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XPS, DRUV-VIS and ESR characterization of the non-stoichiometric compound $Ge_{0.74}V_{0.21}\,\square_{0.05}O_2$

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Microcrystalline powders of the nonstoichiometric $Ge_{0.74}V_{0.21}\,\square_{0.05}O_2$ compound were prepared by conventional high temperature solid-state reactions. The powders were characterized by X-ray diffraction (XRD); scanning electron microscopy (SEM); X-ray photoelectron spectroscopy (XPS); diffuse reflectance ultraviolet-visible spectroscopy (DRUV-VIS) and electron spin resonance (ESR) spectroscopy. From the analysis performed on compound, it was found that: The powders showed a rutile type crystalline structure with a rectangular prismatic crystalline habit. The XPS analysis, confirm the presence of V^{4+} and V^{5+} vanadium ions, the DRUV-VIS spectra show absorption bands in the 200-800 nm wave length interval and the ESR analysis confirms that the V^{4+} ions are within microcrystals, hosted as VO^{2+} at sites of rhombic (C_{2v}) symmetry.

Keywords: Crystal Stoichiometry; X-ray powder diffraction; SEM; XPS; DRUV-VIS; ESR.

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1. Introduction

In the course of recent decades, there has been much interest in vanadium oxides because of their rich crystal chemistry [1], they show some basic solid state phenomena such as; metal-insulator transitions [2], Spin-Peierls transitions [3], doping promoted ferromagnetism in vanadium oxide nanotubes (VONT's) [4]; more recently, novel technical applications based on these compounds have been reported [5,6]. On the other hand, GeO2 exhibits many interesting physicochemical properties, such as photoluminescence, high values of dielectric constant and refractive index, good thermal stability and mechanical strength which make it suitable for applications in optical, electronic and optoelectronic devices [7-11], in particular, as transparent glasses their structural and specific optical properties, make it a valuable candidate for the construction of planar waveguides for optoelectronic communications [12-14].

As mixed oxides, the V_2O_5 and the GeO2 have been synthesized as vitreous materials for several years and their physical and chemical properties have been investigated systematically [15-17]. Later, amorphous coatings of mixtures of these oxides were prepared by the route of sol-gel synthesis and characterized using different spectroscopic techniques [18,19]. Although there is published work related to Ge-V-O based crystalline compounds (see [20,21] and references therein), the information on crystalline solid solutions of type $Ge(1-x)\,V_x\,O_2$ is scarce, so, we start a systematic study of the physical and chemical properties of these solid solutions synthesized from high temperature reaction of mixtures of vanadium and germanium oxide powders.

In this paper we present the characterization of the non-stoichiometric $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound synthesized by our group some years ago [22]. The characterization was performed through the following analysis techniques: X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), diffuse reflectance ultraviolet-visible spectroscopy (DRUV-VIS) and electron spin resonance (ESR) spectroscopy.

2. Experimental Details

The $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ polycrystalline compound was prepared by conventional solid-state reactions, starting from quartz-type GeO_2 (Cerac 99.999%) and V_2O_5 (J.T. Baker 99.7%). To set up the phase transition of q-GeO_2 to r-GeO_2, we employ the K_2CO_3 (J.T. Baker 99.9%) reactive as a catalyst. The educts were mixed and ground in an agate mortar in order to obtain a fine powder, which was placed on a platinum crucible and then heated in a furnace in air at 1123 K for two days. At the end of the heat treatment, a solidified mixture of crystalline and amorphous phases was obtained. The amorphous component was easily removed by dissolution, stirring and washing the mixture wth hot distilled water.

The X-ray powder diffraction measurements were performed on a Bruker D8 Advance Diffractometer: Cu K_{al} radiation, and a goniometer with a lynx-eye detector. The data were collected from $2\theta = 7^\circ$ to 110° and with a step size of 0.019°, the operating conditions of the X-ray generator being 35 kV and 25 mA. The Scanning electron microscopy (SEM) observations were performed on a JEOL JSM 5600 LV microscope.

