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The effect of pressure on luminescence properties of Cr^{3+} ions in $LiSc(WO_4)_2$ crystals—Part I: Pressure dependent emission lineshape

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Abstract

We report the results of high-pressure studies of spectral properties in Cr^{3+}-doped $LiSc(WO_4)_2$ crystals between ambient pressure and 260 kbar. The effect of pressure on the present system has led to a structural transformation for pressure 60–88 kbar and a low-field → high-field spectral transformation of the Cr^{3+} emission for pressure 117–227 kbar. The pressure-induced spectral transformation provided the opportunity to distinguish two distinct Cr^{3+} sites in the host lattice. We have attributed them to the Cr^{3+} ions that occupy the Li^{+} and Sc^{3+} sites. For both sites we observed that energy of the ^2E excited state of Cr^{3+} was lower than 14,000 cm^{-1} and exhibited pressure-induced red shift of about $-2.5\,cm^{-1}$/kbar. We have also observed the large inhomogeneous broadening of the $^4T_2 \rightarrow {}^4A_2$ and $^2E \rightarrow {}^4A_2$ emissions. We have completed a quantitative analysis of the relative emission intensities of the $^2E \rightarrow {}^4A_2$ and $^4T_2 \rightarrow {}^4A_2$ transitions as a function of pressure and temperature to study the distribution of the crystal field and electron–phonon coupling of the Cr^{3+} in the host lattice. As the result we have recovered a functions that describe the distribution of the energy of $^4T_2$ state and electron–lattice coupling $(S-\frac{1}{2})\hbar\omega$ in considered material.

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1. Introduction

Since trivalent titanium doped sapphire (Ti^{3+}:Al_2O_3) was developed as commercial tunable solid state laser in the red and extended red range (about 700–950 nm), the intensive search for new tunable solid state laser materials capable of operating over extended wavelength ranges in the near-infrared, visible, and ultraviolet portions of the spectrum has been ongoing [1,2]. Tetravalent chromium (Cr^{4+}) ions in several host lattices have been discovered as the most promising near-infrared lasing centers ranging over about 1100–1500 nm [1]. Efficient tunable laser materials in the tuning range between 950 and 1100 nm have not yet been found to date. Trivalent chromium (Cr^{3+})-doped materials are promising candidates for designing new efficient laser materials over this tuning range principally because low field Cr^{3+} systems have an efficient spin-allowed, vibronic $^4T_2 \rightarrow {}^4A_2$ emission whose energy is proportional to crystal field strength (Dq) and varies widely over host lattices [2]. A family of double tungstates and molybdates [$M^IM^{III}(M^{VI}O_4)_2$, where M^I = alkali earth metals; M^{III} = transition metals or rare earths and M^{VI} = Mo or W] are found to exist in polymorphic forms [3–7] and to have promising optical, antiferroelectric and ferroelastic properties [8–16]. They have been already shown to be excellent host materials for optical activators like transition metal and rare earth ions [8–14]. Trivalent chromium (Cr^{3+}) ions in some compounds within this family are observed to have either a narrow structured, high-field $^2E \rightarrow {}^4A_2$ emission or a broadband, low-field $^4T_2 \rightarrow {}^4A_2$ emission between 700–1100 nm [8–10]. This fact indicates that the Cr^{3+} luminescence varies very strongly with the M^I and M^{III} cations and the lattice structure of $M^IM^{III}(M^{VI}O_4)_2$ and therefore can be manipulated chemically. Detailed luminescence studies of Cr^{3+}-doped $M^IM^{III}(M^{VI}O_4)_2$ materials have not been reported to date and are needed to establish a systematic property-structure relation.

Previous high-pressure tuning spectroscopy studies on Cr^{3+}-activated materials have clearly demonstrated that pressure is an irreplaceable and powerful tool for quantifying the extent of electronic mixing between the ^2E and $^4T_2$ states of the Cr^{3+} ion [17–19], for identifying the irresolvable multi-site behavior of broadly emitting Cr^{3+} systems [20,21], and for characterizing the inhomogeneous distribution of Cr^{3+} ions in a disordered crystal or a glass host [22]. Since pressure induces the $^4T_2$–^2E level crossing (at high pressure the broad emission band related to the $^4T_2 \rightarrow {}^4A_2$ transition is replaced by the sharp lines related to the $^2E \rightarrow {}^4A_2$ transition) many of the important characteristics of the Cr^{3+} emission may be resolved and systematically investigated through high-pressure experimentation.

The objective of this paper is to apply high pressure to a Cr^{3+}-doped $LiSc(WO_4)_2$, to study the effect of pressure on luminescence properties of Cr^{3+} in a representative tungstate host lattice and to initiate development of a structure-property relation for the general Cr^{3+}-activated $M^IM^{III}(M^{VI}O_4)_2$ system. Ambient condition luminescence experiments on three Cr^{3+}-doped tungstates, $LiSc(WO_4)_2$, $LiIn(WO_4)_2$, and $NaIn(WO_4)_2$ indicate that Cr^{3+}:$LiSc(WO_4)_2$ exhibits the low field, broadband $^4T_2 \rightarrow {}^4A_2$ emission over 900–1100 nm and is therefore good candidate for tunable laser operation. The effect of pressure on the emission properties of Cr^{3+}:$LiSc(WO_4)_2$ has been investigated briefly in our previous paper [23], where a pressure induced low- to high-field transformation of the Cr^{3+} ions has been demonstrated. In this paper we focus on the analysis of inhomogenity of the Cr^{3+} system, specifically considering the distribution of the energy of the $^4T_2$ state and electron–lattice coupling strength.

2. Sample and experiment

2.1. Crystal growth and structure

Cr^{3+}-doped $LiSc(WO_4)_2$ single crystal doped with 0.5 wt% of Cr^{3+} were grown by a melting method developed by Klevtsov et al. [4]. The details were described in our previous paper [23]. $LiSc(WO_4)_2$ crystallizes in a monoclinic structure ($C2/c = C_{2h}^6 z = 4$) with a unit-cell parameters: $a = 9.52$ Å, $b = 11.54$ Å, $c = 4.93$ Å, $\beta = 91.2^\circ$, [4]. The crystal lattice of $LiSc(WO_4)_2$ is basically