Synthesis, characterization and luminescent properties of Sr1-xPbxWO4 solid solution (x=0, 0.5 and 1)

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Abstract. In this work, a study of the role of chemical substitution in the properties of the solid solution $Sr_{1-x}Pb_xWO_4$ (x = 0, 0.5 and 1) is presented. Polycrystalline samples were synthesized by solid state reaction at 1100°C. Using Rietveld method, the structural parameters of all samples were refined. All structures are of scheelite type Scanning electron microscopy showed that a high level of crystallization characterized the samples, with modifications in sizes and shapes depending on composition x. The Infrared and Raman spectroscopies were performed to characterize the evolution of vibrational modes with composition x. Finally, a systematic study of luminescence under X-ray and UV excitations was performed. The energies and intensities of luminescence depended on composition x and on the nature of excitations.

1. Introduction

The first paragraph after a heading is not indented The scheelite tungstate crystals AWO_4 are characterized by tetragonal structures [1,2] (space group $I4_1/a$), with tetrahedral oxyanions WO_4^{2-} and M^{2+}cations forming MO_8groups [3]. They were extensively investigated for their potential applications as laser host materials [4,5], scintillators [6,7], oxide ion conductors [8], materials for microwave applications [9] and magnetic materials [10]. The luminescent properties under different excitations of single-crystals as well as polycrystalline $SrWO_4$ and $PbWO_4$ compounds have been widely studied by several authors [11–15]. Generally, luminescence spectra of scheelite tungstate were decomposed into two main blue and green bands, and to a weaker orange–red emission: the emissions were observed with energies close to 3.0–2.8, 2.7–2.4 and 2.3–2.0 eV [16–20].

In this work we study the luminescent properties of lead and strontium tungstates $Sr_{1-x}Pb_xWO_4$ for the three compositions x= 0 ; 0.5 and 1 under X-ray and UV excitations. We already published the synthesis, characterization and luminescence under X-ray excitation of $Sr_{1-x}Pb_xWO_4$ and $Ca_{1-x}Cd_xWO_4$ solid solutions [21-23]. Presently, we compare the luminescence responses under X-ray and UV excitations of these substituted samples.

2. Experimental

2.1. Synthesis

All samples of $Sr_{1-x}Pb_xWO_4$ with x= 0, 0.5 and 1, were prepared by conventional solid state chemical reaction using WO_3 [Alfa Aesar N° 11828, >99.8%], $SrCO_3$ [Sigma-Aldrich N° 1633-05-2, >99.0%] and PbO [Sigma-Aldrich N° 1317-36-8, > 99.0%]. The elaboration conditions (grinding process, temperature and time of thermal treatment) were optimized and the final process was as follows: the reagents in stoichiometric proportions were thoroughly mixed and ground in an agate mortar for 15 min, then thermally treated at 600°C for 3 h, in pure alumina crucible under air. The samples were ground again thoroughly for 2 h, and then, retreated at 1100 °C for 4 h, under air.

2.2. Characterization techniques

2.2.1. X-ray diffraction: Each sample was analysed by X-ray diffraction using an Empyrean Panalytical diffractometer, equipped with a copper X-ray source (wavelength $\lambda=1.54.10^{-10}$ m, tension V= 45 kV, intensity I= 35 mA), and with a Ni filter eliminating the K_β radiation. The structural parameters of the samples were refined using the Fullprof software [24] based on Rietveld procedure.

2.2.2. Scanning electron microscopy: A systematic analysis of grain sizes and morphologies was performed using a Supra 40 V_pColonne Gemini Zeiss scanning electron microscope (SEM), with a maximum voltage of 20 kV.

2.2.3. Raman spectroscopy analysis: Raman spectroscopy was used to characterize the evolution of the various phases, and to correlate vibration modes with these structural evolutions. The equipment used to perform the various vibration spectra was a spectrometer Horiba Jobin-Yvon HR800 LabRam, spatially resolved to 0.5 μm, by means of an optical microscope with a 100 objective. The latter has a dual function: it allows firstly focusing the laser beam on a small area, and, secondly, visualizing the area of the sample. The 514.5 nm line of an Ar-ion laser was used as the excitation source; the photonic power applied to the samples was limited to 5 μW with an acquisition time of 30 s. Each Raman band was characterized by its wavenumber (in cm-1).

