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Energy levels scheme for Na_2SiF_6:Mn^{4+} nanophosphor

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Na_2SiF_6 assumes a crystalline morphology that resembles the morphology of ice. To explain the experimental data concerning the luminescent properties of Na_2SiF_6 phosphor, doped with Mn^{4+} ion, is necessary to investigate the electronic structure of this ion doped in host lattice. These phosphors have the space group = D_3^2 - *P321* with the lattice constant of *a* = 8.859Å, *c*=5.038Å, and the Mn^{4+} ion substitute for Si ion in octahedral site symmetry. The crystal field parameters and energy for lowest energy levels of Mn^{4+} doped in Na_2SiF_6 crystal have been calculated in the frame of Exchange Charge Model. The obtained results are in satisfactory agreement with experimental data.

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1. Introduction

The recent development of white light-emiting diodes relies on the use of phosphors for converting blue or UV light into longer wavelenght complementary colors [1], [2]. Many phosphors were synthesized by firing host and activated, at high temperatures, with rare earth or transitional metals [3].

Sodium fluorosilicate (Na_2SiF_6) is an interesting material because its refractive index is very similar to that of ice at visible wavelengths. Na_2SiF_6 assumes a crystalline morphology that resembles the morphology of ice [4]. Therefore, Na_2SiF_6 is known as an ice-analog material. Luminescent materials using manganese ion as activator have become popular due their superb properties [3]. After investigating the electronic structure of the ion doped in this host lattice we can explain the experimental data concerning the luminiscent properties of Na_2SiF_6 phosphor, doped with Mn^{4+} ion. The Mn^{4+} ion has the same electronic configuration, with $3d^3$ electrons, as Cr^{3+} ion. Using the standard crystal field theory we have been modeled the crystal field parameters and simulated the energetic levels scheme of this ion. The sequence of the energy levels is determined by the symmetry of ion sites, by interelectronic interactions determined by the Racah parameters *B* and *C* and by the crystal-field parameters. The system Mn^{4+}:Na_2SiF_6 have been experimentally investigated [5], a consistent theoretical analysis on the crystal field parameters and the energy levels scheme have been not yet done.

The aim of this paper is to report on detailed crystal field calculation of the Mn^{4+} energy levels in order to give a reliable explanation for experimental data [5].

2. Method and samples

These phosphors, Na_2SiF_6 (sodium hexafluorosilicate), have the trigonal crystal structure (space group = D_3^2 - *P321)* [5] with the lattice constant of *a* = 8.859Å and *c* = 5.038Å (Fig. 1). After doping Mn^{4+} in sodium hexafluosilicate (Na_2SiF_6, malladrite) crystal this ion will substitutes the Si^{4+} with octahedral coordination formed by F^- ions.

The parameters of the crystal field acting on the Mn^{4+} ion are calculated in the frame of Exchange Charge Model [6], from the crystal structure data. With these parameters we have been diagonalized the crystal field Hamiltonian.

The obtained energy level schemes were compared with experimental data, and a good agreement is demonstrated.

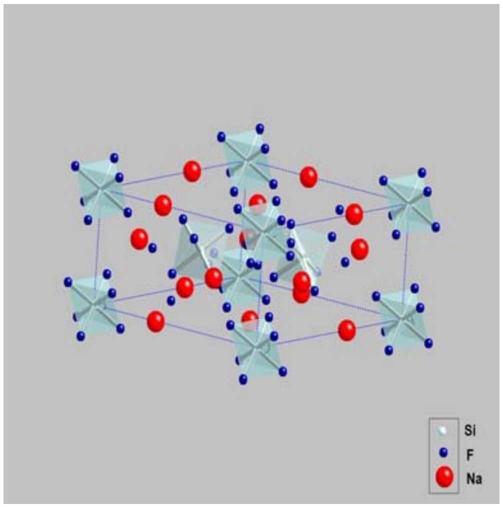

Fig. 1. Na_2SiF_6 structure [5].

The influence of the crystalline field on the energy levels of the $3d^n$ system can be usually interpreted by the Tanabe–Sugano energy-level diagram (Fig. 2).

