

Simulating energy level schemes using SAAS for MgGa_2O_4 ($\text{M} = \text{Mg}, \text{Zn}$) and MgF_2 doped with Co^{2+} and Cr^{3+}

R. NISTORA*, A. S. GRUIA

Faculty of Physics, West University of Timisoara, 300223 Timisoara, Romania

The aim of this paper is to simulate the energy level schemes for some host matrices doped with transition metals ions. These schemes will be calculated in the frame of the Symmetry Adapted Axes System (SAAS). In recent years, some materials doped with tetrahedral Co^{2+} ions have attracted much attention due to their excellent absorption and emission properties. For the considered systems, the energy level schemes are obtained by diagonalizing the Hamiltonian of the system in the base of Co^{2+} and Cr^{3+} . The obtained values of the energy levels are compared with experimental data and a satisfactory agreement is demonstrated.

(Received July 3, 2012; accepted July 19, 2012)

Keywords: Energy levels scheme, Crystal field theory, 3d-ions

1. Introduction

In this paper we have calculated the real crystal field parameters and simulate the energy level schemes for two oxide spinels and magnesium fluoride doped with transition metals ions (Co^{2+} and Cr^{3+}) using the Symmetry Adapted Axes System (SAAS) [1].

In recent years, some materials doped with tetrahedral Co^{2+} ions have attracted much attention due to their excellent absorption and emission properties [2–5]. The Co^{2+} ion has a $3d^7$ electronic configuration.

Magnesium gallium oxide (MgGa_2O_4) and zinc gallium oxide (ZnGa_2O_4) are both spinel-type compounds that have wide energy gaps of 4.4 and 5.0 eV, respectively [6]. Oxide spinels comprise a very large group of structurally related compounds [7-9].

ZnGa_2O_4 is a good phosphor material used for low-voltage cathodoluminescent and vacuum fluorescent display, liquid crystal displays (LCD), and recently reported as a promising candidate for the emitting layer for field emission displays and electroluminescent devices [10, 11].

The MgGa_2O_4 and ZnGa_2O_4 have a cubic structure space group Oh^7 ($\text{Fd}\bar{3}\text{m}$) (no. 227 in International Tables for Crystallography [12]) with point symmetry Td ($\bar{4}3\text{m}$) for tetrahedral sites and D_{3d} ($\bar{3}\text{m}$) for octahedral sites, with cell parameter $a = 8.286 \text{ \AA}$ for MgGa_2O_4 and $a = 8.323 \text{ \AA}$ for ZnGa_2O_4 . After doping Co^{2+} in these host matrices this ion will substitute Mg^{2+} and Zn^{2+} in a tetrahedral coordination. The introduction of Co^{2+} does not change the lattice constant of ZnGa_2O_4 much [13].

Zinc gallate (ZnGa_2O_4) is a normal spinel crystal structure with Zn^{2+} ions in the tetrahedral sites and Ga^{3+} ions in the octahedral sites. It is a kind of multifunctional material [13]. In contrast, a part of MgGa_2O_4 has an inverse spinel structure [6].

Crystals of MgF_2 were used as a standard host material and its optical absorption and emission for the 3d transition-metal doped in this crystal are well known [14]. MgF_2 has a rutile-type structure, with space group P42/mnm (no. 136 in International Tables for Crystallography [12]), two formula units in a unit cell and lattice constants $a = 4.6213 \text{ \AA}$, $c = 3.0159 \text{ \AA}$ [15].

The unit cell of MgF_2 is tetragonal and the Mg^{2+} ion is surrounded by six fluorines occupying the tops of distorted octahedra of D_{2h} site symmetry [16]. In MgF_2 crystals, the ligand distance is primarily restricted by the lattice constant and the nearest neighbor Mg-F distances are of the order of 1.98 \AA . The optical properties of 3d ions in MgF_2 crystals have been confirmed that Cr^{3+} and Co^{2+} ions are substitution in Mg^{2+} sites [16, 17].

2. Method and samples

MgGa_2O_4 and ZnGa_2O_4 are not only excellent phosphors but are also excellent luminescent materials [18–20].

