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Structural characterization of bulk $ZnWO_4$ prepared by solid state method

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Uniform crystals of $ZnWO_4$ have been synthesised from the equimolar mixtures of ZnO and WO_3 by conventional solid state method. For the first time the sample has been characterised detailedly to confirm the formation of pure single phase of perovskite $ZnWO_4$. The formation of $ZnWO_4$ has been confirmed by sintering the mixtures of ZnO and WO_3 at two different temperatures one at 900 °C and other at 1000 °C. It is observed that the sample sintered at 1000 °C for 24 h shows complete formation of the single phase of $ZnWO_4$. The crystallinity and the phase formation has been confirmed by X-ray diffraction technique. X-ray photoelectron spectroscopy measurements have been carried out for the bulk $ZnWO_4$ sintered at 1000 °C for 24 h, showing 16% of Zn, 16% of W and 68% of O indicating stoichiometric $ZnWO_4$. Surface morphology studies by scanning electron microscopy showed uniform crystals of $ZnWO_4$. The purity of the compound has also been checked in depth by Energy Dispersive X-ray method indicating the absence of foreign ions apart from that, the ratio of Zn : W has been calculated and found to be 1 : 1 confirming the stoichiometric $ZnWO_4$ inside the crystals. © *2000 Kluwer Academic Publishers*

1. Introduction

In recent years, there has been growing interest in zinc tungstate ($ZnWO_4$) as a possible new material for scintillator [1, 2], laser host [3], acoustic [4], optical fiber [5] and as a sensor material for the detection of NO_2 gas [6]. It is a promising material for x-ray scintillators because its luminescence output and after glow are comparable to or better than those materials currently in use [1, 2]. In addition, zinc tungstate has the advantage of not being hygroscopic and much cheaper than those used for, like $Bi_4Ge_3O_{12}$ (BGO), a widely used scintillator material. In order to replace other materials, pure and high quality $ZnWO_4$ uniform crystals with good optical quality are needed. Generally, it has been found that reaction sintering is difficult to control, especially when a chemically homogeneous, single phase product with high purity, high density and uniform microstructure is desired. In this present investigation, we have carried out the chemical reaction of equimolar mixtures of ZnO and WO_3 (commercial high purity powders 99.98%) prepared by conventional solid state route and for the first time it has been characterized detailedly by different techniques to illustrate the microstructural properties of the bulk $ZnWO_4$.

2. Experimental procedure

5 gm of ZnO powder (reagent grade; purity 99.98%; Aldrich) is mixed with equivalent molar quantity of 14.243 gm WO_3 powder (reagent grade; purity 99.98%; Aldrich) in an agate mortar and then added 10 ml of distilled ethyl alcohol (C_2H_5OH) which is used as a disparsant to the above mixture. The contents are mixed thoroughly for 3 h to make it slurry and then dried in oven at 100 °C for 24 h. The dried powder is ground in an agate mortar and pestle and the then passed through a 150 mesh sieve to eliminate any large agglomerates. Cylindrical compacts (10 × 6 mm height) are prepared by die pressing at a pressure of 1 ton\cm^2. Sintering of cylindrical compacts are carried out in air at constant heating rate 3 °C\min, at 900 °C and 1000 °C temperatures for 24 h. The schematic flow chart of the synthesis of bulk $ZnWO_4$ has been shown in the Fig. 1. The sintered pellets have been ground in agate mortar and pestle to fine powder and analysed by XRD, EDX, XPS and SEM techniques to find out phase formation, elemental analysis, composition and morphology, respectively.

3. Characterization of bulk $ZnWO_4$

3.1. X-ray diffraction

X-ray diffraction (XRD) (model:SIEMENS D5000) with copper target, K_α radiation ($\lambda = 1.5406$ Å) is used for phase identification recording the diffracted intensities as a function of 2θ. The XRD pattern of the ZnO and WO_3 powder mixtures sintered at 800 °C and 900 °C for 24 h has been shown in the Fig. 2. This spectrum clearly shows the formation of $ZnWO_4$ is not completed even at a sintering temperature of 900 °C, showing the un-reacted mixtures of ZnO and WO_3.

