Physica B 406 (2011) 315–318

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Theoretical and comparative investigations of Yb^{3+} ion in MWO_4 and $M'MoO_4$ scheelites crystals (M=Sr, Pb, Ca, Ba) and (M′=Sr, Pb, Ca, Cd)

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ARTICLE INFO

Article history:
Received 21 September 2010
Received in revised form
5 October 2010
Accepted 6 October 2010

Keywords:
Crystal-field
Scheelites
Ytterbium

ABSTRACT

The crystal-field model is applied to a series of scheelites crystals ($CaWO_4$, $SrWO_4$, $PbWO_4$, $BaWO_4$, $CdMoO_4$, $CaMoO_4$, $SrMoO_4$ and $PbMoO_4$) doped with the Yb^{3+} ion. The calculated crystal-field parameters present a general trend of variation with M^{2+} ionic radius of the host cation. The maximum splitting ΔE of the $^2F_{7/2}$ manifold of the Yb^{3+} ion is then obtained as a function of N_V crystal-field strength parameters. The agreement between experimental results and theoretical predictions for all investigated systems is very satisfactory. The crystal-field effects are very important for the prediction of emission energies of the Yb^{3+} ion in different scheelites.

1. Introduction

Over the last decade there has been increasing interest in the research of Yb^{3+} activated laser crystals [1]. The Yb^{3+} ion in a laser host crystal is the simplest example of electronic levels in an impurity-doped solid, since the Yb^{3+} ion possesses only two electronic states: the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state. The two energy levels are split under the crystal-field, which means that all Yb lasers are quasi-three-level systems. The Yb-doped crystals display some advantages over Nd-doped crystals: the Yb^{3+} doped media generally have longer radiative lifetimes and higher quantum efficiency; the Yb^{3+} ions in the host materials possess no up-conversion effect or excited state absorption in principle, which will greatly reduce thermal effects in the laser crystal; the absorption spectrum shows prominent bands in the range 900–980 nm; the emission spectra of Yb doping materials are broader than those of Nd doping materials, so Yb doping materials may be used to produce pulsed laser or mode-lock lasers. Many kinds of Yb-doped crystals have been reported for efficient Yb laser outputs [2–13]. Scheelites doped with the ytterbium ion have been investigated extensively through paramagnetic resonance, spectroscopy and other techniques, resulting in a large body of data on these systems.

Until now, the most attention has been paid to the scintillation properties of molybdates with a scheelite-type structure: $M'MoO_4$ (M′=Ca, Cd, Sr, Pb); however, all of the crystals studied have a number of drawbacks, i.e., low luminescence intensity, even at low temperatures ($BaMoO_4$); large Z ($PbMoO_4$); or the presence of radioactive cation isotopes ($CdMoO_4$, $PbMoO_4$). Currently, $CaMoO_4$ crystals are considered as the most appropriate. MWO_4 (M=Sr, Pb, Ba and Ca) with scheelite structure has attracted great interest due to its useful properties, such as electro-optics [14,15], high-pressure phase transformation [16,17] and unique spontaneous Raman behaviors [18–20], which are proven to be important for the stimulated Raman scattering (SRS) technique in Raman laser development [21].

In this work, we are interested in ytterbium doped $CaWO_4$, $PbWO_4$, $SrWO_4$, $BaWO_4$, $CaMoO_4$, $PbMoO_4$, $SrMoO_4$ and $CdMoO_4$ and we estimate a general trend for ytterbium ions in MWO_4 and $M'MoO_4$ scheelites.

2. Calculation

Scheelite-type MWO_4 (or $M'MoO_4$) has a tetragonal crystal structure of space group $I4_1/a$ (C_{4h}^6). The M^{2+} (or M'^{2+}) site has eight nearest-neighbor oxygen ions, which can be grouped into two sets of distorted interpenetrating tetrahedra [18,22–24].

