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# CO - doping effects on $SrWO_4$: $Nd^{3+}$ crystals for Raman lasers

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The strontium tungstate ($SrWO_4$) crystals doped with laser active $RE^{3+}$ (rare earths) ions can act as multifunctional systems, combining the laser and Raman scattering properties. To bring some insight in the charge compesation mechanisms connected with substitution of the $Sr^{2+}$ host cations with $RE^{3+}$, the high-resolution optical spectra at low temperatures on Nd: $SrWO_4$ single doped crystals and co-doped with $Nb^{5+}$ or $Na^{+}$ ions were performed. The crystal growth conditions and structural results are presented too. The high-resolution optical absorption data at 15 K reveal a multicenter structure (up to five centers). A comparative analysis of the $Nd^{3+}$ spectra in single doped or in (Nd, Na) and (Nd, Nb) co-doped $SrWO_4$ crystals is presented.

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## 1. Introduction

The necessity of lasers with emission in new spectral wavelengths has extended the search for different materials and generation processes, such as stimulated Raman scattering (SRS). Among the crystals with good nonlinear properties for crystalline nano and picoseconds Raman lasers are the tungstates ($CaWO_4$, $BaWO_4$, $SrWO_4$) [1-5]. The investigations on undoped crystals were directed to obtain crystals of good optical quality and to determine the characteristics of stimulated Raman scattering process.

The tungstates crystals doped with $Nd^{3+}$ are investigated as multifunctional systems combining the laser and non-linear properties [3-6] or doped with other $RE^{3+}$ ions ($Er^{3+}$, $Tm^{3+}$, $Yb^{3+}$) as laser materials [7 - 10]. $SrWO_4$ crystals belong to the uniaxial tetragonal scheelite structure [11] with a space group of $I4_1/a$ $\left(C_{4h}^6\right)$ having the cell parameters a = b =5.417 Å and c = 11.951 Å. The scheelite elementary cell contains four $SrWO_4$ units. The $RE^{3+}$ ions replace $Sr^{2+}$ in sites with eightfold oxygen coordination (distorted dodecahedron, point symmetry $S_4$) [12]. The excess of charge could be compensated by cation vacancies, interstitial oxygen, pairing of $Nd^{3+}$ ions, etc, and by co-doping with $Na^{+}$ (replacing $Sr^{2+}$) or $Nb^{5+}$ (replacing $W^{6+}$) ions [13].

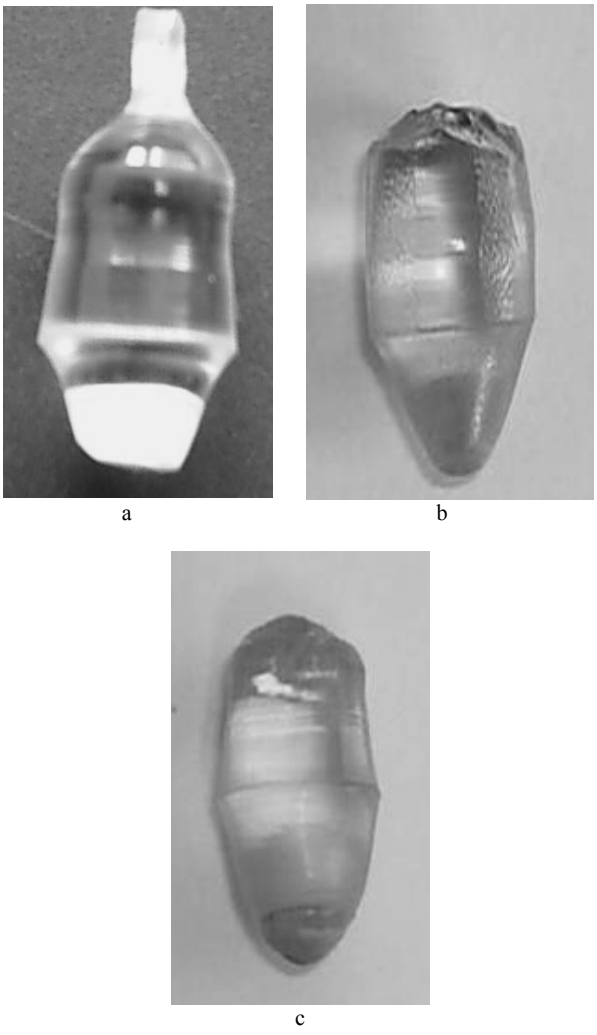
The charge compensation leads generally to multicenter spectral structures. The changes of spectral (optical or EPR) characteristics especially the apparition of a variety of spectra, connected with charge compensation mechanisms function on $RE^{3+}$ ion, sample preparation, doping or co-doping level have been observed [13]. However, no reliable characterization of the charge compensation mechanisms has been given even in the recent publications [6-10].The purpose of this paper is to investigate the crystal growth conditions, structure and preliminary high-resolution spectral characteristics of $SrWO_4$ single crystals doped with $Nd^{3+}$ and co-doped with $Nb^{5+}$ or $Na^{+}$ ions.