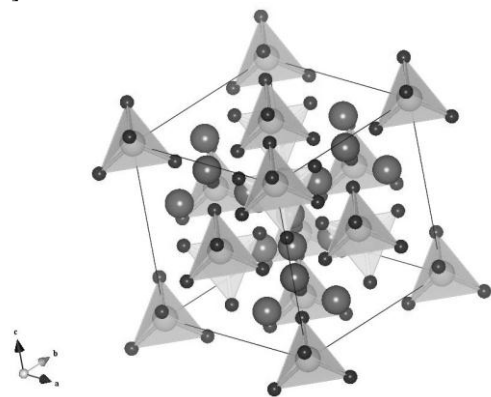


Fig. 1. ZnGa_2O_4 structure.

The effective ionic radius of Mg^{2+} ion is 0.57\AA and 0.60\AA for Zn^{2+} ion and is easily substituted for the Co^{2+} ion with ionic radius 0.58\AA . By doping Co^{2+} in $MgGa_2O_4$ and Co^{2+} in $ZnGa_2O_4$ crystals the Co^{2+} ion will substitute the Mg^{2+} respectively Zn^{2+} with tetrahedral coordination formed by the four O^{2-} ions. Charge compensation is not necessary.

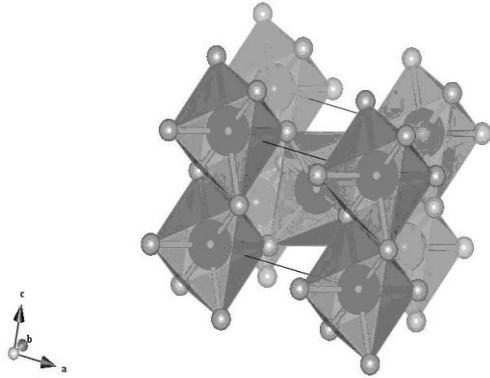


Fig. 2. MgF_2 structure.

These Figs. (Fig. 1 and Fig. 2) were drawn with Vesta developed by Momma and Izumi [21].

In case of magnesium fluoride because the ionic radii for Cr^{3+} and Mg^{2+} are close (0.61\AA for Cr^{3+} and 0.65\AA for Mg^{2+} ion) [22] the local symmetry of Cr^{3+} ion don't change, it keep D_{2h} . After doping Cr^{3+} in MgF_2 crystal this ion will substitute the Mg^{2+} with octahedral coordination formed by F ions.

When doped with tetrahedral Co^{2+} ion, $ZnGa_2O_4$ spinel exhibits strong broad luminescence bands in the visible and near infrared (NIR) spectral regions [23, 24]. This allows us to consider such material as a possible candidate for tunable solid-state laser materials in the visible and NIR [13].

The intense and broad emission band makes the $MgGa_2O_4$ a very attractive material for use as tunable media [25].

3. Results and discussions

In the framework of the Exchange Charge Model (ECM) of crystal field [26] the energy levels of an impurity ion are considered as the Eigen values of the following Hamiltonian:

$$H = \sum_{p=2,4} \sum_{k=-p}^p (B_{p,q}^k + B_{p,s}^k) O_p^k$$

O_p^k are the linear combinations of irreducible tensor operators, and crystal field B_p^k parameters (CFP) containing all information about geometrical structure of an impurity center.

In paper [27] it have been calculated, the Crystal Field Parameters (CFPs) acting on the Co^{2+} ion, in the frame of ECM [26], in the crystallographic axes system for $MgGa_2O_4:Co^{2+}$ respectively $ZnGa_2O_4:Co^{2+}$ systems. In

both cases the site symmetry is apparent, not actual [1] and the CFPs are non-standard. We calculate the CFPs of the crystal field of the host matrixes, acting on the Co^{2+} and Cr^{3+} ion, in the frame of the Symmetry Adapted Axes System (SAAS) [1]. 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. This trigonal axis system is obtained from crystallographic axis system ($[100]$, $[010]$, $[001]$) by rotations with Euler angles $\Phi=45^\circ$, $\theta=54.73^\circ$, $\Psi=0^\circ$. In case of MgF_2 (magnesium fluoride) we applied a rotations (C_2) with Euler angles $\Phi=45^\circ$, $\theta=0^\circ$, $\Psi=0^\circ$.

In Table 1 and Table 3 we present the crystal field parameters for the two host matrixes doped with transition metals ions, Co^{2+} ($3d^7$). The results are presented in different columns, PCC represent the point charge contribution and ECC is the exchange charge contribution, making this sums I obtained the total value of crystal field parameters.