2.2.4. Luminescence experiments: For the luminescence under X-ray excitation, the copper X-ray source of the diffractometer Empyrean-Panalytical was used to irradiate the samples and perform luminescence experiments. The nominal emission conditions (voltage VRX / current IRX) were 45 kV /35 mA. The luminescence emissions of samples were recorded using a UV–visible spectrophotometer MicroHR (JobinYvon) equipped with an optical fiber of 400 μm in diameter.

The equipment used to perform the measurements of luminescence under UV was the previously described spectrometer Horiba Jobin-Yvon HR800 LabRam. The entrance slit, positioned behind the filter, is a diaphragm whose diameter can range from 50 to 500 μm. The 364.5 nm line of an Ar-ion laser was used as the excitation source. The power applied to the samples was fixed to 0.005 mW with an acquisition time set to 100 ms.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD pattern of $Sr_{1-x}Pb_xWO_4$ powders. All diffraction peaks are characteristic of the scheelite tetragonal structure with space group $I4_1/a$. The diffraction peaks are shifted to smaller 2θ angles as x increases.

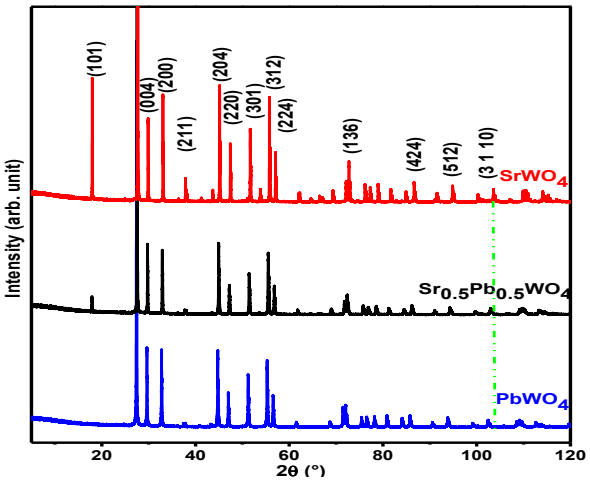

Figure 1.XRD patterns of the tetragonal $Sr_{1-x}Pb_xWO_4$ powders with x = 0, 0.5, 1.

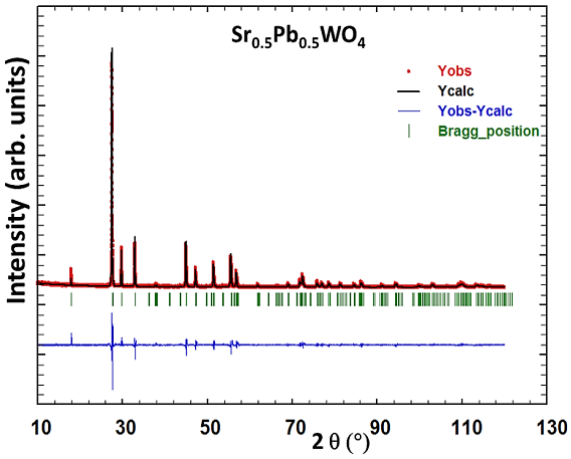

Figure 2. Calculated and observed diffraction profiles from Rietveld analyses for the $Sr_{0.5}Pb_{0.5}WO_4$ phase. Y_{calc}: calculated profile and Y_{obs} : observed profile.

Table 1 reports the refined structural parameters. Fig. 2 shows selected results comparing calculated diffraction profiles to experimental data.

Table 1. Refined structural parameters for $Sr_{1-x}Pb_xWO_4$ compounds with x = 0, 0.5; 1. Cell parameters, Debye-Waller factors B, reliability factors R in %.

x	**0**	**0.5**	**1.0**
a (10^{-10} m)	5.41734(2)	5.43919(3)	5.46220 (3)
b (10^{-10} m)	5.41734(2)	5.43919 (3)	5.46220 (3)
c (10^{-10} m)	11.95599(5)	11.99990(9)	12.04766(8)
Volume Cell (10^{-30} m^3) : V	350.880(2)	355.014 (5)	359.450(4)
B (M) = $(8\pi^2/3).<\Delta r^2>$ ($Å^2$)	0.37(3)	0.77(4)	0.38(2)
B (W) ($Å^2$)	0.21(3)	0.17(3)	0.20(2)
Reliability factors (*)			
R_B %	5.53	7.64	7.01
R_F (%)	5.34	7.24	8.04
R_{exp} (%)	7.08	8.49	8.45
W (x,y,z)	Fixed values : x = 0.00000 ; y = 0.25000 ; z= 0.12500 (**)		
M (x,y,z)	Fixed values : x = 0.00000 ; y = 0.25000 ; z= 0.62500 (**)		
O (x,y,z)	Fixed values : x = 0.23880 ; y = 0.11410 ; z= 0.04290 (**)		