## 2. Results

### 2.1 Samples preparation

The starting material $SrWO_4$ was synthesized by solid-state reaction of $SrCO_3$ and $WO_3$ in stoichiometric ratios. The dopants were added in forms of $Nd_2(WO_4)_3$ (starting from $Nd_2O_3$, $HNO_3$ and $Na_2WO_4$), $NdNbO_4$ (starting from $Nd_2O_3$ and $Nb_2O_5$), and $Nd_2O_3$ + $Na_2CO_3$. The raw materials were completely mixed in a Pt crucible ant sintered in oxygen atmosphere at 1350 °C for 24 hours. X - ray diffraction patterns, performed on the powders of the synthesized samples, proved that the solid-state reactions were completed and that no other parasitic phases are present. Single crystals of $SrWO_4$ doped with $Nd^{3+}$ ions between 0.3 and 3.0 at.%, or co-doped (0.6 at.% Nd, 0.6 at.% Na) and (0.6 at.% Nd, 0.6 at.% Nb) were grown from the melt by Czochralski method with induction heating, without any excess of $WO_3$ into the melt. The doping concentrations refer to the melt composition. The melting point is 1535 ± 20 °C, so it was possible to use platinum crucibles (internal diameter of 35 mm and height of 35 mm) in the 3% $O_2$ + 97% $N_2$ atmosphere. From the first $SrWO_4$: Nd crystal obtained by crystallization on the Pt wire, seeds of [001] orientations were cut and further crystal growths were carried out using crystalline seeds oriented parallel to the c-axis. The temperature was initially maintained for 2 - 3 hours 50 – 60 °C higher than the melting point of crystals (measured with an infrared pyrometer to assure complete melting and homogenization then it was lowered to the melting temperature. The seeds were necked down before they were tapered off to a diameter of about 2 mm. The decreasing of the temperature gradient just above the melt at about 30 – 40 °C/cm allow to obtain single crystals of

[001] orientation free of blocks. To obtain crystals with good optical quality, the pulling rate must not exceed 1.5 mm/h. With substantial increase of dopants concentration ($Nd^{3+}$, $Na^{+}$ or $Nb^{5+}$) the pulling rate has to be decreased to 0.8 mm/h. The rotation rates were between 25 and 30 rpm. The crystals were cooled to room temperature at a rate of 30 ºC/h. Crystals of good optical quality and sizes of 12 mm in diameter and 20 mm long were grown (Fig. 1).



a b c

*Fig. 1. Single crystals of (a) $SrWO_4$: Nd(0.6 at.%), (b) $SrWO_4$: Nd(0.6 at.%), Na(0.6 at.%) and (c) $SrWO_4$: Nd(0.6 at.%), Nb(1.0 at.%).*

Phase identification and determination of lattice parameters of the grown crystals were performed using a TUR M62 diffractometer with Co $K_{\alpha 1}$ radiation ($\lambda$ = 1.78897 Å). The recorded X-ray powder diffraction pattern of the $SrWO_4$: Nd (0.6 at.%) grown crystal is reproduced in Fig. 2.

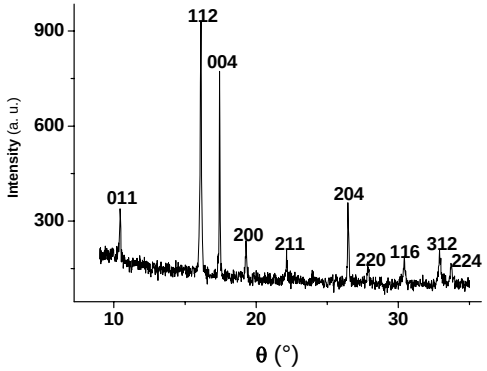



*Fig. 2. X-ray powder diffraction pattern of the $SrWO_4$: Nd(0.6 at.%) grown crystal.*

The pattern matches very well with the data reported for the $SrWO_4$ phase in literature [14].

