



Spectral characterization and energy levels of Cr³⁺:Sc₂(MoO₄)₃ crystal

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ABSTRACT

This paper reports the spectral properties and energy levels of Cr³⁺:Sc₂(MoO₄)₃ crystal. The crystal field strength Dq , Racah parameter B and C were calculated to be 1408 cm⁻¹, 608 cm⁻¹ and 3054 cm⁻¹, respectively. The absorption cross sections σ_{α} of ⁴A₂→⁴T₁ and ⁴A₂→⁴T₂ transitions were 3.74 × 10⁻¹⁹ cm² at 499 nm and 3.21 × 10⁻¹⁹ cm² at 710 nm, respectively. The emission cross section σ_e was 375 × 10⁻²⁰ cm² at 880 nm. Cr³⁺:Sc₂(MoO₄)₃ crystal has a broad emission band with a broad FWHM of 176 nm (2179 cm⁻¹). Therefore, Cr³⁺:Sc₂(MoO₄)₃ crystal may be regarded as a potential tunable laser gain medium.

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1. Introduction

Since tunable solid-state lasers have a wide field application in medicine, ultra short pulse generation, environment and communication [1,2], research on Cr³⁺-doped tunable solid-state laser in the visible and near infrared spectrum has generated strong interest. The Cr³⁺ as a active ion tends to be incorporated into environments which are octahedrally coordinated by ligands. Since in an oxide compound with general formula A₂(BO₄)₃ (A = Al, Sc; B = W, Mo) there are AlO₆ and ScO₆ octahedron, A₂(BO₄)₃ (A = Al, Sc; B = W, Mo) compounds can be considered as the Cr³⁺-doped host materials. The spectroscopic properties of Cr³⁺:Al₂(WO₄)₃ and Cr³⁺:Sc₂(WO₄)₃ crystals were investigated as a tunable solid-state laser material [3,4]. Sc₂(MoO₄)₃ crystal belongs to the orthorhombic symmetry with space group Pnca [5–7]. This paper reports the optical properties of Cr³⁺:Sc₂(MoO₄)₃ crystals.

2. Experimental procedure

Cr³⁺:Sc₂(MoO₄)₃ crystals were grown from a flux of Li₂Mo₂O₇ by the top seeded solution growth (TSSG) method at a cooling rate 1–2 K/d and a rotating rate of 4.5 rpm. The Cr³⁺ ions concentration in Cr³⁺:Sc₂(MoO₄)₃ crystal was determined to be 0.61 at% by ionic coupled plasma (ICP) spectrometry. A sample with dimension of 5 × 4 × 2 mm³ was cut from as-grown crystal for spectral

measurement. The absorption spectrum was recorded using a Perkin-Elmer UV–vis–NIR Spectrometer (Lambda-900) at room temperature. The fluorescence spectrum and fluorescence lifetime were measured using an Edinburgh Instruments FLS920 spectrophotometer with a continuous Xe-flash lamp and R928-P detector at 300 and 10 K.

3. Experimental results and discussion

Fig. 1 shows the absorption spectrum of Cr³⁺:Sc₂(MoO₄)₃ crystals. Two broad absorptions with peak at $\lambda = 499$ and 710 nm are due to the ⁴A₂→⁴T₁ and ⁴A₂→⁴T₂ transitions of Cr³⁺ ions, respectively. The two structures on either side of the ⁴T₂ absorption peak are due to absorption into the ²T₁ and ²E states, which show up as Fano antiresonance structures [8,9]. We take the dips in the absorptions as approximate values of the positions of the ⁴A₂→²T₁, ²E transitions. The absorption cross sections σ_{α} of ⁴A₂→⁴T₁ and ⁴A₂→⁴T₂ transitions were estimated to be 3.74 × 10⁻¹⁹ cm² at 499 nm and 3.21 × 10⁻¹⁹ cm² at 710 nm, respectively.

The Cr³⁺ ions substitute at Sc³⁺ site in Sc₂(MoO₄)₃, where the symmetry is approximately octahedral. The peak energy of the ⁴A₂→⁴T₂ band measures 10Dq [10], thus the Dq was measured to be 1408 cm⁻¹ from the spectrum of Fig. 1. The energy at the peak of the ⁴A₂→⁴T₁ band depends on both Dq and B [11]. The B can be calculated by the following equation [10]:

$$\frac{B}{Dq} = \frac{(\Delta/Dq)^2 - 10(\Delta/Dq)}{15(\Delta/Dq - 8)} \quad (1)$$