The XPS measurements were performed at ultra-high vacuum conditions in a Thermo-VG SCALAB 250 system equipped with a monochromatic Al$K\alpha$ source ($h\nu = 1486.6$ eV) and a hemispherical analyzer. The DRUV-VIS spectra of synthesized powders were taken with a Cary 5000 UV-VI-NIR spectrophotometer, equipped with a DRA-900 integration sphere accessory and politetrafluoroetilen as reflective reference material. The ESR spectra of the synthesized powders were recorded at 310 K using an ESR JEOL (JES-RE3X) spectrometer equipped with a cylindrical TE 011 mode cavity in X band (9.6 or 9.21192 GHz) with a 100 kHz field modulation. The V^{4+} concentration was determined from the double integration of the first derivative of the ESR spectrum of powders and by a comparison with a KCl-pitch standard.

3. Results

After the washing process described above, the "beige" recovered powders (Fig. 1) were subjected to an X-ray diffraction analysis. The Rietveld refinement of the X-ray pattern (see Fig. 2), clearly matches with that of the crystalline model previously reported by Rosales *et al.* [22] for the rutile-type compound $Ge_{0.74}V_{0.21}\square_{0.05}O_2$. In that compound, some percentage of Ge^{4+} is replaced by V^{5+} ions and the charge neutrality is accomplished by the presence of cation vacancies. On the other hand, SEM images show that the synthesized powder consists of long faceted rectangular crystallites (Fig. 3), a shape frequently observed on rutile type nano-crystals grown by sol-gel methods in alkaline environments [23].

In many compounds based on vanadium oxides it is very common to find the vanadium ion in different oxidation states. This leads to the well known chromophoric effect observed in both, glassy and crystalline materials [24,25], then, the "beige" color observed in the recovered powders, is probably caused by combined oxidation states of vanadium ions hosted in the crystal lattice. So, to determine the oxidation state of vanadium we perform an analysis of powders by XPS.

FIGURE 1. Powders of the synthesized $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound

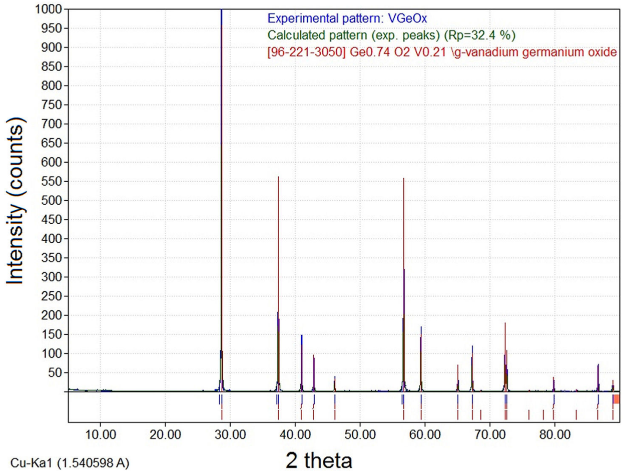

FIGURE 2. Experimental X-ray pattern obtained in the recovered microcrystalline powders compared with that reported by Rosales *et al.* [22].

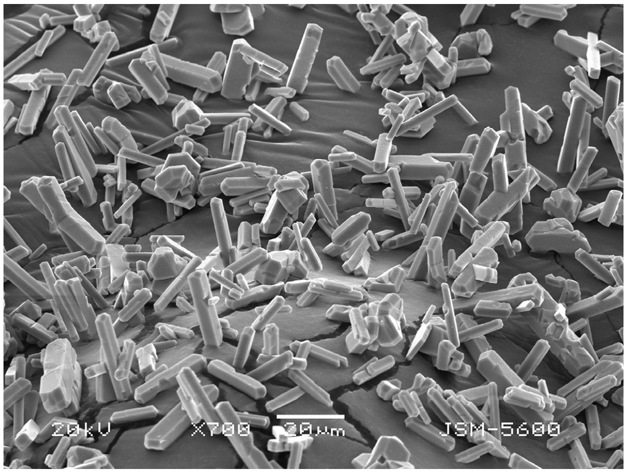

FIGURE 3. SEM image of synthesized microcrystalline powders of the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound.

