COMPARATIVE STUDY BETWEEN CRYSTAL FIELD PARAMETERS FOR
$Mn^{4+}:K_2SiF_6$ AND $Mn^{4+}:Na_2SiF_6$

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Abstract
The aim of this paper is to model the crystal field parameters for Mn^{4+} doped in K_2SiF_6 respectively in Na_2SiF_6 crystal, in the Exchange Charge Model of the crystal field theory. By doping Mn^{4+} in K_2SiF_6 and Mn^{4+} in Na_2SiF_6 crystals the manganese ion will substitutes the Si^{4+} with octahedral coordination formed by F^- ions, but with different site symmetry. The theoretical parameters of the crystal field acting on the Mn^{4+} ion will be calculated in the frame of the symmetry adapted axes system of the local symmetry for each host matrix and will be compared between them. Using these parameters we simulated the energy level schemes for each considered system and the comparison with experimental data and between them shows a satisfactory agreement.

1. Introduction

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

Luminescent materials using manganese ion as activator have become popular due their grates properties [3]. In order to explain experimental data concerning the luminescent properties of K_2SiF_6 phosphor, doped with Mn^{4+} ion, and Na_2SiF_6 phosphor, doped with Mn^{4+} ion, is necessary to investigate the electronic structure of this ion doped in host lattice.

Potassium hexafluorosilicate, K_2SiF_6, have a cubic structure space group Oh^5 [4] (no. 225 in International Tables for Crystallography [5]), with one formula per unit cell and the lattice constant of a=8.13Å [4]. Si ions have the position *192 l* (in Wyckoff notation) and O_h site symmetry [4]. Malladrite, Na_2SiF_6 (sodium hexafluorosilicate), have the trigonal crystal structure

with space group D_3^2-*P321*[6](no.150 in International Tables for Crystallography [4]), with the lattice constants of *a*=8.859Å and *c*=5.038Å [6]. The Si ions have the position *6g* (in Wyckoff notation), and D_3 site symmetry [6]. In these crystals the Si ions have a similar octahedral coordination, but different local symmetry. In this paper we model the crystal field for each host matrix in the frame of the Exchange Charge Model (ECM) [7], calculate the crystal field parameters and simulate the energy levels scheme for Mn^{4+} ions doped in these crystals.

2. The ECM for K_2SiF_6 and Na_2SiF_6 doped with Mn^{4+}

The Mn^{4+} ion has the effective ionic radius of 0.54Å [8] and is easily substituted for the Si^{4+} ion with ionic radius 0.40Å [8] in the SiF_6^{2-} complex. By doping Mn^{4+} in K_2SiF_6 and Mn^{4+} in Na_2SiF_6 crystals the manganese ion will substitutes the Si^{4+} with octahedral coordination formed by F^- ions.

In paper [9] and [10] it have been calculated, the Crystal Field Parameters (CFPs) acting on the Mn^{4+} ion, in the frame of ECM [7], in the crystallographic axes system for $Mn^{4+}:K_2SiF_6$ and $Mn^{4+}:Na_2SiF_6$ systems. In both cases the site symmetry is apparent, not actual [11] and the CFPs are non-standard. In order to make a comparison between the sets of CFPs for $Mn^{4+}:K_2SiF_6$ and $Mn^{4+}:Na_2SiF_6$, in this paper we calculate the CFPs of the crystal field of the host matrixes, acting on the Mn^{4+} ion, in the frame of the Symmetry Adapted Axes System (SAAS) [11]. Even if the energy levels do not depend on axes system of the coordinates, the use of SAAS allows to obtain the standard CFPs, their number are according with the predictions of the group theory and can made comparison of different sets of such parameters. In both cases we used the SAAS with origin in Mn^{4+} ion and x ∥ [11$\bar{2}$], y ∥ [$\bar{1}$10] and z ∥ [111] directions [12]. This trigonal axis system is obtained from crystallographic axis system ([100], [010], [001]) by rotations with Euler angles Φ=45°, θ=54.73°, Ψ=0°.

