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Structural, vibrational and photoluminescence properties of $Sr_{(1\text{-}x)}Pb_xMoO_4$ solid solution synthesized by solid state reaction

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ABSTRACT

In this paper, strontium lead molybdate $Sr_{1\text{-}x}Pb_xMoO_4$ polycrystalline samples with $0 \leq x \leq 1$ were prepared by solid state preparation method at 1000 °C. These materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and micro-Raman spectroscopy. Their photoluminescence responses were analyzed under X-ray excitation. Rietveld refinements indicate that all the materials present a scheelite-type tetragonal structure. Micro-Raman spectra confirmed the formation of the solid solution with a specific effect due to Sr-O-Mo and Pb-O-Mo links in the scheelite structure. SEM images showed modifications in the shapes and grain sizes as x increased. Broad photoluminescent emission bands were observed in the energy range 2.1–2.9 eV. The emission bands were decomposed into four gaussian components. The intensities of all components presented a strong maximum in the composition range $0.1 < x < 0.4$.

1. Introduction

In recent years, tungstates and molybdates have attracted a great deal of interests due to their broad potential to industrial application, including optic fiber, humidity sensor, catalysts, scintillation detector, solid-state lasers, photoluminescent devices and microwave applications [1–26]. Molybdates are significant luminescent materials with scheelite-type tetragonal structure, $I4_1/a$ space group, with two formula units per primitive cell. The scheelite structures $MMoO_4$ are characterized by a juxtaposition of $[MoO_4]$ tetrahedra and $[MO_8]$ hexahedra [27–31], with chemical links M-O-Mo. The pure molybdate phases $MMoO_4$ were synthesized from various methods: flux method [32], Czochralski technique [33,34], floating zone-like technique [35], co-precipitation process [36–40], sonochemical [41,42], citrate complex method [43,44], hydrothermal technique [45–50], solvothermal routines [51–57], microemulsion method [58], microwave-assisted synthesis method [59,60] and solid state reaction [61]. The two pure strontium and lead molybdate phases were previously synthesized by solid state reaction [62], flux [63], Czochralski [64], co-precipitation [65], hydrothermal [66] and pulsed laser ablation method [67].

Presently, we deal with the modifications of properties of solid solutions $A_{1\text{-}x}B_x(Mo, W)O_4$: in these materials, the atoms A and B (or Mo and W) can be distributed on the same crystallographic site, in ordered or disordered way. A high crystallization level of each compound can be reached (regular lattice) after specific synthesis method, despite the existence of a full disorder of atoms on their sites. In the case of luminescence properties of solid solutions, this disorder can play a prominent role in emission intensities.

Recently, photoluminescence properties in solid solutions $Sr_{1\text{-}x}Pb_xWO_4$, $Ca_{1\text{-}x}Cd_xWO_4$ and $Ba_{1\text{-}x}Sr_xMoO_4$ ceramics were analyzed as a function of the composition x [1–3,68]. The general aim was to better understand the role of substitution in the photoluminescence of tungstates and molybdates. The phase diagram of the $SrMoO_4$-$PbMoO_4$ system was partly determined by Zhuravlev et al. [69]. In our previous work on this system under X-ray excitation, we observed a significant increase of emission intensities in the range x = 0.2 to 0.4. Therefore in this paper, a new study of this molybdate based solid solution, we try to better understand the role of substitution on photoluminescence in molybdate materials. A series $Sr_{1\text{-}x}Pb_xMoO_4$ has been synthesized and characterized using X-ray diffraction (XRD), Raman spectroscopy (RS), and scanning electron microscopy (SEM). Finally, the photoluminescence properties (PL) have been analyzed under X-ray excitation.

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2. Experimental details

2.1. Synthesis by solid state method

Several series of eleven samples $Sr_{(1-x)}Pb_xMoO_4$ with $0 \leq x \leq 1$, were prepared by conventional solid state chemical reaction using polycrystalline precursors MoO_3 [Sigma-Aldrich N° 1313-27-5, >99.5%], $SrCO_3$ [Sigma-Aldrich No. 1633-05-2, >99.0%] and PbO [Sigma-Aldrich No. 1317-36-8, >99.0%]. The elaboration conditions (grinding process, temperature and time of thermal treatment) were optimized to reach a high crystallization level. 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 1000 °C for 6 h, under air. The main difficulty in this synthesis is the high volatility of PbO and MoO_3. A 1.5 wt% and 2 wt% excess amounts of MoO_3 and PbO respectively were added to the mixture to compensate for the volatilization of MoO_3 and PbO during synthesis of the polycrystalline powders.

2.2. X-ray diffraction analyses

Each sample was analyzed 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 $K\beta$ radiation. The diffractometer was equipped with a Pixcel-1D-Detector. The XRD analysis was carried out using the classical θ–2θ configuration, in continuous mode, with a step size of 0.00164, a scan speed of 0.002/s. All polycrystalline samples were compacted in a specific sample holder.