The X-ray powder diffraction patterns of grown crystals confirm the presence of single phases of $SrWO_4$: Nd, $SrWO_4$: (Nd, Na) and $SrWO_4$: (Nd, Nb) respectively, and show that the unit cell parameters decrease slightly with the increasing $Nd^{3+}$ and $Na^{+}$ concentration. This is determined by the difference between the ionic radii of the $Nd^{3+}$ and $Na^{+}$ cations (1.04 Å and 0.97 Å) that substitute the much larger $Sr^{2+}$ (1.12 Å) cations. The influence of $Nb^{5+}$ ions on the unit cell parameters is very small as a consequence of the very closed ionic radii of $W^{6+}$ and $Nb^{5+}$ (0.62 Å and 0.69 Å respectively).

### 2.2 Spectroscopic data and discussion

The spectral investigations on oriented crystalline samples include high-resolution absorption, emission at 15 K and 300 K. An experimental set-up containing a tungsten halogen lamp, a GDM (0.3 $cm^{-1}$ resolution) monochromator and a photon counting system in connection with a MCS multichanel analyzer for detection and a closed cycle He cryostat (for low temperatures) was used.

In the case of $SrWO_4$: Nd single doped crystals, the high-resolution spectra (taken with unpolarized light along c axis) show a complex multicenter structure. At least five lines of different intensities (separated by up to 25 $cm^{-1}$) are observed, as illustrated in Fig. 3 with the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ absorption at 15 K for a sample with 0.6 at. % Nd in the melt. In this transition a single line is expected for each center. A similar structure is observed in other transitions too such as for the absorption to the first Stark level of the $^4F_{5/2}$ manifold (Fig. 4). Obviously, this situation is determined by the compensation of electric charge difference between the doping $Nd^{3+}$ ions and the host cations ($Sr^{2+}$) and indicates that different charge compensation are accomplished by lattice defects, such as cation vacancies, near the doping ion, by formation of doping ion clusters, other defects or impurities.

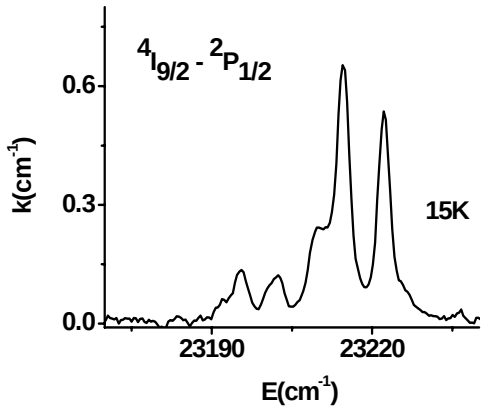



*Fig. 3. The $^4I_{9/2} \rightarrow {}^2P_{1/2}$ absorption of 0.6 at. % Nd: $SrWO_4$ at 15 K.*

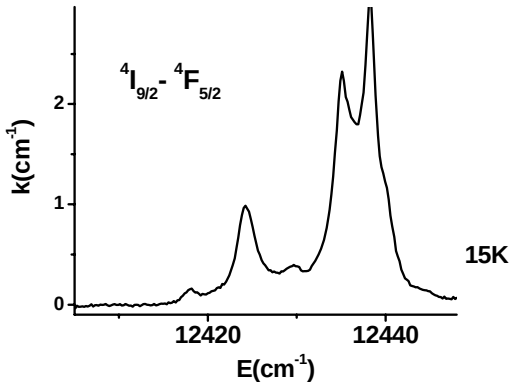



*Fig. 4. The $^4I_{9/2} \rightarrow {}^4F_{5/2}$ absorption of 0.6 at. % Nd: $SrWO_4$ at 15 K.*

In order to observe the effects of co-doping on the spectroscopic properties, the high-resolution absorption spectra were recorded, in the same conditions, for crystalline samples co-doped with $Na^+$ and $Nb^{5+}$. The absorption spectra corresponding to $Nd^{3+}$ $^4I_{9/2} \rightarrow {}^4F_{3/2}$ and $^4I_{9/2} \rightarrow {}^4F_{5/2}$, transitions of interest for diode laser pumping in $SrWO_4$ crystals doped either with 0.6 at.% Nd, (0.6 at.% Nd, 0.6 at.% Na), or (0.6 at.% Nd, 0.6 at.% Nb) (concentrations in melt) are comparatively illustrated in Fig. 5 and 6. As observed, the spectra are slightly different, the relative intensity of different centers lines change, or other lines -centers appear. Co-doping with $Na^+$ leads to a simplification of the spectra, as illustrated in the transitions to the first Stark of the $^4F_{3/2}$ (Fig. 5) or $^4F_{5/2}$ (Fig. 6) that show one prevailing center.