Notes :
(*)$R_B = 100.\{\sum | I_k^{obs} - I_{ki}^{calc} | / \sum | I_k^{obs} | \}$; $R_F = 100.\{\sum w_i | (I_{iobs})^{1/2} - (I_{ical})^{1/2} | / \sum (I_{iobs})^{1/2} | \}$; $R_{exp} = 100.\{[(N-P) / \sum w_i | y_i^{obs} |^2]^{1/2} \}$ where N, P are the number of observations and parameters respectively.
(**) Sr, W and O coordinates from author [25] have been fixed.

3.2. Raman spectra

Fig. 3 shows the Raman spectra of the three compositions at room temperature. The vibration modes of $SrWO_4$ and $PbWO_4$ were already interpreted by authors *Priya et al.* and *Ling et al.* [26, 27] and

Crane et al. [28]. The decrease with composition x of Raman wavenumbers clearly suggests a continuous modification of chemical bonds W–O due to W–O–Pb interactions: as Pb–O bonds present a more covalent character, the W–O bonds probably present a weaker covalent character, with decreasing rigidity, due to electron displacement in favor of the Pb–O bond. In addition, a mass effect, due to a mass of Pb stronger than the mass of Sr, should play a role in the decrease of wavenumbers.

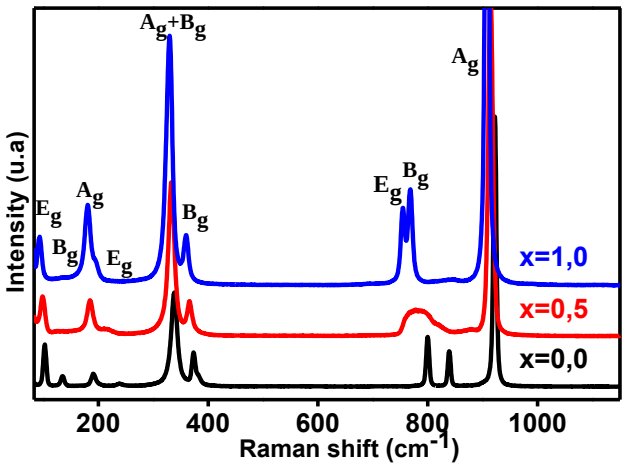

Figure 3. Room temperature Raman spectra of $Sr_{1-x}Pb_xWO_4$, for x = 0, 0.5, 1. (λ (excit.) = 514.5 nm).

3.3. Scanning electron microscopy

The SEM analyses of the x= 0.1, 0.5, 1 samples (Figures 4a, 4b and 4c, successively) show a progressive increase of crystallite sizes as x increases. In Figure 4a, we have inserted a magnified image to better illustrate the morphologies. In the case of the x=0.5 sample (Fig. 4b), a majority of large and regular crystallites is observed. For $PbWO_4$ (Fig. 4c) a mix system of crystallites with large and small grains is observed.

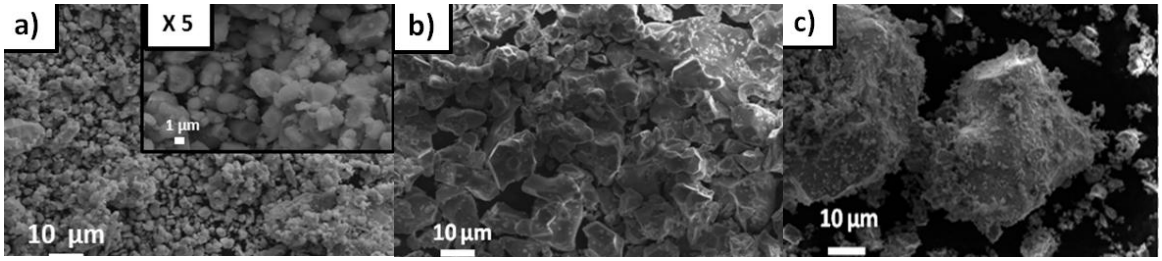

Figure 4. Scanning electron microscopy micrographs of the $Sr_{1-x}Pb_xWO_4$ samples (a) x=0 In inset : magnification of image (a) (x5), (b) x=0.5, and (c) x= 1.

