Spectra properties of Cr-doped and Cr, La-co-doped PbWO$_4$ single crystals

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Abstract

We report in this paper the spectra properties of Cr-doped and Cr, La-co-doped PbWO$_4$ (PWO) crystals grown by the Czochralski method. It is found that low-field Cr^{3+} ions and Cr^{4+} ions in tetrahedral sites co-exist in the crystals studied. In the case of Cr-doped PWO samples, Cr^{3+} is supposed to reside primarily at the Pb-site, and this results in the relaxation of lattice, which is confirmed by FT-IR analysis. The crystal-field parameters of Cr^{3+} in a distorted octahedral environment are estimated, and they are $Dq = 1351$ cm^{-1} and $Dq/B = 2.11$, respectively. The NIR absorption of the crystals confirms the formation of Cr^{4+} and it is suggested that this is situated in the W^{6+} position. In particular, the co-addition of La^{3+} can induce a remarkable increase of absorption coefficient in the NIR region, on the grounds that La^{3+} ions preferably occupy the Pb^{2+} sublattice and force Cr to enter the W^{6+} position in the form of Cr^{4+}. Cr-doped PWO crystals may be of interest as a new passively Q-switched laser material considering their high absorption coefficient in the NIR spectrum.

1. Introduction

Since the approval of PbWO$_4$ (PWO for brevity) as the basic crystal for the CMS and ALICE projects at CERN in 1994, extensive attention has been directed towards improving its scintillation characteristics and identifying related possible defect structures. Up to now, it has been well established that most trivalent or tetravalent ion doping in the PWO host [1–3] can effectively ameliorate the transmittance and radiation hardness of the resultant crystals. PWO crystal is also expected to be a promising laser host by doping Nd^{3+}; this finds applications in lidar technology and for the generation of specific wavelengths, e.g. as pump sources for upconversion fibre lasers [4]. This is a valuable result because doping with appropriate ions might enable PWO crystals to be employed in a new practical way in a photoelectron field in view of its low cost and the well-developed growth technique of large-size single crystals.

Chromium (IV) ions with tetrahedral symmetry, as found in single crystals of forsterite [5, 6] and $Y_3Al_5O_{12}$ [7], have found applications as saturable-absorbers for passive Q-switched lasers [8], as tunable solid state lasers in the NIR, and for ultrashort laser pulse generation [9]. Under normal growing conditions, it follows that only a few per cent of the chromium correspond to the tetrahedral Cr^{4+} active species [10] in these materials. The tendency of Cr^{4+} to disproportionate into Cr^{3+} is the major difficulty in preparing pure Cr(IV) solids. In recent years, renewed studies of optical performances for Cr^{3+} ions in crystals and in glasses have been conducted because of the exploitation of these materials as active media for infrared tunable lasers, and to aid the fundamental understanding of the interaction between impurity and host lattice [11–13].

This paper describes the spectra properties of a series of Cr-doped and Cr, La-co-doped PWO single crystals. We propose that the formation of Cr^{4+} is related not only to the initial Cr content in the melt but also more importantly to the co-addition of La^{3+} ions. The doping mechanism is also discussed. To our knowledge, this is the first report about Cr(IV) in a tungstate host.

2. Experimental details

Single crystals were grown in air atmosphere by the Czochralski technique, in which the raw materials of 5N pure PbO and WO_3 powders were prepared according to the stoichiometric composition. Cr and La impurities were introduced in the form of Cr_2O_3 and La_2O_3. Their starting concentrations were: (a) Cr 0.1, (b) Cr 0.2, (c) Cr 0.3 + La 0.6, and (d) Cr 0.4 + La 0.8 (at.%). The crystals were transparent and free from cracks, inclusions and precipitations. The investigated crystals were cut into dimensions of about $10 \times 10 \times 2$ mm^3 and $6 \times 5 \times 0.3$ mm^3 with two large facets polished and their faces perpendicular to the c-axis. Samples for FT-IR measurement were also prepared from the same parent bulk crystals by grinding them into fine powders, and pressing with KBr into plates.