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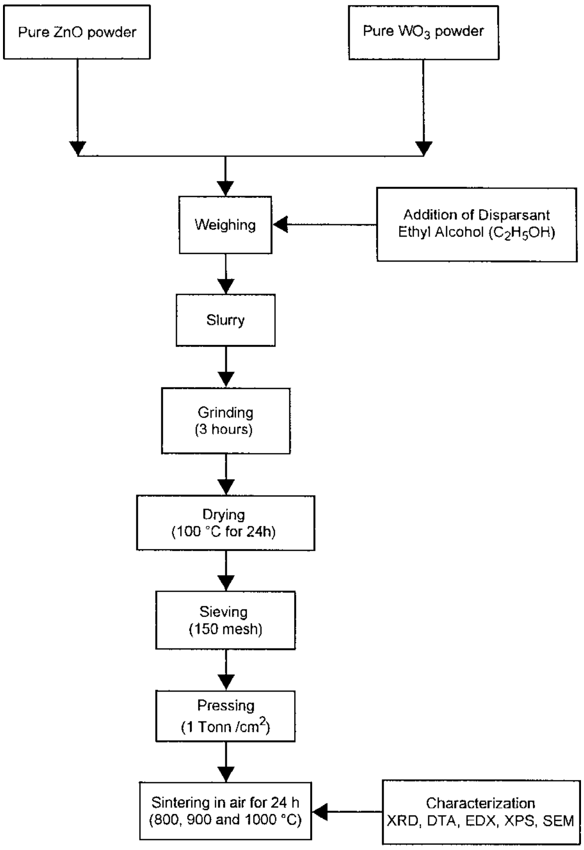

Figure 1 Schematic flow chart for the preparation of single phase $ZnWO_4$.

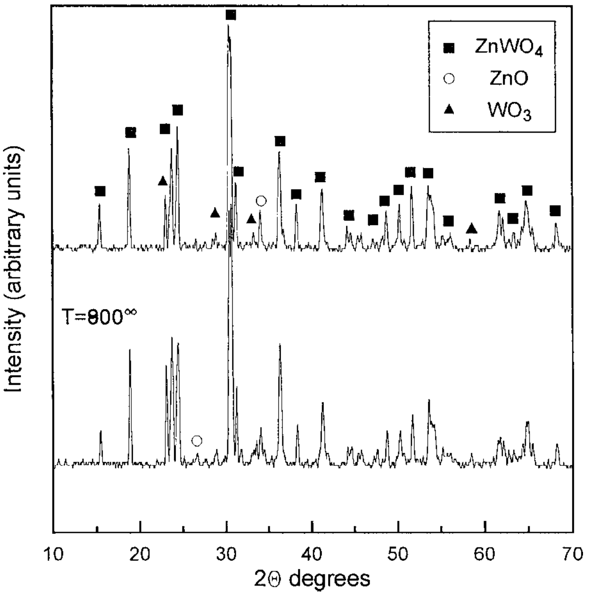

Figure 2 X-ray diffraction pattern of $ZnWO_4$ sintered at 800 °C and 900 °C/24 h.

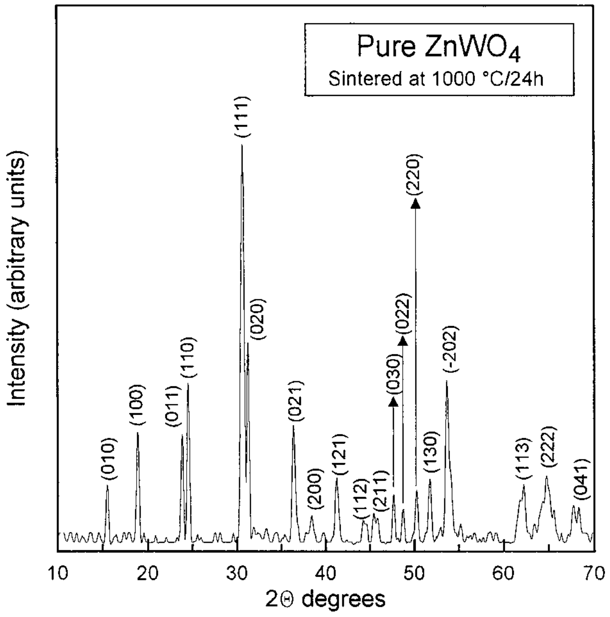

Figure 3 X-ray diffraction pattern of $ZnWO_4$ sintered at 1000 °C/24 h.

