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Optical properties of rare earth sodium double molybdates $Na_5RE(MoO_4)_4$, RE = Pr, Nd, Eu

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Abstract

Absorption and emission measurements at liquid-helium temperature, liquid-nitrogen temperature and room temperature have been performed on tetragonal scheelite-type rare earth sodium double molybdates $Na_5RE(MoO_4)_4$ and on RE-doped $Na_5Gd(MoO_4)_4$ samples. The rare earth occupies one single crystallographic position with S_4 as point symmetry. The spectra were analysed according to the crystal field theory. From the experimental data, nearly complete energy level schemes of the Pr^{3+} and Nd^{3+}, on the $4f^2$ and $4f^3$ configurations were derived. Very good correlation was obtained between the experimental and simulated energy level schemes, first for the approximated D_{2d} and then for the true S_4 symmetries. The crystal field parameters vary smoothly with the atomic number of the rare earth, when compared with those determined previously for Eu^{3+} in the same matrix.

1. Introduction

The development and successful use of the rare earth compounds as solid-state laser materials and their application in modern technology as luminescence enhancers have renewed interest in rare earth spectroscopy. In particular, the scheelite-type rare earth sodium double molybdates $Na_5RE(MoO_4)_4$ (or tungstates $Na_5RE(WO_4)_4$), are good stoichiometric host luminiscent materials. Optical properties have been extensively studied in recent years [1–4], particularly in the case of pure and doped Eu^{3+} compounds.

The aim of the present work is to continue the previous study on the spectroscopic data [3] and extend the knowledge of the free ion and crystal field effects, obtaining energy level schemes on the most interesting remaining rare earth isotype compounds.

2. Experimental details

2.1. Preparation of samples

Polycrystalline powder samples were prepared by using high purity rare earth oxides RE_2O_3, Na_2CO_3 and MoO_3. The synthesis method consists of a heating the well mixed components at about 800 K for 1 week. All samples, the pure $Na_5RE(MoO_4)_4$ and the 5% RE activated $Na_5Gd(MoO_4)_4$, were tested by X-ray diffraction analysis, and appeared to be free of other phases.

2.2. Optical measurements

The absorption spectra of the pure praseodymium and neodymium compounds were obtained from polycrystalline powders mixed and pelletized with KBr, on a 3.4-m Jarrell-Ash grating spectrograph using photographic detection, and on a CARY 2400 spectrometer. The measurements were carried out at 300, 77 and 9 K. The fluorescence emission of the Pr-doped samples were recorded at 300, 77 and 9 K, under various excitations: the blue lines of a CW argon ion laser and/or a dye laser excitation accorded on selected crystal field levels.

3. Crystallographic background

Double molybdates (and tungstates) of sodium and rare earth $Na_5RE(MoO_4)_4$ are isostructural throughout the whole lanthanide series, including Y [5,6]. They crystallize in the $CaWO_4$ scheelite-type structure, with $Z=4$, and space group $I4_1/a$ (No. 88) [7]. In this structure, the RE atoms are located at the same positions as Ca in the scheelite, and are surrounded by eight O atoms, the arrangement being that of a slightly distorted dodecahedron with point symmetry S_4 (Fig. 1). The deviation of the oxygen atoms from an ideal dodecahedron of symmetry D_{2d} is very small, affording an

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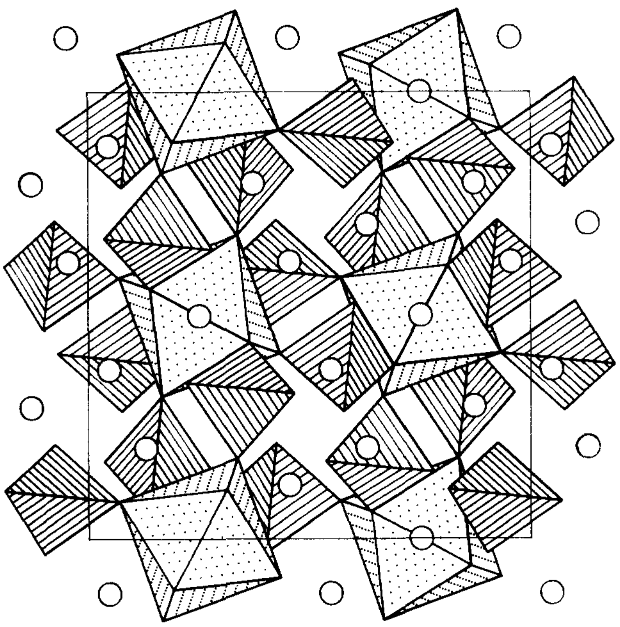