The structural parameters of the samples were refined using the Fullprof software [70] based on Rietveld procedure. The experimental profiles were fitted with the most suitable pseudo-Voigt analytical function. For both $K\alpha_1$ and $K\alpha_2$ profiles, the line broadening function and the symmetric part of instrumental function may be represented by the pseudo-Voigt (pV) function:

$$pV(x) = \sum I_{nt}[\eta L(x) + (1-\eta)G(x)] \quad (1)$$

In this expression, $L(x) = (1 + x^2)^{-1}$ is the Lorentzian component, and $G(x) = \exp[(\ln 2)\, x^2]$ is the Gaussian component, $x = (2\theta - 2\theta_0)/\mathrm{FWHM}$ (FWHM = Full Width at Half Maximum of the Bragg peaks), η is the gaussian character of X-ray profiles, θ_0 the Bragg angle of $K\alpha_1$ peak and I_{nt} is the scale factor. Considering the integrated intensity of the peaks as a function of structural parameters only, the Marquardt least-squares procedures were used to minimize the difference between the observed and simulated powder diffraction patterns. The minimization was carried out using the reliability index parameters such as Bragg factors (R_{Bragg}) comparing the calculated and observed intensities ($I_{i_{cal}}$ and $I_{i_{obs}}$), R_F factors comparing the calculated and observed structure factors ($F_{i_{obs}}$ and $F_{i_{cal}}$), and expected factors R_{exp}. All these parameters were used to characterize the quality of the fit between calculated and experimental diffraction profiles. The main reliability factors are defined as follows:

$$R_{Bragg_{(\%)}} = 100_{(\%)}.\frac{\sum_i |I_{i_{obs}} - I_{i_{cal}}|}{\sum_i I_{i_{obs}}} \quad (2)$$

$$R_{F_{(\%)}} = 100_{(\%)} \cdot \left\{ \frac{\sum_i |I_{i_{obs}} - I_{i_{cal}}|}{\sum_i \sqrt{I_{i_{obs}}}} \right\} \quad (3)$$

$$R_{\exp_{(\%)}} = 100_{(\%)} \cdot \left[\frac{n-p}{\sum_i w_i \left(y_{i_{obs}}\right)^2} \right]^{1/2} \quad (4)$$

In these expressions, $y_{i(obs)}$ is the intensity of experimental profile for a given 2θ angle, $w_i = (1/y_{i_{obs}})$ is the weight of profile determination, n is the number of experimental observations and p is the number of fitting parameters. A detailed description of the mathematical procedures implemented in the Rietveld analysis has been earlier reported by Rietveld and Pradhan et al. [71–75].

We used the atom coordinates obtained by Nogueira et al. on $SrMoO_4$ [76] and by authors Gurmen et al. on $PbMoO_4$ [77], to initiate the refinements of the various structures. The coordinates of oxygen atoms of intermediate compounds ($0 < x < 1$) were determined by interpolation, using the oxygen coordinates of $SrMoO_4$ and $PbMoO_4$; then these coordinates were fixed during the refinement procedure (see section results 2.2, below). These coordinates cannot be refined because of the high difference of scattering factors of oxygen and heavy atoms (Sr, Pb, Mo). The coordinates of W and average M (Sr, Pb) atoms were fixed because they occupy particular Wyckoff positions in the space group of scheelite structures. The average atoms M were considered as a mix of the Sr and Pb atoms with occupancy factors fixed by composition x. Cell parameters and Debye-Waller (DW) factors of heavy atoms were refined.

2.3. Scanning electron microscopy analysis

A systematic analysis of grain sizes and morphologies was performed using a Supra 40 Vp Colonne Gemini Zeiss scanning electron microscope (SEM), with a maximum voltage of 20 kV. Local chemical analysis using an Oxford EDS X-Max system, with a spatial resolution of 0.1 μm was carried out to control the homogeneity of powders.

2.4. Micro-Raman spectroscopy analysis

Raman spectroscopy was used to analyze the effect of substitution on vibration modes, and to correlate these vibration modes with the structural evolutions. The equipment used to record 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 100X 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 emission band was characterized by its wavenumber (in cm^{-1}).

2.5. Luminescence experiments analysis

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 V_{RX}/current I_{RX}) were 45 kV/35 mA. The resulting excitation energies ranged between 0 and 45 000 eV, with a maximum located at about 20 000 eV. It should be noted that the X-ray source also delivered the classical transition energies of copper source. All samples were in form of 2 mm thick cylindrical pellets, compacted under a pressure of 5 kbars, placed at a constant distance of the X-ray source, set with a fixed distance to the incident X-ray beam of about 10 cm. The luminescence emissions of samples were recorded using a UV – visible spectrophotometer MicroHR (Jobin