Fig. 3 shows the formation of single phase of $ZnWO_4$ at sintering temperature of 1000 °C for 24 h. The effects of sintering temperature on crystallographic structure and crystallite size for the samples sintered at 800 °C and 900 °C revealed low intensity and broad peaks indicating the crystallinity is not well defined. On the other hand, sharp and intensive peaks are observed for the sample sintered at 1000 °C for 24 h, indicating a higher degree of crystallinity. For the sample sintered at 1000 °C for 24 h, all the diffraction lines agree with reported values and match with the JCPDS data confirming the formation of monoclinic $ZnWO_4$ structure. From the spectra the lattice parameters have been calculated and found to be $a = 4.692$ Å, $b = 5.719$ Å, $c = 4.924$ Å which are in good agreement with the reported values from the JCPDS data. The crystallite size is calculated and found to be 456 Å by Scherrer formula applied to the (111) orientation which is the maximum reflection of the monoclinic structure of $ZnWO_4$ at $2\theta = 30.5°$. $ZnWO_4$ has the monoclinic wolframite structure with C_{2h} point group symmetry and P 2/c space group. It has two formula units per unit cell, with lattice parameters $a = 4.72$ Å, $b = 5.72$ Å, $c = 4.93$ Å and $\beta = 90°05'$. The unit cell of $ZnWO_4$ is isomorphic to those of a group of tungstates (Cd, Mg, Ni, Fe, Co and Mn) that contain octahedral WO_6 groups [6].

3.2. Thermogravimetric and differential thermal analysis

Thermo-gravimetric analysis (TGA) and Differential Thermal Analysis (DTA) of the sample sintered at

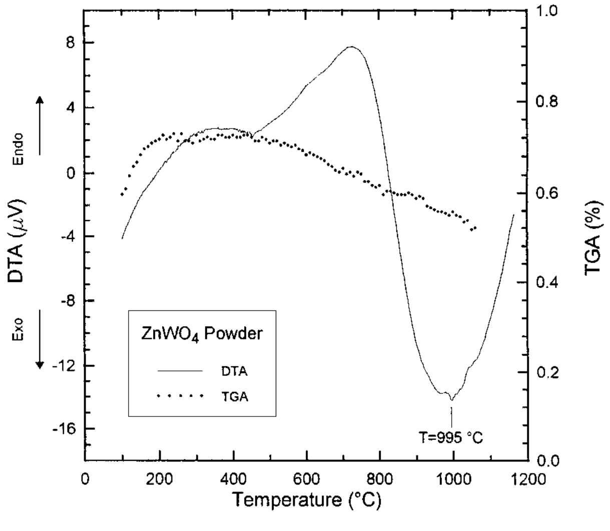

Figure 4 Thermo Gravimetric and Differential Thermal Analysis of pure bulk $ZnWO_4$.

1000 °C for 24 h have been carried out to determine the weight loss as well as the exact temperature for the formation of $ZnWO_4$. The DTA and TGA curves for $ZnWO_4$ powder in the temperature range 20–1200 °C at a heating rate of 10 °C min^{-1} are shown in the Fig. 4. The TGA curve indicates that there is a negligible weight loss. On the other hand, we have observed an exothermic peak at 995 °C, which is attributed to the heat loss during the formation of single phase $ZnWO_4$ from the mixtures of ZnO and WO_3. This has been further confirmed by the X-ray diffraction technique for the same sample sintered at 1000 °C for 24 h by which, we have observed the formation of single phase of $ZnWO_4$. The broad shoulder between 600 and 700 °C is due to the effect of radiant heat between the crucibles and the tube wall of the furnace.

