OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 8, No. 5-6, May - June 2014, p. 608 - 611

Investigations of the optical spectra and spin-Hamiltonian parameters for VO(II) ion in mixed alkali cadmium phosphate glasses

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The aim of this paper is the theoretical investigation of the optical spectra and spin-Hamiltonian parameters for vanadium ion doped in a tetragonal compressed octahedral site, in three different LiNaCdP glasses. The crystal field parameters were calculated and the simulation of the optical energy levels scheme have been done for all three samples. The spin-Hamiltonian parameters (g-factors - $g_{\parallel}, g_{\perp}$) and hyperfine structure constants ($A_{\parallel}, A_{\perp}$), were evaluated by using the perturbation theory of Macfarlane and complete diagonalization method of the Hamiltonian of the systems. Both methods give very close results with the experimental data.

(Received January 5, 2013; accepted May 15, 2014)

Keywords: Vanadyl, Phosphate glasses, Crystal field parameters, Spin-Hamiltonian parameters

1. Introduction

Mixed-alkali in glasses has attracted much attention, due to its technological and theoretical interests in describing the physics and chemistry of glasses [1]. So, these glasses have attracted a great deal of attention because of their potential applications in the development of new tunable solid-state lasers, solar-energy converters, and fiber-optic communication devices. Transition metal ions are used to probe the glass structure, because their responses to surrounding actions are very sensitive [1, 2].

Interesting changes in electron paramagnetic resonance (EPR) spectra have been found in different crystal field environments, due to vanadyl ions and these changes are reflected in the values and anisotropy of the *g* and *A* tensors. Due to this, VO(II) is used extensively as a dopant in various systems for EPR studies, to investigate defect properties, structural changes and host lattice effects on molecular ions [3,4].

The optical absorption and EPR data of vanadyl ion incorporated into LiNaCdP glasses confirm that the V^{4+} site symmetry is octahedral, which decrease as the Jahn-Teller static effect, to C_{4v} symmetry [2]. In this paper the crystal field parameters were calculated and the simulation of the optical energy levels scheme have been done for three samples: x Li_2O + (20-x) Na_2O + 20 CdO + 59.5 P_2O_5 + 0.5 V_2O_5, with varying concentration $5 \le x \le 15$. The spin-Hamiltonian parameters were calculated by using the perturbation theory method (PTM) of Macfarlane [5] and complete diagonalization (of energy matrix) method (CDM) [6-9].

2. Optical spectra

Vanadyl ion (VO^{2+}) has the electronic configuration [Ar] $3d^1$ and the free ion term is ^2D. The behavior of unpaired electron in VO^{2+} complexes is determined by strong V=O bonding, as a result most of the complexes possess C_{4v} symmetry [10]. In an octahedral field the ^2D term split into ^2E_g and $^2T_{2g}$ terms. In our case the vanadium ion enters in the LiNaCdP glass matrix and due to the Jahn–Teller static effect, the octahedron is compressed and the symmetry descents to C_{4v} [2]. In this new lower symmetry the $^2T_{2g}$ term is split into a doublet ^2E_g and a singlet $^2B_{2g}$, with $^2B_{2g}$ ground state and the ^2E_g term splits into two nondegenerate orbital singlets $^2A_{1g}$ and $^2B_{1g}$.

For d^1 ions in the tetragonal symmetry with the ground states $^2B_{2g}$, according to the crystal field theory, the three optical absorption bands can be expressed as [6]:

$$E_1 = E(^2B_{2g}) \rightarrow E(^2E_g) = -3Ds + 5Dt \qquad (1)$$

$$E_2 = E(^2B_{2g}) \rightarrow E(^2B_{1g}) = 10Dq \qquad (2)$$

$$E_3 = E(^2B_{2g}) \rightarrow E(^2A_{1g}) = 10Dq - 4Ds - 5Dt \qquad (3)$$

where Dq is the cubic crystal field parameter, Ds and Dt are the tetragonal crystal field parameters. For vanadyl ion in LiNaCdP glasses (LiNaCdP1 x = 5, LiNaCdP2 x = 10, LiNaCdP3 x = 15) the values of these parameters are given in [2]. The relation between the crystal field parameters B_{kq} and Dq, Dt and Ds are [6, 11]:

$$B_{20} = -7Ds \qquad (4)$$

$$B_{40} = 21(Dq - Dt) \quad (5)$$

$$B_{44} = 3\sqrt{70}\,\frac{Dq}{2} \quad (6)$$

From these equations the B_{kq} parameters can be calculated and the results are listed in Table 1.

Table 1. The crystal field parameters (in cm^{-1}) for vanadyl ion doped in LiNaCdP.