The XPS spectra we obtained for this compound in the binding energy interval 510-540 eV, shows the characteristics Vp3/2, Vp1/2, Os1 bands assigned to vanadium and oxygen (Fig. 4). A detailed analysis through the deconvolution of the band corresponding to Vp3/2 zone (Fig. 5) clearly shows that this consists of two peaks located at 516 eV and 517 eV which have been assigned to V^{4+} and V^{5+} ions respectively [26], so we can assert that this two types of vanadium ions are present, at least, in the first atomic layers of synthesized microcrystals if we consider that the XPS is a surface analysis technique. Additionally, DRUV-VIS spectra taken on the recovered powders show broad absorption bands in the interval of 200 to 800 nm, which invariably can be matched by six Gaussian-shape bands centered at 230, 310,

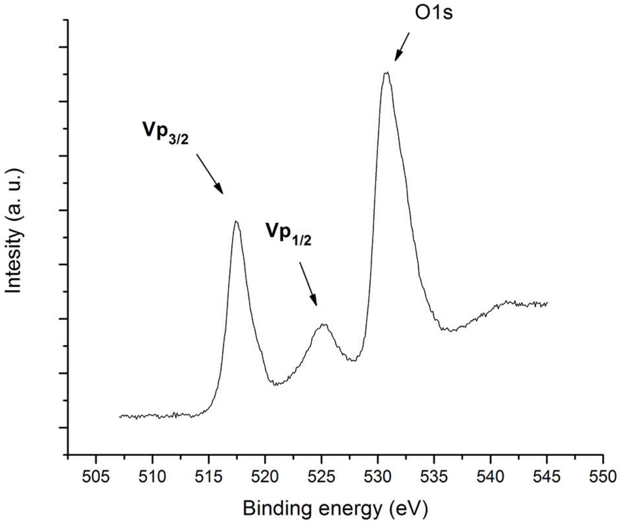

FIGURE 4. V2p and O1s bands of vanadium and oxygen detected on the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound.

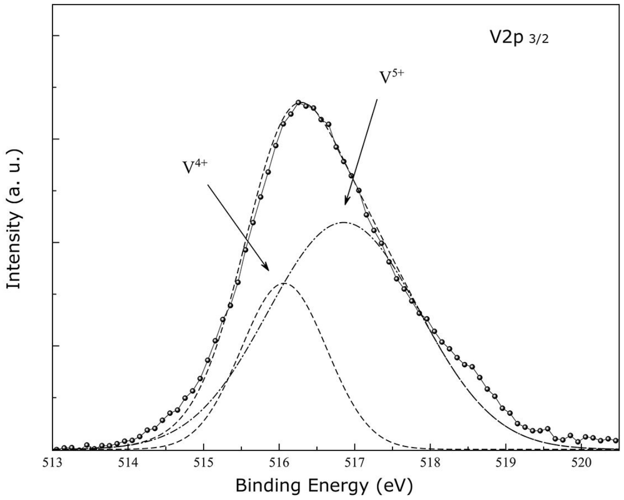

FIGURE 5. Fitting of V2p3/2 band with two peaks assigned to V^{4+} and V^{5+} oxidation states of vanadium.

400, 505, 620 and 751 nm (see Fig. 6). In this spectral region charge-transfer (C-T) and d-d transition bands of the V^{5+} and V^{4+} ions hosted in based vanadium oxide compounds have been reported [27].

On the other hand, it is well known that some physical properties of compounds based on vanadium oxide such as electronic conductivity and magnetic susceptibility are linked with the presence of vanadium ions in mixed oxidation states (as an example see Ref. 28), so to understand the physical processes that give rise to these properties, it is first necessary to determine the crystalline sites occupied by the different vanadium ions.

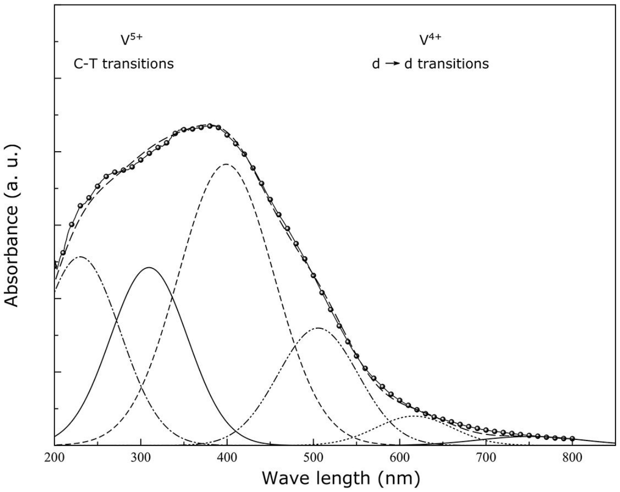

FIGURE 6. DRUV-VIS spectrum (displayed in absorbance) of recovered powders of the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound.