The absorption spectra were recorded at room temperature on a spectrophotometer (Lambda900, Perkin–Elmer) with a spectral range from 200 to 2600 nm. FT-IR spectra were collected with a Digilab-FTS-80 spectrophotometer.

3. Results and discussions

Figure 1 presents the UV–VIS absorption spectra of Cr-doped and Cr, La-co-doped PWO crystals at room temperature. The spectra are complex due to the overlap of the Cr(III) and Cr(IV) absorption bands for the Cr-doped crystals. To be clear, the absorption spectra at wavelength range from 360 nm to 550 nm of La-free and La-containing PWO crystals are fitted by three and two Gaussian curves, respectively, as shown in figure 2. The presence of the Cr^{3+} centre is reflected in the existence of broad absorption bands at 510 and 740 nm, which associate with the transitions from the $^4A_2$ ground state to the $^4T_1$, $^4T_2$ excited states of Cr^{3+} in a nearly octahedral site, respectively. Thereby, the crystal field parameters are estimated and they are $Dq = 1351$ cm^{-1} and $Dq/B = 2.11$. The results are agreement with those of Cr^{3+} in $ZnWO_4$ single crystal [14], and suggest that the Cr^{3+} ions are submitted to a weak crystal field. On the other hand, the weakness of these bands exhibits only a small quantity of Cr^{3+} ions in the crystal. In contrast to samples (a) and (b), the 510 nm peak cannot be found and only one symmetrical band centred around 710 nm can be seen for the Cr, La-co-doped PWO crystal. It seems that it is difficult for the Cr^{3+} ion to exist in this crystal.

A possible interpretation about the 420 nm band is that it is due to a charge-transfer and its shoulder peak at 475 nm is attributed to Cr^{4+} [7, 15]. The symmetry allowed $^3A_2 \rightarrow {}^3T_1$
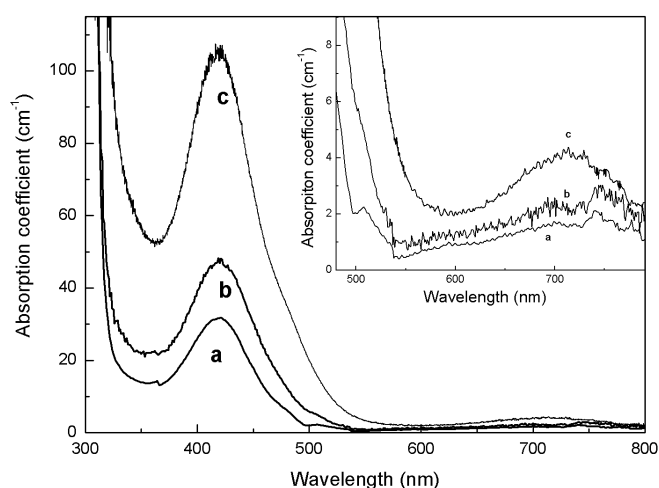
Figure 1. UV–VIS absorption spectra of doped PWO crystals. The crystals contain (a) 0.1 at.% of Cr, (b) 0.2 at.% of Cr, and (c) 0.3 at.% of Cr and 0.6 at.% of La, with a thickness of 0.3 mm along the excitation direction (c-axis). The inset shows the absorption spectra at the long wave region.

Table 1. The spectra performances of PWO:Cr^{4+} samples in the NIR.

Sample number	(a)	(b)	(c)	(d)
Sample colour	Orange	Brown	Brown	Puce
AC at 870 nm (cm^{-1})[a]	0.11	0.13	1.3	5.51
Multiple[b]	1	1.2	12	50
AC at 1060 nm (cm^{-1})[a]	0.05	0.08	0.7	2.57
Multiple[b]	1	1.6	14	51

[a] AC = absorption coefficient.
[b] Compared to the result of sample (a).