B_{kq}	***LiNaCdP1***	***LiNaCdP2***	***LiNaCdP3***
B_{20}	24661	24703	24738
B_{40}	23436	23415	23247
B_{44}	18448	18398	18448

In tetragonal crystal field for a 3d^1 ion, the Hamiltonian can be written as [6, 12]:

$$H = H_f + H_{CF}(B_{20}, B_{40}, B_{44}) \quad (7)$$

where H_f and H_{CF} re the free-ion term and the crystal field interaction (with the crystal field parameters B_{20}, B_{40}, B_{44}) respectively. Using the Eqs.(1)-(3), and the complete diagonalization method (CDM) of the Hamiltonian (7), with the crystal field parameters from Table 1, we have calculated the energy of optical levels for all three doped glasses.

In Table 2 are given the positions of the calculated optical spectral bands for all three host matrix and comparison with experimental data.

Table 2. The optical spectral band positions (in cm^{-1}) for VO(II) in LiNaCdP glasses.

VO(II):LiNaCdP1	**Eqs(1-3)**	**CDM**	**Exp. [2]**
$^2B_2 \rightarrow {}^2E_1$	12339	12244	12345
$^2B_2 \rightarrow {}^2B_1$	14700	14713	14705
$^2B_2 \rightarrow {}^2A_1$	27022	27029	27027
VO(II):LiNaCdP2	**PTM**	**CDM**	**Exp. [2]**
$^2B_2 \rightarrow {}^2E_1$	12342	12246	12345
$^2B_2 \rightarrow {}^2B_1$	14660	14675	14662
$^2B_2 \rightarrow {}^2A_1$	27021	27029	27027
VO(II):LiNaCdP3	**PTM**	**CDM**	**Exp. [2]**
$^2B_2 \rightarrow {}^2E_1$	12417	12321	12422
$^2B_2 \rightarrow {}^2B_1$	14700	14714	14705
$^2B_2 \rightarrow {}^2A_1$	27021	27029	27027

As can see from this table the results of the calculations are in good agreement with the experimental data.

3. Spin-Hamiltonian parameters

For vanadyl ion doped in mixed alkali cadmium phosphate glasses, with the ground state $^2B_{2g}$, the spin-Hamiltonian is [2]:

$$H = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (8)$$

where β is the Bohr magneton, while g||, $g_{\perp}$ and $A_{\parallel}$, $A_{\perp}$ are the components of the gyromagnetic tensor g and hyperfine structure tensor A, respectively. B_x, B_y and B_z are components of the magnetic field, S_x, S_y, S_z and I_x, I_y, I_z are the spin operators of the electron and the nucleus, respectively.

According to the perturbation method, in the third-order perturbation formulas for spin-Hamiltonian parameters, we have [5, 6, 13-15]:

$$g_{\parallel} = g_e - \frac{8k\zeta}{E_2} - \frac{(k+g_e)\zeta^2}{E_1^2} - \frac{4k\zeta^2}{E_1E_2} \quad (9)$$

$$g_{\perp} = g_e - \frac{2k\zeta}{E_1} + \frac{(k-g_e)\zeta^2}{E_1^2} - \frac{2g_e\zeta^2}{E_2^2} \quad (10)$$

$$A_{\parallel} = P\left[-\kappa - \frac{4}{7} + (g_{\parallel} - g_e) + \frac{3}{7}(g_{\perp} - g_e)\right] \quad (11)$$

$$A_{\perp} = P\left[-\kappa + \frac{2}{7} + \frac{11}{14}(g_{\perp} - g_e)\right] \quad (12)$$

Here g_e =2.0023 is the free electron value, k is the orbital reduction factor, κ is the core polarization constant, in our case κ = 0.73 (LiNaCdP1), κ = 0.72 (LiNaCdP2) and κ = 0.73 (LiNaCdP3) [2]. P are the dipolar hyperfine structure constant (in our case $P = -132 \cdot 10^{-4} cm^{-1}$ for LiNaCdP1 glass, $P = -134 \cdot 10^{-4} cm^{-1}$ for LiNaCdP2 glass and $P = -134 \cdot 10^{-4} cm^{-1}$ for LiNaCdP3 glass [2]) and ζ is spin-orbit coupling parameters.

Considering the covalence reduction effect for 3d^1 ions in crystals [16], we have:

$$\zeta = k\zeta_0,\ P = kP_0 \quad (13)$$

here ζ_0 and P_0 are the corresponding parameters for free state: $\zeta_0 = 248 cm^{-1}$ [6, 12] and P_0=172×10^{-4} cm^{-1} [6, 12]. The unknown orbital reduction factor k is obtained using Eq. (13).