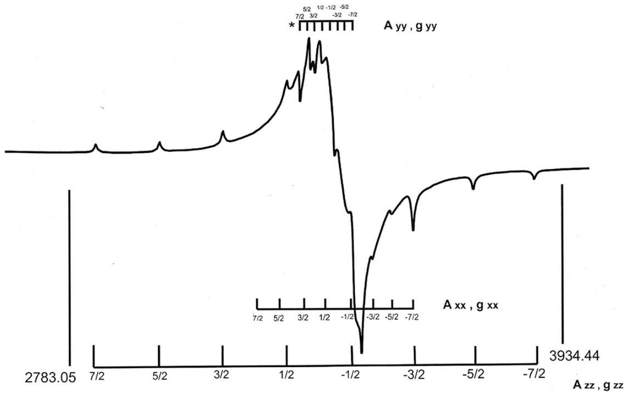

FIGURE 7. ESR spectrum taken on the synthesized powders of the compound $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound.

As we saw, the XPS measurements performed on the non-stoichiometric $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound detected the presence of V^{4+} ions hosted, at least, in the first layers of crystallites. Taking into account that V^{4+} is a paramagnetic ion, from ESR measurements it is possible to obtain information about the environment of the crystalline sites occupied by these ions trough the analysis of the spin Hamiltonian data.

The paramagnetic V^{4+} ion has the $3d^1$ electronic configuration and an electronic spin $S = 1/2$, and a nuclear spin for its V 51 isotope (natural abundance 99.5%) of I = 7/2, then an eight component hyperfine structure is expected in the ESR spectra of synthesized compound.

In this case, we used a full spin Hamiltonian to describe the spectra of V^{4+}:

$$H = \beta(gxHxSx + gyHySy + gzHzSz) + AxIxSx + AyIySy + AzIzSz$$

where β is the Bohr magneton; Hx, Hy and Hz are the components of the static magnetic field; Sx, Sy, and Sz are the spin operators of the electron; Ix, Iy, and Iz are the nuclear spin operators of the nucleus; gx, gy, and gz are the values of the anisotropic g-tensor; Ax, Ay and Az are the parallel and perpendicular hyperfine values of the hyperfine A-tensor. The experimental ESR spectrum taken on a sample of synthesized powders shows three sets of eight hyperfine transitions

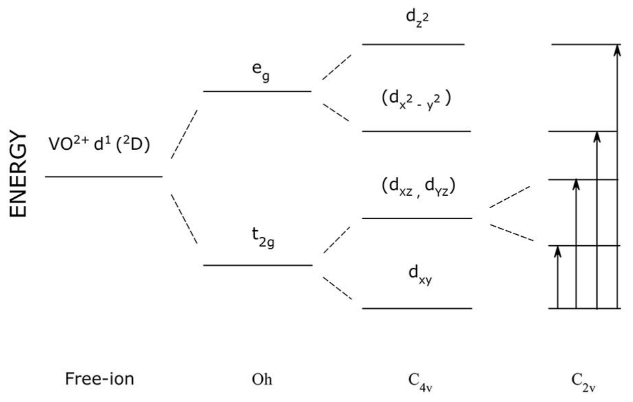

FIGURE 8. Diagram of energy levels with the assignment of the optical transitions of VO^{2+} in the symmetry C_{2V}.

(Fig. 5), one of them due to a parallel site and the other two due to perpendicular sites for the applied external magnetic field.

The spin Hamiltonian parameters deduced from computer simulation for the three sets of eight hyperfine transitions are: The parallel site to the z axis, has a hyperfine splitting $A_{zz} = 146.54$ gauss with a $g_{zz} = 1.9623$. The two perpendicular sites have splittings of; $A_{xx} = 40.69$ gauss whit $g_{xx} = 1.9514$ and $A_{yy} = 19.84$ gauss with $g_{yy} = 1.9198$. Therefore it is evident that recovered powder contains V^{4+} ions hosted at crystalline sites with orthorhombic ligand field symmetry, $i.e.$, the V^{4+} ions are possibly located at sites with a bi-axially distorted octahedral symmetry.