Table 2. Physical parameters [17] of some of the ions in this work.

Ions	Pb^{2+}	W^{6+}	Cr^{3+}	Cr^{4+}	Cr^{5+}	La^{3+}
CN[a]	8	4	6	4	4	8
Ionic radii (Å)	1.20	0.42	0.62	0.41	0.35	1.16
Electronegativity	1.8	1.7		1.66		1.10

[a] CN = coordination number.

transition of Cr^{4+} is considered to correspond to the absorption band at around 700 nm [16]. The absorption spectra in the NIR region are displayed in figure 3, and a double-humped band extends from 850 to 1200 nm, which is assigned to the $^3A_2 \rightarrow ^3T_2$ transition of Cr^{4+} in a tetrahedral environment [10]. In the case of Cr-doped PWO samples, with the Cr content altering from 0.1 to 0.2 at.%, the absorption coefficient at 1060 nm slightly increases from 0.05 to 0.08 cm^{-1}. It is interesting that the intensity of the absorption is significantly enhanced by the co-doping with La^{3+}. The ratio of absorption coefficient between samples (d) and (a) is 50 when the concentration of Cr shifts from 0.1 to 0.4 at.%. This is high enough to make the system possible as a passively Q-switched laser material. The results are presented in table 1.

To understand the experimental data well, it is necessary to give a short introduction of the PWO crystal structure and to evaluate the possible doping mechanisms. Lead tungstate exhibits a tetragonal scheelite-type symmetry, in which a Pb atom is surrounded by eight O atoms and a W atom four-coordinated with O atoms. Both coordination polyhedra are in S4 symmetry. This structure can be derived from fluorite-type symmetry.
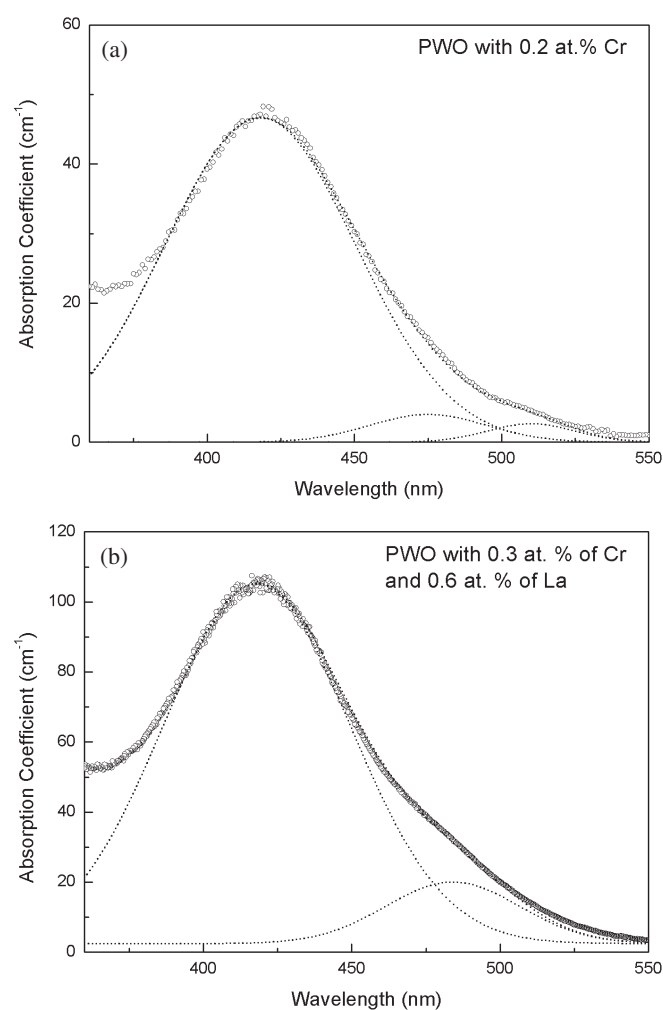
Figure 2. The absorption spectra of (a) La-free (0.2 at.% Cr) and (b) La-containing (Cr 0.3 at.% and La 0.6 at.%) PWO crystals were fitted by three and two Gaussian curves (dot curves), respectively.