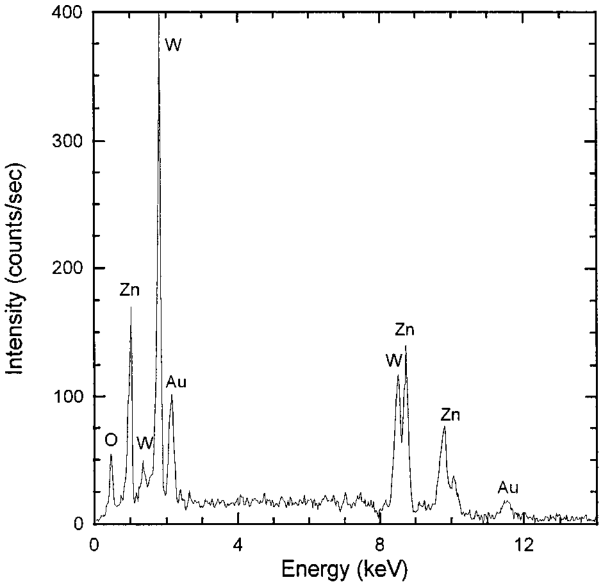

Figure 5 Energy Dispersive X-ray Spectrum of $ZnWO_4$ powder sintered at 1000 °C/24 h.

3.3. Energy dispersive X-ray analysis

Energy Dispersive X-ray Analysis (EDX) has been carried to find out the elemental analysis for the sample sintered at 1000 °C for 24 h as shown in the Fig. 5.

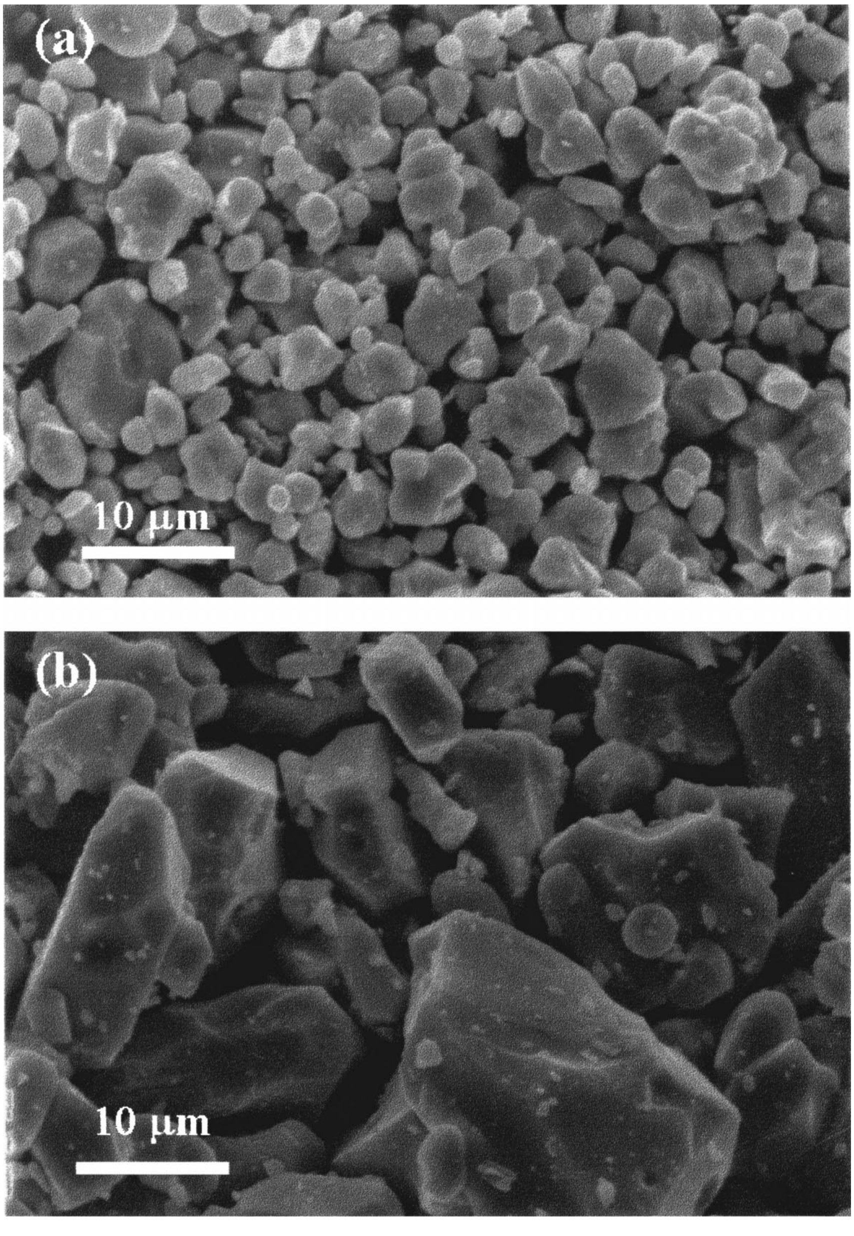

Figure 6 Scanning Electron Micrographs of $ZnWO_4$ powder sintered at (a) 900 °C (b) 1000 °C.