Fig. 1. Coordination polyhedra in the scheelite-type structure of $Na_5RE(MoO_4)_4$; circles represent Na cations.

explanation of the experimental intensity distribution seen in the optical spectra of $Na_5RE(MoO_4)_4$, satisfying to a first approximation the selection rules for the higher symmetry model of REO_8 polyhedra.

The MoO_4 tetrahedra share pairs of vertices with isolated REO_8 dodecahedra, creating a tridimensional framework $\{RE(MoO_4)_4^{5-}\}_{3\infty}$. (Fig. 1), stabilized by Na atoms.

4. Energy level schemes simulation

The rare earth compounds offer an almost unique opportunity to compare the theory of the atomic spectra with high-precision experimental data, even when interactions of secondary importance are taken into account. The central field approximation considers the Hamiltonians corresponding to the free ion and crystal field interactions separately. According to the nomenclature of a recent paper [8], the Hamiltonian used in the present study can be written as

$$H = H_0 - \sum_{k=0}^{k=3} E^k(nf, nf)e_k + \zeta_{4f}A_{so} + \alpha L(L+1)$$

$$+ \beta G(G_2) + \gamma G(R_7) + \sum_{\lambda=2,\ \lambda\neq 5}^{\lambda=8} T^\lambda t_\lambda$$

where E^k and ζ_{4f} are the Racah parameters and the spin-orbit coupling constant, and e_k and A_{so} represent the angular parts of the electrostatic repulsion and spin-orbit coupling, respectively.

In the present case, seven free ion parameters can adequately describe the $4f^2$ configuration of Pr^{3+}. β and γ two-body parameters are fixed to standard values (Table 1). For the $4f^3$ configuration of Nd^{3+}, the T^λ parameters are also introduced. Some of these parameters (T^2 and T^8) are also fixed to values used in earlier studies.

The crystal field calculations are usually carried out within the single-particle crystal field theory [9,10]. Following Wybourne's formalism, the crystal field Hamiltonian is expressed as a sum of products of spherical harmonics and crystal field parameters:

$$H_{cf} = \sum_{k,q}(B_q^k[C_q^k + (-1)^q C_q^k] + iS_q^k[C_q^k - (-1)^q C_{-q}^k])$$

The number of non-zero B_q^k and S_q^k depends on the crystallographic point site symmetry of the lanthanide ion.

For S_4 point symmetry, the crystal field potential involves five real B_q^k and two imaginary S_q^k crystal field parameters, immediately reduced to six parameters by an appropriate choice of the reference axis system, which cancels S_4^4. For D_{2d} symmetry, the Hamiltonian is the same except that the imaginary crystal field parameters are zero. Then, in order to make the process accurate, the first calculation is performed for the approximate D_{2d} symmetry, and the crystal field parameters obtained are considered as starting parameters for the simulation of the S_4 symmetry.

TABLE 1. Phenomenological spectroscopic parameters of rare earth double molybdates $Na_5RE(MoO_4)_4$[a]

	Pr	Nd	Eu
E_0	9500(2)	23558(1)	
E_1	4484(2)	4937(1)	
E_2	21.84(2)	23.31(2)	
E_3	460.2(1)	480.97(4)	
α	22.99(7)	19.79(4)	
β	[−673]	[−621.5]	
γ	[1520]	[750]	
ζ	737.6(9)	872.5(7)	
T^2		[274]	
T^3		38(2)	
T^4		95(3)	
T^6		−231(5)	
T^7		248(6)	
T^8		[22]	
B_0^2	179(12)	193(16)	217(15)
B_0^4	−96(29)	−91(47)	−302(27)
B_4^4	−1351(14)	−1104(17)	−871(15)
B_0^6	−693(45)	−529(33)	−422(32)
B_4^6	−423(40)	−301(26)	−386(29)
S_4^6	−52(165)	−137(93)	−113(179)
No levels	35	76	21[b]
Residue	3547	15203	195
rms	12.4	15.9	3.6

[a] Values in brackets are fixed for the simulation.
[b] Simulation performed only on a part of the ^7F_J multiplet.