The ECM [7] has been successfully applied for the calculations of the energy levels of both rare earth [13-15] and transition metal ions in different hosts as well [16–18] and we recommend to interested reader kindly advised to Refs.[9, 10, 16-18] for use this known model.

3. Results and Discussions

Based on the geometrical data [4, 6] and using the SAAS we calculated the following parameters: a) Mn^{4+} doped in K_2SiF_6 - the Racah parameters $B = 413cm^{-1}$, $C = 4264cm^{-1}$, the

parameter of ECM, $G=4.748$ and the crystal field parameters (in cm^{-1}) $B_4^0 = -3552$, $B_4^3 = 100475$; b) Mn^{4+} doped in Na$_2$SiF$_6$ - the Racah parameters $B = 775$cm^{-1}, $C= 3491$cm^{-1}, the parameter of ECM, $G=4.46$ and the crystal field parameters (in cm^{-1}) $B_2^0 = -444$, $B_4^{-3} = 97946$, $B_4^0 = -3403$. The number of the CFPs corresponds with the octahedral site symmetry for first case and to trigonal symmetry for second one. After the Racah parameters, G parameter of ECM were fitted and CFPs are found the crystal field Hamiltonian:

$$H = \sum_{p=2,4} \sum_{k=-p}^{p} B_p^k O_p^k$$

(with O_p^k being the combination of the irreducible tensor operators [7]), is diagonalized in the basis set spanned by the wave functions of the manganese ion. The calculated values for energy levels of the considered ion in both crystals are given in Table 1.

Table 1.   Calculated (this work) and observed energy levels (in cm^{-1})

Energy levels (Oh)	Mn^{4+}:K$_2$SiF$_6$				Mn^{4+}:Na$_2$SiF$_6$			
	This work		Experi-mental values [19]	Calcula-ted Tanabe Sugano diagram	This work		Experi-mental values [20]	Calcula-ted Tanabe Sugano diagram
	Calcula-ted	Avera-ged			Calcula-ted	Avera-ged		
$^4A_2$	0	0	0	0	0	0	0	0
^2E	16100 16100	16100	16100	16126	16202 16202	16202	16201	16201
$^2T_1$	16335 16335 16335	16335	-	16789	16831 16914 16914	16886	-	16884
$^4T_2$	20299 20299 20299	20299	20300	20300	19627 19739 19739	19702	19700	19700
$^2T_2$	24398 24398 24398	24398	-	24416	24389 24389 24570	24449	-	24444
$^4T_1$	24892 24892 24892	24892	24900	28099	27429 27429 27596	27485	27481	27480
$^2A_1$	34743	34743	-	33790	33274	33274	-	32270

As it can be seen from this table the obtained results are in good agreement with experimental data and very close in both host matrix. This means that the influence of the potassium and sodium ions on energy levels is small.

The covalence effects play an essential role in both considered systems. It can be revealed by using the following non-dimensional quantity [21]:

$$\beta = \frac{1}{2}\sqrt{\left(\frac{B_1}{B_0}\right)^2 + \left(\frac{C_1}{C_0}\right)^2}$$

where the subscripts "1" and "0" are related to the values of the Racah parameters in a crystal and in a free state, respectively. This quantity can serve as a qualitative measure of the nephelauxetic effect (significant decrease of the Racah parameters for 3d ions in a crystal with respect to those in a free state). For free ions these parameters are [22] $B_0 = 1065 \text{cm}^{-1}$, $C_0 = 4919 \text{cm}^{-1}$ for Mn^{4+}. With the above values of B, C parameters for Mn^{4+} the obtained values for β are: 0.4748 for Mn^{4+}:K_2SiF_6 and 0.5082 for Mn^{4+}:Na_2SiF_6. This means that the covalence effect is "strong" in these systems and ECC contribution to CFPs are important.

Conclusions

The actual crystal field parameters and energy for lowest levels of Mn^{4+} doped in K_2SiF_6 crystal and Mn^{4+} doped in Na_2SiF_6 crystal have been calculated and the obtained results are compared with experimental data and between them. The calculations have been performed in the frame of the symmetry adapted axes system and 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 both systems the covalent effects are strong and the obtained results for the energy level schemes are in good agreement with experimental data.

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