3.4. Luminescence under X-ray excitation

Figure 5 compares the intensities emitted by the three different materials (x=0, 0.5, 1). We observe a clear difference between the intensity of the substituted compound (x=0.5) and those of x= 0 and 1 samples, with a very strong intensity for the x=0.5 sample. The average energy of the emission band is close to 2.8 eV (blue region).

3.5. Luminescence under UV excitation

Figure 6 shows the intensities of luminescence under UV excitation. In this case, no stronger intensity is observed for the substituted sample. This difference between the two emissions under UV and X-ray excitations can be ascribed to the low penetration of UV beam and to the high penetration of X-ray beam in samples. In the case of low energy UV excitation (3.6 eV), the observed luminescence is

mainly due to the external areas of crystallites and irregular surfaces of powdered samples, which is not the case for high energy X-ray excitations (from 0 to 45000 eV) that concern larger volumes of material. The average energy of the emission band is close to 2.25 eV (green region).

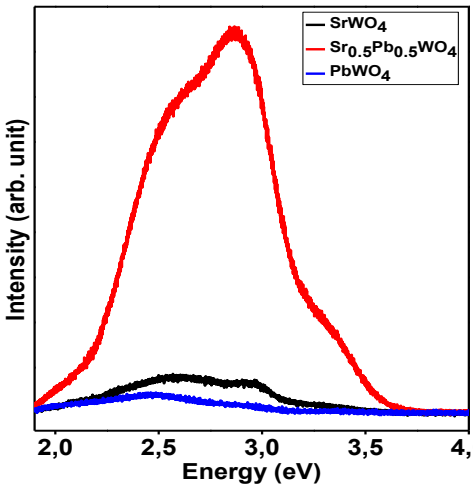

Figure 5. Photoluminescence spectra of $SrWO_4$, $Sr_{0.5}Pb_{0.5}WO_4$ and $PbWO_4$ under X-ray excitation (excitation energies in the continuous range 0 to 45000 eV).

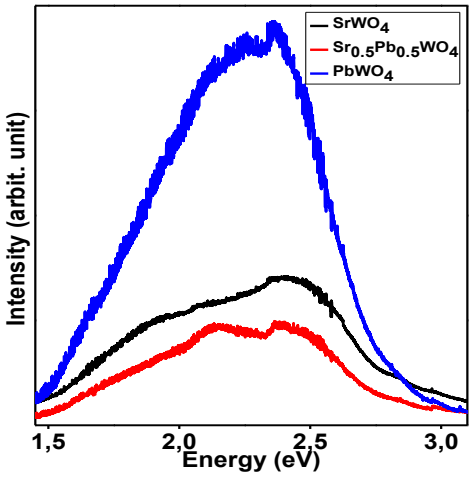

Figure 6. Photoluminescence spectra of $SrWO_4$, $Sr_{0.5}Pb_{0.5}WO_4$ and $PbWO_4$ under UV excitation (λ =364.5 nm or E=3.6 eV.

4. Conclusion

In this work, we have observed a complex influence of the chemical substitution on the luminescence signals under X-Ray excitation and UV excitation, in the series $Sr_{1-x}Pb_xWO_4$. Generally the origin of the emission in tungstate materials is related to the classical $^3T \rightarrow A_1$ transitions in the oxyanions WO_4^{2-}, and cations or anions vacancies in the material. The emission energies under X-ray and UV excitations are in the blue and green regions respectively. The luminescence experiments under X-ray excitation show that the emission of $Sr_{0.5}Pb_{0.5}WO_4$ presents intensity stronger than the intensity observed in $SrWO_4$ and $PbWO_4$. This behavior is fully different from the one observed in experiments under UV excitation: the emission intensity observed in the case of x=0.5 sample is lowered in comparison with the one of $SrWO_4$ and $PbWO_4$.

In these studies, we have shown that the effects of chemical substitution are complex, and that substitution can be used to obtain variable luminescence properties. The extension of these studies of substituted luminescent materials is now in progress: a major objective should be to better understand the different roles of substitution and of crystallization in luminescence efficiency.

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