The phenomenological crystal field parameters of the Eu^{3+} are a convenient set of starting values for crystal field calculations. Since the ground ^7F_J septet of the $4f^6$ configuration is well isolated from the rest of the configuration and is the only one of that multiplicity, an accurate simulation of the crystal field effect is allowed by considering only the strongly reduced $^7F_{JM}$ basis. In addition, crystal field parameters should vary smoothly in an isostructural series. All simulations are performed by the FORTRAN computer programs REEL and IMAGE [11].

5. Analysis of the spectra

Pure and activated Pr and Nd sodium double molybdates samples give absorption and fluorescence spectra with sharp and well resolved transitions. As an example, Fig. 2 shows some well characterized zones in the absorption spectra at 9 K for the Pr and Nd compounds. Some unexpected lines in the Nd spectrum are also detected in the hypersensitive transition region; they correspond to $NaNd(MoO_4)_2$.

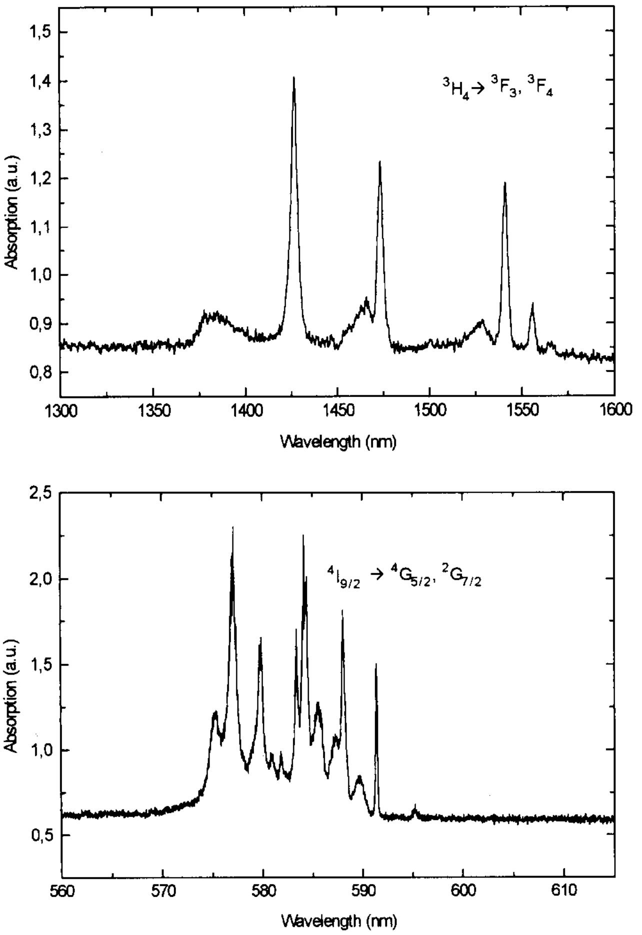

Fig. 2. Part of the absorption spectra at 9 K for $Na_5RE(MoO_4)_4$, RE = Pr (top) and Nd (bottom).