The parallel and perpendicular components of the g-tensor and the parallel and perpendicular components of the hyperfine tensor *A* can be calculated by PTM, using Eqs (9)–(12). The obtained results are given in Table 3.

Table 3. The g factors and hyperfine structure constants in $10^{-4}cm^{-1}$ calculated by PTM and CDM.

LiNaCdP1	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}\times10^{-4}$	$A_{\perp}\times10^{-4}$
Calculated by PTM	1.9217	1.9777	184	61
Calculated by CDM	1.9217	1.9777	184	61
Observed value [2]	1.9254	1.9772	183	61
LiNaCdP2				
Calculated by PTM	1.9189	1.9769	186	61
Calculated by CDM	1.9194	1.9769	186	61
Observed value [2]	1.9283	1.9772	185	61
LiNaCdP3				
Calculated by PTM	1.9202	1.9774	186	61
Calculated by CDM	1.9202	1.9774	186	62
Observed value [2]	1.9237	1.9785	185	62

The second method used for calculations the spin-Hamiltonian parameters is CDM of the matrix of the Hamiltonian (7) [6-9]. As the result the $|\psi_+\rangle$ and $|\psi_-\rangle$ of ground state were obtained (Appendix). Using these wave functions of the ground state and the equivalence between the spin-Hamiltonian parameters and the Zeeman interaction, the *g*-factors can be expressed as [6, 9, 17]:

$$g_{\parallel} = 2\langle\psi_+|kL_z + g_eS_z|\psi_+\rangle \qquad (14)$$

$$g_{\perp} = 2\langle\psi_+|kL_x + g_eS_x|\psi_-\rangle \qquad (15)$$

in which L_j and S_j $(j = x, y, z)$ are the operators of orbit and spin angular momentum.

The expressions of $A_{\parallel}$ and $A_{\perp}$ are the same as those in Eqs. (11) and (12). The calculated results are also listed in Table 3.

4. Conclusions

The simulation of energy levels scheme, the modeling of the crystal field parameters, and calculation of spin-Hamiltonian parameters for VO^{2+}:LiNaCdP system have been made.

Diagonalizing the energy matrix, the energy levels and the wave functions of ground state are obtained. We simulated the energy levels scheme of the system, which is in agreement withexperimental data.

The g-factors ($g_{\parallel}, g_{\perp}$) and hyperfine structure constants ($A_{\parallel}, A_{\perp}$), calculated using the perturbation theory method and complete diagonalization method give very close results and they are in good agreement with the experimental data. This suggests that both methods are adequate for the investigations of spin-Hamiltonian parameters for VO(II) ions in the title host.

Appendix

The eigenfunctions $|SLM_SM_L\rangle$ of ground state $^2B_2$ of VO(II) ion doped in LiNaCdP glasses, are as follows:

LiNaCdP1:

$$|\psi_+\rangle = -0.716211\left|\frac{1}{2}2\frac{1}{2}-2\right\rangle +$$

$$+0.010941\left|\frac{1}{2}2-\frac{1}{2}-1\right\rangle + 0.697798\left|\frac{1}{2}2\frac{1}{2}2\right\rangle$$

$$|\psi_-\rangle = -0.697798\left|\frac{1}{2}2-\frac{1}{2}-2\right\rangle -$$

$$-0.010941\left|\frac{1}{2}2\frac{1}{2}1\right\rangle + 0.716211\left|\frac{1}{2}2-\frac{1}{2}2\right\rangle$$

LiNaCdP2:

$$|\psi_+\rangle = -0.716379\left|\frac{1}{2}2\frac{1}{2}-2\right\rangle +$$

$$+0.011112\left|\frac{1}{2}2-\frac{1}{2}-1\right\rangle + 0.697623\left|\frac{1}{2}2\frac{1}{2}2\right\rangle$$

$$|\psi_-\rangle = -0.697623\left|\frac{1}{2}2-\frac{1}{2}-2\right\rangle -$$

$$-0.011112\left|\frac{1}{2}2\frac{1}{2}1\right\rangle + 0.716379\left|\frac{1}{2}2-\frac{1}{2}2\right\rangle$$

LiNaCdP3:

$$|\psi_+\rangle = -0.716307\left|\frac{1}{2}2\frac{1}{2}-2\right\rangle +$$

$$+0.010988\left|\frac{1}{2}2-\frac{1}{2}-1\right\rangle + 0.697699\left|\frac{1}{2}2\frac{1}{2}2\right\rangle$$

$$|\psi_-\rangle = -0.697699\left|\frac{1}{2}2-\frac{1}{2}-2\right\rangle -$$

$$-0.010988\left|\frac{1}{2}2\frac{1}{2}1\right\rangle + 0.716307\left|\frac{1}{2}2-\frac{1}{2}2\right\rangle$$

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