Table 1. CFP for Co^{2+} in $MgGa_2O_4$.

Parameter	PCC	ECC	Total value
B_4^0	429	150	579
B_4^3	-12129	-4252	-16382

Table 2. Energy levels of Co^{2+} ion in $MgGa_2O_4$ ($B=868$ cm^{-1} , $C=3456$ cm^{-1} , $G=1.147$).

Energy levels (Td group notations)	This work	Observed [24, 28]
	Calculated	
4A_2	0	0
4T_2	3309	~3300
4T_1	5801	6500-7700
2E	15514	-
2T_1	16022	-
4T_1	16249	15385-16000

Table 3. CFP for Co^{2+} in $ZnGa_2O_4$.

Parameter	PCC	ECC	Total value
B_4^0	324	394	718
B_4^3	-9166	-11150	-20316

Table 4. Energy levels of Co^{2+} ion in $ZnGa_2O_4$ ($B=880$ cm^{-1} , $C=3142$ cm^{-1} , $G=4.118$).

Energy levels (Td group notations)	This work	Observed [24]
	Calculated	
4A_2	0	0
4T_2	4104	4103
4T_1	7143	~7800
2E	14758	-
2T_1	15383	-
4T_1	15891	~15527

Table 5. CFP for Co^{2+} in MgF_2 .

Parameter	PCC	ECC	Total value
B_2^0	19	-951	-932
B_2^2	1037	5873	6910
B_4^0	-108	89	-10
B_4^2	-2264	-6757	-9021
B_4^4	1332	6242	7574

 Table 6. Energy levels of Co^{2+} ion in MgF_2 ($B=900\text{ cm}^{-1}$, $C=3685\text{ cm}^{-1}$, $G=7.12$).

Energy levels (Td group notations)	This work	Observed [14]
	Calculated	
4T_1	0	0
4T_2	6296	6297
2E	11056	11798
4A_2	13619	13597
${}^4T_1(P)$	19275	19095

 Table 7. CFP for Cr^{3+} in MgF_2 .

Parameter	PCC	ECC	Total value
B_2^0	21	1476	1497
B_2^2	1189	2085	3274
B_4^0	-126	-505	-631
B_4^2	-2640	-17744	-20384
B_4^4	1554	11925	13479

 Table 8. Energy levels of Cr^{3+} ion in MgF_2 ($B=516\text{ cm}^{-1}$, $C=3797\text{ cm}^{-1}$, $G=3.302$).

Energy levels (Td group notations)	This work	Observed [17]
	Calculated	
${}^4A_{2g}$	0	0
${}^4T_{2g}$	14942	14948
2E_g	15258	15267
${}^2T_{1g}$	15697	-
${}^4T_{1g}(P)$	20394	20284

As can see from the Table 1 and Table 3 the point charge contribution is significant for the first case and for the second one the covalence effects play an essential role.

In Table 5 and Table 7 we present the real crystal field parameters for the MgF_2 doped with Co^{2+} ($3d^7$) and Cr^{3+} ($3d^3$) ions and we can observe that the covalent effect are strong and in Table 6 and Table 8 the energy levels schemes.

Using the SAAS we have obtained values for the energy levels (Table 2, Table 4, Table 6 and Table 8) that were not observed experimentally yet.

4. Conclusions

The crystal field parameters and energy for lowest levels of Co^{2+} doped in MgGa_2O_4 , ZnGa_2O_4 and MgF_2 crystal and Cr^{3+} doped in MgF_2 crystal have been calculated and the obtained results are compared with experimental data. 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 number of the crystal field parameters is less than in case of ECM and the use of SAAS allows to obtain the effects from doped lattice. Using SAAS the standard CFPs, their number are according with the predictions of the group theory and can made comparison of different sets of such parameters. The energy levels do not change using SAAS then in case of ECM because the Hamiltonian is invariant. The obtained results for the energy level schemes are in good agreement with experimental data.

Acknowledgments

The author (R. Nistora) would like to acknowledge the European Social Fund through the Sectoral Operational Program for Human Resources Development 2007-2013 for financial support under the project POSDRU/88/1.5/S/49516 coordinated by West University of Timișoara and also expresses his thanks to Professor N. M. Avram for the constant support and encouragement.