The ESR spectra of V^{4+} ions at crystalline sites with this kind of ligand symmetry are characterized by A_{iso} and g_{iso} values in (60-90) and (1.920-1.95) intervals respectively [29]. In our case, the calculated A_{iso} (69.02) and g_{iso} (1.945) values fall within these ranges, and are very similar to those reported in a pioneering research related to a paramagnetic resonance in polycrystalline and single crystals of rutile-type GeO_2 slightly doped with V^{4+} ions [30,31].

Finally, following the quantification procedure described in the experimental section, the V^{4+}/V_{total} proportion was estimated as 0.002.

4. Discussion

To prepare the polycrystalline $Ge_{0.74}V_{0.21}\square_{0.05}O_2$, we employed K_2CO_3 as flux and catalyst. This carbonate decomposes in K_2O and CO_2 at temperatures reached in our synthesis procedure, then, the microcrystals were grown from the melted mixtures of quartz-type GeO2 and V_2O_5 in an alkaline ambient and in a reducing atmosphere. This would account for the shape of crystallites obtained, as in the case of sol-gel methods of synthesis of rutile nanoparticles in alkaline environments [23] and for the reduction of V_{5+} to V_{4+}, which diffuses in small quantities into crystallite lattice, as we detected by ESR.

The deconvolution of the XPS spectra taken on recovered powders of synthesized compound, invariably shown the presence of vanadium as V^{5+} and V^{4+} ions, whose electronic configuration are [Ar] $3d^0$ and [Ar] $3d^1$ respectively. It is known that the V^{4+} reacts readily to form some oxy-cations such as the VO^{2+}, this molecular oxy-cation can be thought as consisting of a V^{4+} ($3d^1$) ion and a closed shell O^{2-} ion. The VO^{2+} ion has a single d electron, which gives raise the free ion term ^2D. In a crystal field of octahedral geometry, this electron occupies the t_{2g} orbital. When the electron absorbs energy it is excited to eg orbital, so, in this geometry only one optical absorption band is expected. Nevertheless, due to the non-symmetrical alignment of V=O bond in the molecular oxy-cation VO^{2+}, this ion could be hosted in lower symmetrical sites such as tetragonal (C_{4v}) or rhombic (C_{2v}). In these cases, three absorption bands are expected for tetragonal and four for the rhombic symmetry [27] (see Fig. 8).

As we see, the absorption spectra taken in the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound we synthesized, invariably can be adjusted with four bands in the region of d-d transitions of the V^{4+} ion. This result could indicate that this ion is hosted as VO^{2+} oxy-cation with a (C_{2v}) rhombic symmetry in the crystal lattice of the rutile-type $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound. Moreover, a ESR spectrum with three sets of hyperfine lines are expected for VO^{4+} in a (C_{2v}) symmetry [27], just as we from our ESR measurements on the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ compound. Similar absorption bands and ESR signals have been reported for the VO^{2+} cation hosted in sites of (C_{2v}) symmetry on CsCl single crystals [32].

In a subsequent paper we will make a detailed theoretical analysis of our ESR and DRUV-VIS results.

5. Conclusions

The characterization of microcrystalline powders of the $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), diffuse reflectance ultraviolet-visible spectroscopy (DRUV-VIS) and electron spin resonance spectroscopy (ESR) let us conclude:

- The synthesized powders of compound $Ge_{0.74}V_{0.21}\square_{0.05}O_2$ grow as long faceted rectangular micro-crystals.

- In these micro-crystals, the Ge^{4+} ions are partially replaced by V^{5+} and V^{4+}, the latter, to a lesser extent as deduced from the ESR measurements.

- The detection of four absorption bands on the DRUV-VIS spectra in a region of d-d transitions of ion V^{4+} indicates that this ion possibly is hosted in the lattice of the micro-crystallites as the VO^{2+} oxy-cation.

- The three sets of hyperfine lines obtained in the ESR spectra and the four bands of the DRUV-VIS spectra, points out that the symmetry of crystalline sites occupied by VO^{2+} cations must be the rhombic (C_{2v}).

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