescence: the $^5D_0 \rightarrow {}^7F_0$ transition in the $-1800<\Delta\bar{\nu}<-1700$ cm^{-1} range, the $^5D_0 \rightarrow {}^7F_1$ transition in the $-1500<\Delta\bar{\nu}<-1350$ cm^{-1} region and the $^5D_0 \rightarrow {}^7F_2$ transition in the $-900<\Delta\bar{\nu}<-600$ cm^{-1}. The $^5D_0 \rightarrow {}^7F_4$ bands located in the 1050–1350 cm^{-1} range, are very strong for $0 \leq x \leq 0.50$ and cannot be represented.

Table 1
Experimental and calculated energy level schemes of $Eu_{0.10}Bi_{0.90}V_{0.60}As_{0.40}O_4$. Units in cm^{-1}

$^{2S+1}L_J$ level	E_{exp}	$E_{calc.}$ in C_{2v}
$^7F_0$	0	0
$^7F_1$	332	331
	350	353
	420	418
$^7F_2$	908	908
	1002	1000
	1002	1005
	1126	1129
	1158	1155
$^7F_3$	1850	1852
	–	1871
	–	1875
	1883	1877
	1941	1946
	–	1959
	–	1980
$^7F_4$	–	2713
	–	2786
	–	2790
	2806	2804
	2846	2846
	2943	2941
	2980	2977
	–	2994
	–	3049
$^5D_0$	17 219	–

zircon form and two others lines at 16 370 and 16 216 cm^{-1} for the distorted scheelite form.

Also, according to the presence of the $^5D_0 \rightarrow {}^7F_0$ transition and to the existence of three lines for the $^5D_0 \rightarrow {}^7F_1$ transition, the europium ion must be located at a site of lower point symmetry than the S_4 point site expected for the scheelite phase. It will be supposed to be a C_2 symmetry site, but treated as C_{2v} for the crystal field calculation. From the energy scheme deduced from the fluorescence spectrum (Table 1) a crystal field calculation is performed on the reduced $^7F_{0-4}$ manifold taking into account 16 observed emission lines from 25, in which the spin–orbit coupling is included implicitly [6,7]. The result of the simulation is presented in Table 1 and the phenomenological parameters in Table 2. As expected, the extra parameters corresponding to those appearing in the

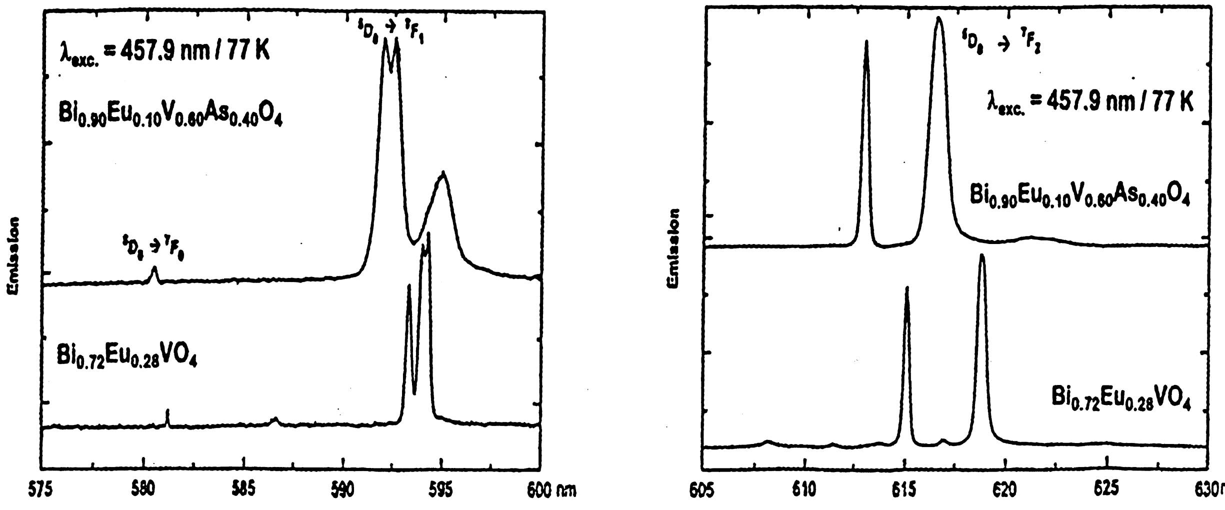

Fig. 3. Fluorescence spectra of Eu^{3+} at 77 K of arsenovanadates with structure deviated from the zircon and scheelite forms.

Table 2
Phenomenological crystal field parameters for $Eu_{0.10}Bi_{0.90}V_{0.60}As_{0.40}O_4$ (values in cm^{-1})

B_q^k	C_{2v}
B_0^2	267
B_2^2	51
B_0^4	−548
B_2^4	75
B_4^4	−880
B_0^6	−519
B_2^6	−45
B_4^6	−347
B_6^6	−260
Residue	131
σ	4.3
N_v	1848

$S_4 \rightarrow C_2$ (C_{2v}) descending symmetry procedure are small. The crystal field strength parameter, $N_v = 1848$ cm^{-1} [8] is close to the value found for the europium in the typical scheelite compound $Na_5Eu(MoO_4)_4$ ($N_v = 1651$ cm^{-1}) [6,7].

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