The autor (A. S. Gruia) would like to acknowledge that this work was partially supported by the strategic grant POSDRU/CPP107/DMI1.5/S/78421, Project ID 78421 (2010), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007 – 2013.

References

- [1] C. Rudowicz, J. Qin, J. Lumin., **110**, 39 (2004).
- [2] N. V. Kuleshov, V. P. Mikhailov, V. G. Scherbitsky, P. V. Prokoshin, K. V. Yumashev, J. Lumin. **55**, 265 (1993).
- [3] K. V. Yumashev, Appl. Opt. **38**, 6343 (1999).
- [4] M. B. Camargo, R. D. Stultz, M. Birnbaum, M. Kokta, Opt. Lett. **20**, 339 (1995).
- [5] I. A. Denisov, M. L. Demchuk, N. V. Kuleshov, K. V. Yumashev, Appl. Phys. Lett. **77**, 2455 (2000).
- [6] Hailiang Lü, Jiyong Du, Yi Ma, Wenling Ma, Junqi Liu, Powder Technology **203**, 428 (2010).
- [7] E. J. W. Verwey, E. L. Heilmann, J. Chem. Phys. **15**, 174 (1947).
- [8] E. W. Gorter, Philips Res. **9**, 295 (1954).
- [9] R. J. Hill, J. R. Craig, G. V. Gibbs, Phys. Chem. Miner. **4**, 317 (1979).
- [10] T. Minami, Y. Kuroi, T. Miyata, H. Yamada, S. Takata, J. Lumin. **72**, 997 (1997).
- [11] T. Minami, Y. Kuroi, T. Maeno, T. Miyata, J. Appl.

- Phys. Japan **34**, L684 (1995).
- [12] "International Tables for Crystallography", edited by Theo Hahn, Fifth edition, Vol. **A**, Springer Verlag, Berlin (2006).
- [13] X. L. Duan, D. R. Yuan, L. H. Wang, F. P. Yu, X. F. Cheng, Z. Q. Liu, S. S. Yan, Journal of Crystal Growth **296**, 234 (2006).
- [14] S. Kuck, Appl. Phys. **B 72**, 515 (2001).
- [15] W. H. Baur, A. A. Khan, Acta Crystallogr. **B 27**, 2133 (1971).
- [16] H. Manaa, Y. Guyot, R. Moncorge, Phys. Rev. **B1, 48**, 3633 (1993).
- [17] S. A. Payne, L. L. Chase, W. F. Krupke, J. Chem. Phys., **86**(6), (1987).
- [18] L. Chen, Y. Liu, Z. Lu, et al Materials Chemistry and Physics **97**(2-3), 247 (2006).
- [19] L. P. Sosman, T. Abritta, Solid State Communications **82**(10), 801 (1992).
- [20] T. Suzuki, G. S. Murugan, Y. Ohishi, Journal of Luminescence **113**(3-4), 265 (2005).
- [21] K. Momma, F. Izumi, Journal of Applied Crystallography, **41**(3), 653 (2008).
- [22] Y. Suzuki, W. A. Sibley, O. H. El Bayoumi, T. M. Roberts, B. Bendow, Phys. Rev. **B 35**, 4472 (1987).
- [23] T. Abritta, F. H. Blak, J. Lumin. **48/49**, 558 (1991).
- [24] L. P. Sosman, A. D. Tavares, T. Abritta, J. Phys. D: Appl. Phys. **33**, L19 (2000).
- [25] L. P. Sosman, A. Dias Tavares Jr., R. J. M. Da Fonseca and A. R. R. Papa, J. Opt. A: Pure Appl. Opt. **10**, 104025 (6pp) (2008).
- [26] B. Z. Malkin, Spectroscopy of solids containing rare-earth ions, edited by A. A. Kaplyanskii, B. M. Macfarlane, North Holland, Amsterdam, pp. 33-50 (1987).
- [27] M. G. Brik, N. M. Avram, C. N. Avram, Analele Universitatii de Vest din Timisoara, **51**, 24-27 (2007).
- [28] X. L. Duan, D. R. Yuan, F. P. Yu, L. H. Wang, Appl. Phys. Lett. **89**, 183119 (2006).

*Corresponding author: nistora_ramona@yahoo.com