The Yb^{3+} ion in MWO_4 or $M'MoO_4$ crystal occupies the M^{2+} site. Strictly speaking, the M^{2+} site has S_4 point symmetry. Since this point symmetry is very nearly D_{2d}, some authors [25,26] applied D_{2d} symmetry as a good and realistic approximation to study the optical spectra for rare-earth ions in MWO_4 or $M'MoO_4$ crystals. For simplicity, we apply D_{2d} symmetry here. In MWO_4:Yb^{3+} or $M'MoO_4$:Yb^{3+}, the energy levels and wave functions of the above-mentioned Kramer's doublets can be calculated by diagonalizing a 14×14 energy matrix of the $4f^{13}$ ion in tetragonal (D_{2d}) symmetry related to the Hamiltonian

$$H = H_{CF}(D_{2d}) + H_{SO} \tag{1}$$

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doi:10.1016/j.physb.2010.10.012

where H_{SO} is the spin–orbit coupling term and the crystal-field term is

$$\hat{H}_{CF}(D_{2d}) = B_0^2\hat{C}_0^2 + B_0^4\hat{C}_0^4 + B_4^4(\hat{C}_{-4}^4+\hat{C}_4^4) + B_0^6\hat{C}_0^6 + B_4^6(\hat{C}_{-4}^6+\hat{C}_4^6) \quad (2)$$

The empirical crystal-field parameters (CFPs) are obtained by a least-square fitting program that minimizes the root mean square (rms) deviation between calculated and experimental energy levels derived from optical spectra. This rms is given by [27]

$$\sigma = \sqrt{\sum_i \frac{(E_i^{cal} - E_i^{\exp})^2}{N-P}} \quad (3)$$

where N denotes the number of levels and P is the number of independent free-parameters.

As useful tools to measure the CF interaction strength, mainly in order to establish quantitative comparisons between CaWO$_4$, PbWO$_4$, SrWO$_4$, BaWO$_4$, CaMoO$_4$, PbMoO$_4$, SrMoO$_4$ and CdMoO$_4$, the crystal-field strength parameters have also been calculated with the formalism defined by Ref. [28]

$$N_V = \left[\sum_{k,q} \frac{4\pi}{2k+1}\left(B_q^k\right)^2\right]^{1/2} \quad (4)$$

3. Results and discussion

3.1. Yb^{3+} doped in MWO$_4$ and M′MoO$_4$ crystals

Trivalent ytterbium has the simplest energy level structure with only two manifolds, the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, which are separated by approximately 10,000 cm^{-1}.

The starting sets of CFPs were taken from Ref. [29] corresponding to the Yb^{3+} ion in MWO$_4$ (M=Sr, Pb, Ba and Ca) and M′MoO$_4$ (M′=Sr, Pb, Cd and Ca) crystals. The fitting procedure was described in our previous work (Yb^{3+} doped YAB) [30]. In this case, the number of energy levels for Yb^{3+} in different scheelites included in the fits was 7. Table 1 shows the final set of CFPs of ytterbium in CaWO$_4$, PbWO$_4$, SrWO$_4$ and BaWO$_4$ obtained for the best fit, which was (with quite good rms) about 3.5, 7.9, 9.5 and 17 cm^{-1}, respectively. All obtained parameters are meaningful then compared to the CFPs of Yb^{3+} in CaWO$_4$ occupying the D$_{2d}$ symmetry site [31]. Table 2 shows the final set of CFPs of ytterbium in CaMoO$_4$, PbMoO$_4$, SrMoO$_4$ and CdMoO$_4$ obtained for the best fit, which was (with quite good rms) about 7.5, 10.8, 7.3 and 3.7 cm^{-1}, respectively. This resulting root square deviation confirms the consistency of the fit. A good agreement is obtained between experimental and calculated energy levels. Table 3 presents a comparison of experimental and calculated $^2F_{7/2}$ and $^2F_{5/2}$ Stark energy levels of the Yb^{3+} ion occupying a D$_{2d}$ symmetry site inside MWO$_4$ (M=Sr, Pb, Ba and Ca) and M′MoO$_4$ (M′=Sr, Pb, Cd and Ca) crystals.

Table 1
Fitted crystal-field parameters values (cm^{-1}) for Yb^{3+} doped CaWO4, PbWO$_4$, SrWO$_4$ and BaWO$_4$ crystals.