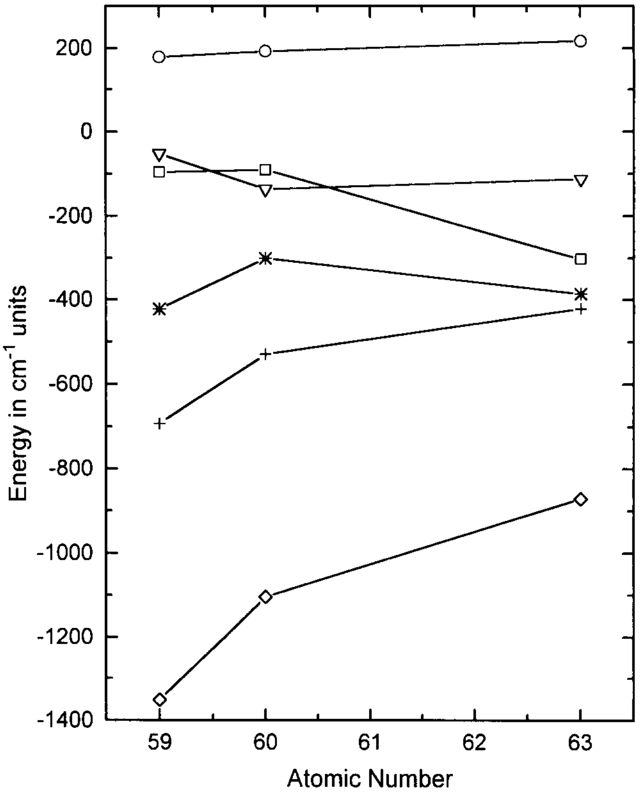

Fig. 3. Evolution of the B^k_q and S^k_q crystal field parameters throughout the $Na_5RE(MoO_4)_4$ series for RE = Pr, Nd and Eu. ○, B^2_0; □, B^4_0; ◆, B^4_4; +, B^6_0; ★, B^6_4; ▽, S^6_4.

All measurements were performed on powders. Attributing irreducible representations to their associated Stark levels is then difficult. However, the comparison of some transitions with different emitting levels (and different irreducible representations) towards the same final level gives more precision, due to different selection rules. Although the selection rules spectra is compatible with a S_4 point symmetry, the relative weakness of certain lines suggests that the point symmetry is not far from D_{2d}. This remark is of interest for the simulation of the energy level positions because some irreducible representations differ for the two groups, as well as electronic transition selection rules. For example, the B(A) one-dimensional irreducible representation is undifferentiated in S_4 but is split into $B_1(A_1)$ and $B_2(A_2)$ in D_{2d}. Transitions like $A_1 \rightarrow B_2$ are allowed as electric dipole for D_{2d}, but not $A_1 \rightarrow B_1$. These features, associated with the relative weakness of certain transitions, help to attribute irreducible representations and fix the relative signs of B^4_4 and B^6_4.

Schemes of 35, 76 and 21 energy levels were considered in simulations for Pr, Nd and Eu materials, respectively. These calculations yielded simulated energy level schemes in very good agreement with the experimental data. The simulations were undoubtedly improved when the S_4^6-parameter was introduced since the rms standard deviations as well the residues decreased significantly. Table 1 gives the phenomenological spectroscopic parameters obtained for S_4 rare earth point symmetry, and Fig. 3 shows the evolution of the crystal field parameters for Pr, Nd and Eu compounds.

References

1 G. Changxin, L. Bilin, H. Yuefen and C. Hongbin, *J. Lumin., 48&49* (1991) 489.

2 G. Changxin and L. Bilin, *Proc. Int. Conf. on Luminescence*, Beijing, China, 1991, p. 177.

3 J. Huang, J. Loriers, P. Porcher, G. Teste de Sagey, P. Caro and C. Levy Clement, *J. Chem. Phys., 80* (1984) 6204.

4 E.J. Baran, M.B. Vasallo, C. Cascales and P. Porcher, *J. Phys. Chem. Solids, 54* (1993) 1471.

5 M.V. Mokhosoev, F.P. Alekseev and E.I. Get'man, *Zh. Neorg. Khim., 14* (1969) 596.

6 V.K. Trunov, T.A. Berezina, A.A. Evdokimov, V.K. Ishunin and V. Krongauz, *Zh. Neorg. Khim., 23* (1978) 2645.

7 V.A. Efremov, T.A. Berezina, I.M. Averina and V.K. Trunov, *Kristallografiya, 25* (1980) 254 [*Sov. Phys. Crystallogr., 25* (1980) 146].

8 W.T. Carnall, G.L. Goodman, K. Rajnak and R.S. Rana, *J. Chem. Phys., 90* (1989) 3443.

9 B.G. Wybourne, *Spectroscopic Properties of Rare Earths*, Wiley, New York, 1965.

10 S. Hüfner, *Optical Spectra of Transparent Rare Earth Compounds*, Academic Press, New York, 1978.

11 P. Porcher, Computer programs REEL and IMAGE for simulation of d^n and f^n configurations involving real and complex crystal field parameters, 1989, unpublished.