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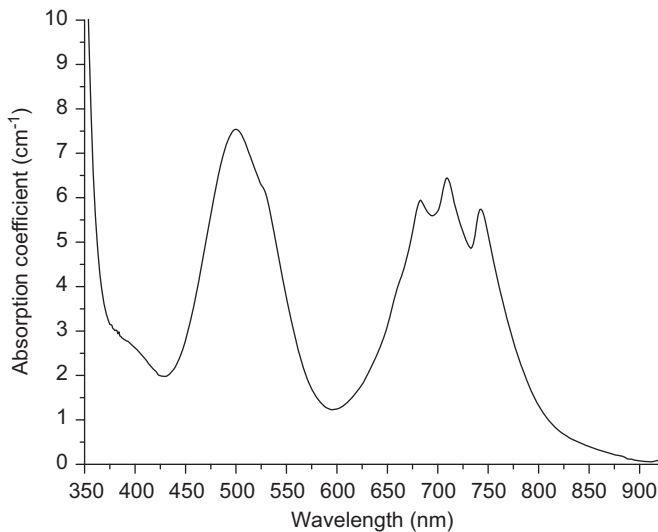


Fig. 1. Absorption spectrum of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal at 300 K.

Table 1

Comparison of crystal field parameters for $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ with other Cr^{3+} -doped crystals.

Material	Dq (cm^{-1})	B (cm^{-1})	Dq/B	C (cm^{-1})	C/B
Al_2O_3 [13]	1664	640	2.6	3300	5.2
YAB [14]	1680	672	2.5	3218	4.8
GAB [15]	1695	673	2.52	3380	5.0
YSB [15]	1539	644	2.39	–	–
GSB [15]	1563	638	2.45	–	–
LSB [16]	1529	675	2.27	3448	5.1
GSGG [17]	1563	638	2.45	–	–
$\text{Sc}_2(\text{WO}_4)_3$ [4]	1449	630	2.3	–	–
$\text{Al}_2(\text{WO}_4)_3$ [4]	1495	650	2.3	–	–
$\text{Sc}_2(\text{MoO}_4)_3$	1408	608	2.32	3054	5.0

where Δ is the difference in energy at the peaks of the two ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ bands, which is 5955 cm^{-1} . Substituting the measured values of Dq and Δ into Eq. (1), the value of B was calculated to be 608 cm^{-1} , from which the value of Dq/B was calculated to be 2.32. To calculate C requires a knowledge of the energy of the ${}^2\text{E}$ level, $E({}^2\text{E})$. C is obtained from the formula [10]:

$$E({}^2\text{E}) \cong 3.05C + 7.90B - 1.80B^2/Dq \quad (2)$$

for the range of values $1.5 < Dq/B < 3.5$ and $3 < C/B < 5$, where $E({}^2\text{E})$ is the dip energy 13643 cm^{-1} (733 nm) of broad band ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Cr^{3+} ions in $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal [12]. Using obtained values of B and Dq , the C was calculated to be 3054 cm^{-1} . The values of Dq , B and C for $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal are compared with other laser gain media in Table 1.

Fig. 2 shows the fluorescence spectrum of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystals at 300 and 10 K. The dominant feature of fluorescence spectrum of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal is a broad band with a peak at 880 nm and a full width at half maximum (FWHM) of 176 nm (2179 cm^{-1}) corresponding to ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition at 300 K. On cooling to 10 K, the fluorescence spectrum is still broad emission, showing that the ${}^4\text{T}_2$ zero-vibrational level is below the ${}^2\text{E}$ level. The weak field site in $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal gives rise the Cr^{3+} fluorescence in the ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition.

As well known, in the Cr^{3+} -doped tunable laser crystals the fluorescence line shape as a function of temperature is determined by the energy splitting $\Delta E = E({}^4\text{T}_2) - E({}^2\text{E})$, where $E({}^4\text{T}_2)$ is the energy of the zero-vibrational ${}^4\text{T}_2$ state [17]. When the value of ΔE is large positive, the ${}^4\text{T}_2$ level is above ${}^2\text{E}$ level, the R-line and

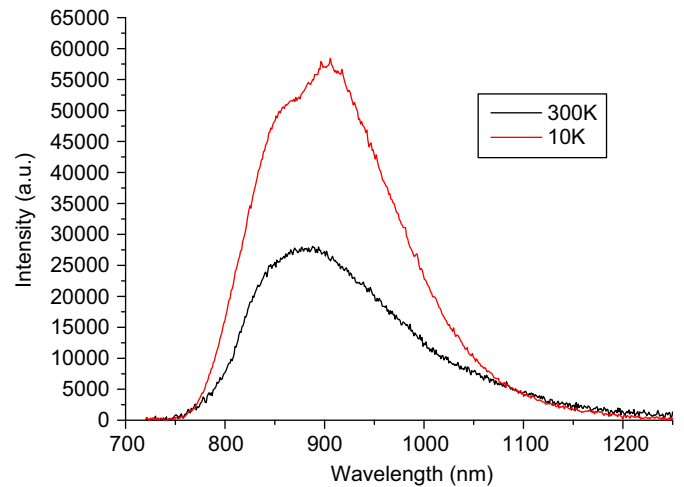


Fig. 2. Photoluminescence spectrum of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ measured excitation with 710 nm radiation at 300 and 10 K.