Based on the ionic radius, electrovalent and electronegativity, Cr^{3+} is supposed to primarily enter the Pb^{2+} sublattice when PWO crystal is doped by Cr with low concentration. Some physical parameters of the ions studied in this work are given in table 2.

$$Cr_2O_3 + PWO \rightarrow 2(Cr_{Pb}^{3+})^{\bullet} + V_{Pb}'' + 3PbO. \tag{1}$$

In this equation, PWO represents the PWO bulk crystal as a whole. It seems that the substitution of Pb^{2+} by Cr^{3+} makes the Cr^{3+} to be coordinated by eight oxygen ions. As a matter of fact, Cr^{3+} ions prefer to occupy approximately octahedral symmetry sites in inorganic crystals because both the ionic radius and the 'octahedral crystal field stabilization' energy favour six-fold coordination [18]. Our absorption spectra also suggest that the Cr^{3+} is in a nearly octahedral environment. One can tentatively say that the octahedron is formed by moving six of the oxygen ions towards the Cr^{3+} and forcing the two others further away, resulting in the relaxation of the crystal lattice. Similar issues for Cr^{3+} were also found in fluorite-structure hosts [19]. FT-IR spectra (figure 4) are exploited to further clarify this fact. Characteristic infrared absorption corresponding to O–W–O stretches ($\nu_3 A_u + \nu_3 E_u$) occurs between 900 and 750 cm^{-1} [20]. Compared with that of pure PWO crystal, the characteristic peak of O–W–O in
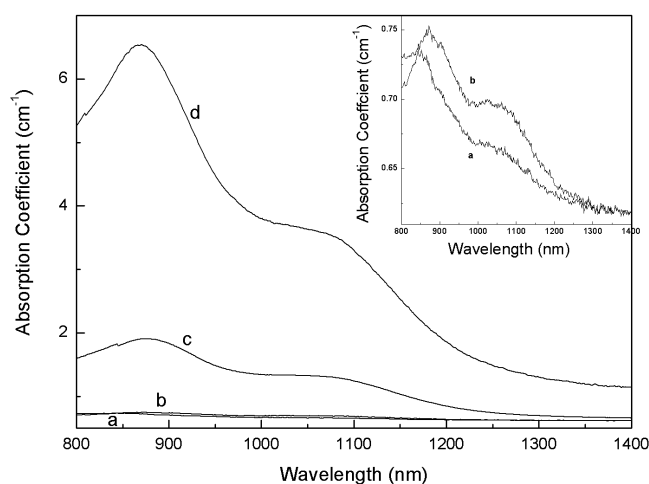
Figure 3. NIR absorption spectra of PWO crystals doped with Cr (a) 0.1 at.%, (b) 0.2 at.%, and co-doped with (c) Cr 0.3 at.% and La 0.6 at.%, (d) Cr 0.4 at.% and La 0.8 at.%. All the crystals are of 2 mm thickness along the excitation direction (c-axis). For clarity, the spectra of (a) and (b) are enlarged in the inset.
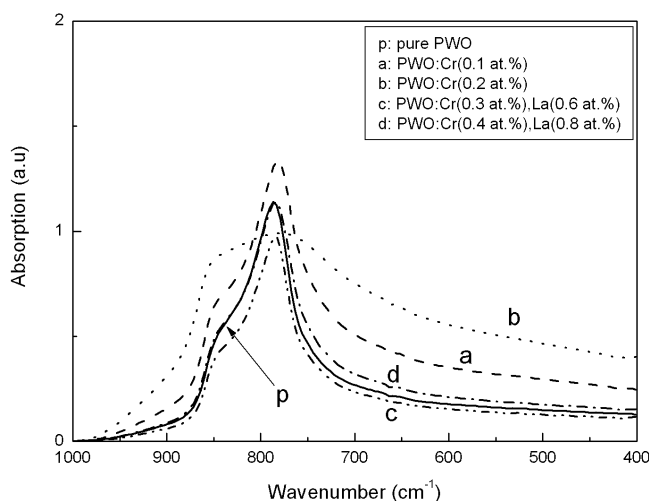

Figure 4. The FT-IR spectra of undoped and doped PWO single crystals.