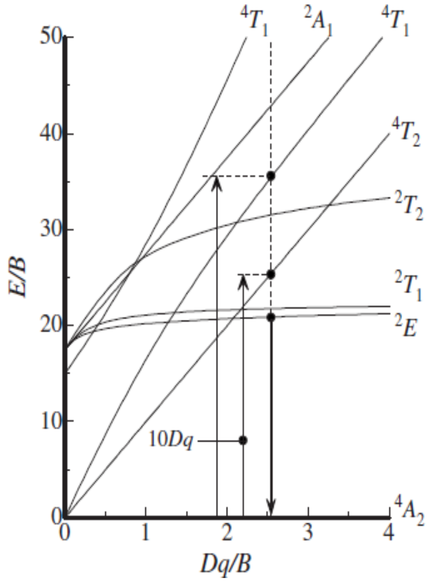

Fig. 2. Tanabe–Sugano energy-level diagram for a $3d^3$ system in the octahedral symmetry (Mn^{4+}).

In order to analysis the crystal field for Mn^{4+} doped in Na_2SiF_6 crystal we follow paper [3]. In the framework of the exchange charge model (ECM) of crystal field the energy levels of an impurity ion are considered as the Eigen values of the following Hamiltonian [6]:

$$H = \sum_{p=2,4}\sum_{k=-p}^{p}\left(B^{k}_{p,q} + B^{k}_{p,S}\right)O^{k}_{p} \qquad (1)$$

Here O^k_p are the linear combinations of irreducible tensor operators, and crystal field B^k_p parameters (CFP) are defined as:

$$B^k_{p,q} = -K^k_p e^2 \left\langle r^p \right\rangle \sum_i q_i \frac{V^k_p \left\langle \theta(i), \varphi(i) \right\rangle}{R(i)^{p+1}} \qquad (2)$$

$$B^k_{p,S} = K^k_p e^2 \frac{2(2p+1)}{5} \sum_i \left(G_S S(S)^2_i + G_\sigma S(\sigma)^2_i + \gamma_p G_\pi S(\pi)^2_i\right) \frac{V^k_p(\theta_i, \varphi_i)}{R_i} \qquad (3)$$

The last term includes all effects of the covalent bond formation and exchange interaction. The sums are carried out over lattice ions denoted by i with charges q_i; $R(i), \theta(i), \varphi(i)$ are the spherical coordinates of the i-th ion of crystal lattice in the system of reference centered at the impurity ion. The averaged values $\left\langle r^p \right\rangle$ of p-th power of the impurity ion electron radial coordinate can be found in Ref. [7]. The values of the numerical factors K^k_p, γ_p and expressions for the polynomials V^k_p are given in [6]. $S(s), S(\sigma), S(\pi)$ correspond to the overlap integrals between d - functions of the central ion and p- and s-functions of the ligands: $S(s) = \langle d0|s0\rangle, S(\sigma) = \langle d0|p0\rangle, S(\pi) = \langle d1|p1\rangle$. These integrals are numerical evaluated.

G_s, G_σ, G_π are dimensionaless adjustable parameters of the model, whose values can be determined from the positions of the first three absorption bands. We assume that they can be approximated to a single value, i.e. $G_s = G_\sigma = G_\pi = G$, that can be estimated from only one (the lowest in energy) absorption band. This is usually a reasonable approximation.

The dependence of the overlap integrals on distance between both ions is described by the following exponential functions [8]:

$$\begin{aligned} S_s &= \langle d0 | s0 \rangle = 2.9481 \ \exp(-1.1738\ R) \\ S_\sigma &= \langle d0 | p0 \rangle = 1.2177 \ \exp(-0.8233\ R) \\ S_\pi &= \langle d0 | p0 \rangle = 1.9908 \ \exp(-1.1314\ R) \end{aligned}$$

The strong advantage of the ECM is that if the G parameter is determined to fit the first absorption band, the other energy levels, located higher in energy, will also fit experimental spectra fairly well. Another advantage of this model is connected with the fact the all CFP can be calculated from available crystal structure data, but not obtained *a posteriori* as a result of a fitting procedure. Also the obtained results are reliable (deviation between the calculated and observed energy levels is about several hundred cm^{-1} for $3d$ ions and several tens cm^{-1} for $4f$ ions). The ECM gives possibility to analyze covalent effects for different impurity centers by comparing bilinear form constructed from the overlap integrals calculated using wave functions of the impurity ions and ligands. The ECM has been successfully applied for the calculations of the energy levels of both rare earth [9-11] and transition metal ions in different hosts as well [12–14].

The obtained energy levels were compared with results of experimental data and discussed. During the diagonalization of the Hamiltonian the estimated Racah parameters B, C and G parameter of the exchange charge model have done.

3. Results and discussion

The calculated CFPs values of Mn^{4+} doped in Na_2SiF_6 are shown in Table 1 (the point charge and exchange charge contributions are denoted by PCC and ECC, respectively, and shown separately).