Crystal	B_{20}	B_{40}	B_{60}	B_{44}	B_{64}	ζ	σ
CaWO$_4$: Yb^{3+} (this work)	500.7	−483.8	−386	802	366	2904	3.5
PbWO$_4$: Yb^{3+} (this work)	468.8	−327.9	−364.6	718.4	259.6	2903.4	7.9
SrWO$_4$: Yb^{3+} (this work)	487.3	−328.8	−339.5	759.3	202.9	2903.2	9.5
BaWO$_4$: Yb^{3+} (this work)	463.4	−283	−379	653	145	2902.2	17
CaWO$_4$: Yb^{3+} [31]	484	−614	−16	739	509	2906	15.2

Table 2
Fitted crystal-field parameters values (cm^{-1}) for Yb^{3+} doped CaMoO$_4$, PbMoO$_4$, SrMoO$_4$ and CdMoO$_4$ crystals.

Crystal (this work)	B_{20}	B_{40}	B_{60}	B_{44}	B_{64}	ζ	σ
CdMoO$_4$: Yb^{3+}	436.3	−495	−388	876	324.6	2901.3	3.7
CaMoO$_4$: Yb^{3+}	470	−435.7	−358	809	284	2901.3	7.5
PbMoO$_4$: Yb^{3+}	427	−313	−334	731.5	281	2900.3	10.8
SrMoO$_4$: Yb^{3+}	444	−297.4	−336	773	203	2902.2	7.3

Table 3
Observed and calculated energy levels (cm^{-1}) of Yb^{3+} in CaWO$_4$, PbWO$_4$, SrWO$_4$, BaWO$_4$, CaMoO$_4$, PbMoO$_4$, SrMoO$_4$ and CdMoO$_4$ crystals.

M label[a]	**CaWO$_4$: Yb^{3+}**			**PbWO$_4$: Yb^{3+}**		
	Cal. val.[b]	Exp. val.[d]	Δ	Cal. val.[b]	Exp. val.[d]	Δ
$^2F_{5/2}$	10663	10665	−2	10599	10604	−5
	10367	10366	1	10316	10314	2
	10279	10278	1	10263	10260	3
$^2F_{7/2}$	490	489	1	427	423	4
	367	366	1	324	323	1
	213	214	−1	160	162	−2
	0	0	0	0	0	0
M label[a]	**SrWO$_4$: Yb^{3+}**			**BaWO$_4$: Yb^{3+}**		
	Cal. val.[b]	Exp. val.[d]	Δ	Cal. val.[b]	Exp. val.[d]	Δ
$^2F_{5/2}$	10612	10605	7	10560	10549	11
	10315	10318	−3	10286	10291	−5
	10260	10264	−4	10248	10254	−6
$^2F_{7/2}$	442	446	−4	400	408	−8
	331	332	−1	282	291	−3
	152	150	2	131	127	4
	0	0	0	0	0	0
M label[a]	**CaMoO$_4$: Yb^{3+}**			**PbMoO$_4$: Yb^{3+}**		
	Cal. val.[c]	Exp. val.[d]	Δ	Cal. val.[c]	Exp. val.[d]	Δ
$^2F_{5/2}$	10633	10628	5	10579	10586	−7
	10347	10349	−2	10312	10309	3
	10260	10263	−3	10250	10246	4
$^2F_{7/2}$	469	473	−4	411	406	5
	356	357	−1	329	327	2
	194	193	−1	163	166	−3
	0	0	0	0	0	0
M label[a]	**SrMoO$_4$: Yb^{3+}**			**CdMoO$_4$: Yb^{3+}**		
	Cal. val.[c]	Exp. val.[d]	Δ	Cal. val.[b]	Exp. val.[d]	Δ
$^2F_{5/2}$	10596	10601	5	10655	10653	2
	10315	10313	2	10380	10381	−1
	10254	10251	3	10265	10267	−2
$^2F_{7/2}$	424	420	4	487	489	−2
	334	333	1	385	385	0
	152	154	−2	226	226	0
	0	0	0	0	0	0

[a] Multiplet label reflects principal SLJ parentage of the calculated energy level.

[b] Calculated levels based on the Hamiltonian parameters listed in Table 1.

[c] Calculated levels based on the Hamiltonian parameters listed in Table 2.

[d] Experimental energy levels taken directly from Ref. [29].

The confidence in these phenomenological parameters and the physical meaning of the fits are supported not only by the low σ values obtained, but also by their smooth variation with ionic radius of the host cation. Figs. 1 and 2 show the evolution of calculated CFPs with ionic radius of substitutional ions M^{2+} in MWO$_4$ and M′$^{2+}$ in M′MoO$_4$, respectively. We noted a smooth