Cr-doped PWO sample is badly deformed. It suffices to say that the WO$_4^{2-}$ group is distinctly affected. XRD analysis reveals that all crystals investigated are homogeneous scheelite-type structure and impurities well enter the crystal lattice. Therefore, it is impossible that there exist lots of such Cr^{3+} ions in this material in order to keep the crystal structure unchanged. For a heavily Cr-doped PWO crystal, some Cr^{3+} ions could be oxidized into the Cr^{4+} state and replace W^{6+} because all crystals were grown under air atmosphere conditions.

$$3Cr_2O_3 + PWO + \tfrac{1}{2}O_2 \rightarrow 4(Cr_{Pb}^{3+})^\bullet + 2(Cr_W^{4+})'' + 2PbWO_4 + 2PbO. \qquad (2)$$
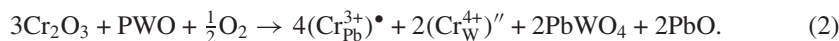
Since the radius of Cr^{4+} is very close to that of W^{6+}, a perfect substitution can happen and this gives rise to optical absorption in the NIR field.

The above-mentioned method can also apply for the understanding of Cr, La-co-doped PWO crystals. La^{3+} is considered to preferably occupy the Pb^{2+} position in view of radii [21], and thus leaves little chance for Cr^{3+}. Cr is forced to go into the W^{6+} sublattice in the form of Cr^{4+}, which is revealed by NIR absorption.

$$Cr_2O_3 + 2La_2O_3 + PWO + \tfrac{1}{2}O_2 \rightarrow 4(La_{Pb}^{3+})^\bullet + 2(Cr_W^{4+})'' + 2PbWO_4 + 2PbO. \qquad (3)$$
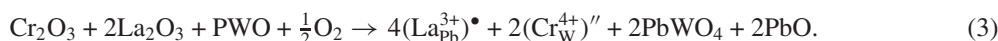
This only requires a small relaxation of the crystal lattice, and is confirmed by FT-IR data. Little change of the characteristic absorption band for the WO_4^{2-} group is found in Cr, La-co-doped PWO crystals. The absence of the 510 nm band in figure 1 can be accordingly accounted for.

Missing from this work is any information about the luminescence performance of the materials. Further experiments are under way.

4. Conclusions

The spectra properties of Cr-doped and Cr, La-co-doped PWO crystals are investigated. All absorption bands are defined to corresponding electronic transitions. In the case of Cr-doped samples, Cr^{3+} is supposed to primarily occupy the Pb-site, with resulting lattice relaxation. The corresponding crystal field parameters are estimated and they are $Dq = 1351$ cm^{-1} and $Dq/B = 2.11$ respectively. Cr^{3+} is in a weak crystal field here. With the increase of Cr concentration, Cr^{3+} will be oxidized into Cr^{4+} and situate in the W^{6+} position. La^{3+} preferably substitutes for Pb^{2+} and forces Cr to enter the W^{6+} site in the form of Cr^{4+} for Cr, La-co-doped samples. Therefore, the Cr^{4+} population evidently rises in the PWO host and the absorption intensity in the NIR region significantly increases. The absorption coefficient at 1060 nm of sample (d) is increased to 2.57 cm^{-1}. The crystal may be a potential candidate as a new passively Q-switched laser material. The FT-IR data provide further support for the visible and NIR absorption spectra interpretation.

Acknowledgments

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