From electric charge and size considerations, the $Na^+$ ions will substitute $Sr^{2+}$, while the small $Nb^{5+}$ions could substitute $W^{6+}$; thus co-doping with these ions could reduce the need for charge compensation of $Nd^{3+}$ by $Sr^{2+}$ vacancies. The charge compensation with these ions in the vicinity of the $Nd^{3+}$ ion determines different crystal field perturbations at the $Nd^{3+}$ site and this leads to the modification of the multicenter structure or to inhomogeneous broadening of the optical spectra (or EPR). This structure cannot be observed at the room temperature or in the low resolution optical spectra of $RE^{3+}$ ions [6-10]. Thus, an envelope of our high resolution spectra (Fig. 3) gives a similar width to that reported (~ 25 cm$^{-1}$) for $^4I_{9/2} \rightarrow {}^2P_{1/2}$ absorption of Nd: $SrWO_4$ grown by flux technique [6]. Our spectra suggest that the co-doping with $Na^+$ is appropriate for increasing the intensity of one center. In our study a 1:1 ratio Nd: Na in the raw material was used. However, taking into account the ionic radii differences, a higher quantity of $Na^+$ relatively to $Nd^{3+}$ could probably simplify even more the spectra. This is important since the laser emission at more wavelengths is possible in a multicenter system. Obviously, the placement of the $Na^+$ or $Nb^{5+}$ ions at the available lattice sites is correlated with the distribution of the $Nd^{3+}$ in crystals and it depends also on crystal growth conditions, such as the thermal regime and crystal growth speed.

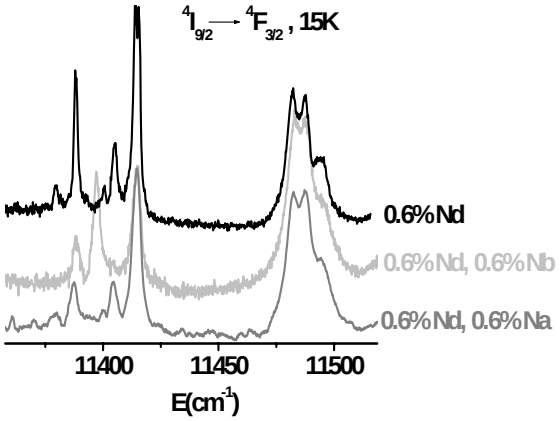



*Fig. 5. The 15 K $Nd^{3+}$ $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra.*

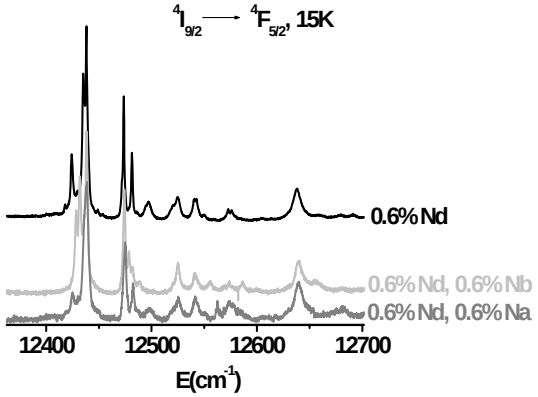



*Fig. 6. The 15 K $Nd^{3+}$ $^4I_{9/2} \rightarrow {}^4F_{5/2}$ absorption spectra.*

## 4. Conclusion

Single crystals of $SrWO_4$: $Nd^{3+}$ (with different $Nd^{3+}$ concentrations), or co-doped $SrWO_4$: Nd(0.6 at.%), Na(0.6

at.%) and $SrWO_4$: Nd(0.6 at.%), Nb(1.0 at.%) with constant diameter of 12 mm and 20 mm long having no polycrystalline or crust regions, and good transparency were grown by the Czochralski pulling technique.

Preliminary high-resolution spectral data of $SrWO_4$ crystals single doped with $Nd^{3+}$ and co-doped samples were performed and show composition-dependent multicenter spectral structures. Selective excited emission or decays measurements on these centers are in progress.

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