The value of the ECM fitting parameter G was determined from the position of the first absorption band in the corresponding absorption spectra and is equal to 4.458.

Table 1. Crystal field parameters for $Mn^{4+}:Na_2SiF_6$.

Parameter	PCC	ECC	Total value
B_2^{-2}	51	88	139
B_2^{-1}	153	214	367
B_2^{0}	-63	-106	-169
B_2^{1}	-527	-813	-1340
B_2^{2}	-93	-136	-229
B_4^{-4}	-1243	-7667	-8910
B_4^{-3}	2750	17003	19753
B_4^{-2}	973	6016	6989
B_4^{-1}	1359	8388	9747
B_4^{0}	-164	-1010	-1174
B_4^{1}	968	5958	6926
B_4^{2}	-3127	-19313	-22440
B_4^{3}	-2761	-17074	-19835
B_4^{4}	2363	14574	16937

The Racah parameters $B = 775$ cm^{-1}, $C = 3491$ cm^{-1} are used during diagonalization of the Hamiltonian of the system. Calculated energy levels are shown in Table 2.

As seen from this Table 2, the calculated values are in good agreement with experimental data, they are obtained by fitting experimental data from ref [5].

Table 2. Observed and calculated (this work) energy levels (in cm^{-1}) of Mn^{4+} ion in Na_2SiF_6.

Energy levels (Oh group rotations)	This work		Experi-mental values [5]	Calculated Tanabe Sugano diagram
	Calculated ECM	Averaged ECM		
$^4A_2$	0	0	0	0
^2E	16200 16202	16201	16201	16201
$^2T_1$	16830 16915 16915	16887	-	16884
$^4T_2$	19620 19736 19746	19701	19700	19700
$^2T_2$	24386 24388 24573	24449	-	24444
$^4T_1$	27414 27439 27597	27483	27481	27480
$^2A_1$	32373	32373	-	32270

4. Conclusions

The crystal field parameters and energy for lowest levels of Mn^{4+} doped in Na_2SiF_6 (sodium hexafluorosilicate) crystal have been calculated and the obtained results are compared with experimental data. The calculations have been performed in the frame of ECM of crystal field, taken into account site symmetry of the impurity ion, the contributions from ions charges of lattices and covalent effects from doped lattice. For this system the covalent effects are strong and obtained results for energy level schemes are in satisfactory agreement with experimental data.

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References

[1] R. Mueller-Mach, G. O. Mueller, M. R. Krames, T. Trottier, IEEE J. Sel. Top. Quantum Electron. **8**, 339 (2002).
[2] E. F. Schubert, J. K. Kim, Science, **308**, 1274 (2005).
[3] K. Narita in Phospor Handbook, S. Shionoya, W. M. Yen, Editors, CRC Press, Boca Raton, FL (1999) p.317.
[4] H-L. Jeong, Y-D. Huh, Materials Letters, (2010), doi:10.1016 / j.matlet. 2010.05.023.
[5] Yan Kai Xu, Sadao Adachi, Journal of Applied Physics **105**, 013525 (2009).
[6] B. Z. Malkin, “Crystal field and Electron-Phonon Interaction in Rare-Earth Ionic Paramagnets” in Spectroscopy of solids containing rare-earth ions, edited by A. A. Kaplyanskii, B. M. Macfarlane, North Holland, Amsterdam, pp. 33-50, 1987.
[7] A. G. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford, Clarendon, 1970.
[8] M. G. Brik, N. M. Avram, AIP Proceedings, **1131**, 86 (2009).
[9] M. N. Popova, E. P. Chukalina, B. Z. Malkin, A. I. Iskhakova, E. Antic-Fidancev, P. Porcher, J. P. Chaminade, Phys. Rev. **B 63**, 075103 (2001).
[10] M. N. Popova, S. A. Klimin, E. P. Chukalina, E. A. Romanov, B. Z. Malkin, E. Antic-Fidancev, B. V. Mill, G. Dhalenne, Phys. Rev. **B 71**, 024414 (2005).
[11] A. E. Nikiforov, V. A. Chernyshev, V. P. Volodin, N. M. Avram, C. N. Avram, AIP Proceedings **1131**, 96 (2009).
[12] C. Jousseaume, D. Vivien, A. Kahn-Harari, B. Z. Malkin, Opt. Mater, **24**, 143 (2003).
[13] M. G. Brik, N. M. Avram, J. Phys: Condens. Matt. **21**, 155502 (2009).
[14] N. M. Avram, M. G. Brik, C. N. Avram, I. Sildos, A. M. Reisz, Solid Stat. Comm. **149**, 2070 (2009).

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