its vibronic sideband is only observed. For example, the laser action of ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) is driven by the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ R-line emission; for large negative value of ΔE the ${}^4\text{T}_2$ level is below ${}^2\text{E}$ level, the broad emission band of ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition is only observed as observed for $\text{Cr}:\text{LiCAF}$ and $\text{Cr}:\text{LiSAF}$ crystals; when the value of ΔE is close to $\Delta E \approx 0$, the observed emission band shape is an intimate mélange of R-line and the broadband process. For $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal, the peak of the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ absorption corresponds to a transition into a higher vibrational level ${}^4\text{T}_2$ state, and does not give the zero-phonon-transition level. Very approximately, one can predict that the position of the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ zero-phonon transition is midway between the absorption and emission peaks, approximately 12724 cm^{-1} above the ${}^4\text{A}_2$ level. Then, $\Delta E = -918 \text{ cm}^{-1}$. Therefore, the ${}^4\text{T}_2$ level is below the ${}^2\text{E}$ level, and a broad emission should be observed at all temperatures.

The emission cross section σ_e was calculated using the formula [11]

$$\sigma_e = \frac{\lambda^2}{4\pi^2 \tau_f n^2 \Delta\nu} \quad (3)$$

where λ is the wavelength of emission peak, n the refractive index which was estimated to be 2.0 by Abbe retractometer at 589 nm wavelength, $\Delta\nu$ the frequency at FWHM ($\Delta\nu = 6.54 \times 10^{13} \text{ s}^{-1}$) and τ_f the fluorescence lifetime. The fluorescence lifetime was measured to be $0.2 \mu\text{s}$ at 300 K. Thus, the emission cross section σ_e was calculated to be $375 \times 10^{-20} \text{ cm}^2$ at 880 nm at 300 K.

4. Conclusion

The spectral characterization of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal was investigated. $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal exhibits a broad emission band. The emission band is extended from 750 to 1200 nm with a peak at 880 nm and an FWHM of 176 nm at 300 K. Of course, another major interest is the broad absorption bands of $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal, one of which is near $\lambda = 710 \text{ nm}$ due to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition, which has the potential for efficient pumping using visible-range diode laser. In comparison with the other Cr^{3+} -doped materials (see Table 2), $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal has a broad emission band, larger absorption and emission cross sections. $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal has a very short fluorescence lifetime, however, it can be used as a short pulse tunable laser gain medium. Therefore, $\text{Cr}^{3+}:\text{Sc}_2(\text{MoO}_4)_3$ crystal may be regarded as a potential tunable laser gain medium.

Table 2
Spectral parameters of Cr³⁺:Sc₂(MoO₄)₃ crystal and other Cr³⁺-doped materials.

Material	⁴ A ₂ → ⁴ T ₁		⁴ A ₂ → ⁴ T ₂		⁴ T ₂ → ⁴ A ₂				Ref.
	λ (nm)	σ _z (10 ⁻²⁰ cm ²)	λ (nm)	σ _z (10 ⁻²⁰ cm ²)	λ (nm)	FWHM	σ _e (10 ⁻²⁰ cm ²)	τ _f (μs)	
BeAl ₂ O ₄	420	10.0	600	20.0	750	–	0.5	260	[12]
K ₂ NaScF ₆	430	1.4	630	0.7	760	–	1.3	285	[12]
GSGG	488	5.1	647.1	3.3	777	–	0.75	114	[18]
LiCaAlF ₆	425.5	–	625	–	780	2000 cm ⁻¹	1.23	175	[19]
LaSc ₃ (BO ₃) ₄								17	[11]
El x	457	1.18	654	1.68	948	200 nm	6.13		
El y	456	1.72	655	1.01	948	210 nm	5.83		
El z	458	1.32	655	0.81	948	280 nm	4.33		
KAl(MoO ₄) ₂								33	[20]
σ-Polarization	480	8.44	669	3.72	823	146 nm	2.74		
π-Polarization	481	5.03	668	2.25	823	135 nm	2.93		
Cr ³⁺ :Sc ₂ (MoO ₄) ₃	499	37.4	710	32.1	880	176 nm (2179 cm ⁻¹)	375	0.2	This work

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