The spectrum shows the presence of Zn, W and O, apart from the Au which has been used for avoiding the charging effect, indicating the purity of the compound. The ratio of Zn and W has been calculated and found to be about 50% and 50% (within the experimental accuracy) respectively when compared to 50% and 50% of Zn and W in stoichiometric $ZnWO_4$.

3.4. Scanning electron microscopy

Fig. 6 shows the scanning electron micrographs of bulk $ZnWO_4$ samples after sintering at 900 °C (a) and 1000 °C for 24 h (b), respectively. Since no change has been observed for 800 °C and 900 °C samples we show here only 900 °C sintered sample. The effect of sintering temperature on crystallite size for the sample sintered at 900 °C for 24 h, reveals the formation of small crystals of $ZnWO_4$ along with unreacted ZnO and WO_3 indicating that the crystallinity of $ZnWO_4$ is not well defined. The presence of unreacted ZnO and WO_3 crystallites has been deduced from EDX analysis on different grains and comparing the obtained results. From an accurate analysis of these results, one can distinguish the different nature of the grains even if the dominant signal, obtained with this technical analysis, comes from the bulk of the sample.

On the other hand, sample sintered at 1000 °C for 24 h shows a well crystallisation of $ZnWO_4$. In fact, on this sample EDX analysis on several grains has not shown sizeable variation on the crystallite stoichiometry. Furthermore, from the image a growth of the crystal size can be observed.

3.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy studies of the samples sintered at 800 °C, 900 °C and 1000 °C for 24 h have been performed using the PHI ESCA system equipped with an Al K_α photon source ($h\nu = 1486.6$ eV) and a concentric hemispherical analyser. Fig. 7 shows the survey scans acquired in the range of 0–1100 eV of WO_3 and ZnO powders and of $ZnWO_4$ sample sintered at different temperatures. No contaminant species are detectable within the sensitivity of the technique. Only a small amount of adsorbed carbon is present on the spectra. This peak was used to calibrate the acquired spectra, and the position of the C 1s peak was located at binding energy (BE) of 284.5 eV [7]. From the detailed spectra of the Zn 2p, W 4f and O 1s peaks, we can obtain the exact composition of the compound, by calculating the atomic concentration of the individual species using the sensitivity factors [7]. We have found 1 : 1 for Zn and W and 1 : 4 for W : O indicating the stoichiometric composition of $ZnWO_4$ for all the sintered samples. Both XPS and EDX composition analyses, obtained from the peak area values, are not able to distinguish between a mixture of ZnO, WO_3 and a stoichiometric $ZnWO_4$ sample. In fact, an equimolar mixture of ZnO and WO_3 and $ZnWO_4$ compound have the same atomic percentage concentration.

In our case this idea is confirmed from the X-ray diffraction analysis where we have obtained a mixture of different phases (ZnO, WO_3 and $ZnWO_4$) for samples sintered at 800 °C and 900 °C and a correct crystalline structure of $ZnWO_4$ for the sample sintered at 1000 °C, while the XPS composition analysis applied on all these three samples gives the same result. The formation of the right $ZnWO_4$ phase is, instead, clearly evident when a detailed analysis on the binding energy of the Zn 2p and W 4f peaks is performed. In Fig. 8 the detailed spectra of the Zn 2p and W 4f peaks for different samples are reported. It is note worthy to mention here that our samples have shown no shift for tungsten 4f and a small shift towards higher binding energy for zinc 2p, on going from 800 °C to 1000 °C sintering temperature. This behaviour can be explained on the basis of the crystalline structure of the $ZnWO_4$, where the unit cell of $ZnWO_4$ is isomorphic to those of a group tungstates that contain octahedral WO_6 groups [5]. This confirms the unshifted W 4f binding energy in the sintered samples. On the other hand, the shift obtained for the Zn 2p can be explained by the chemical

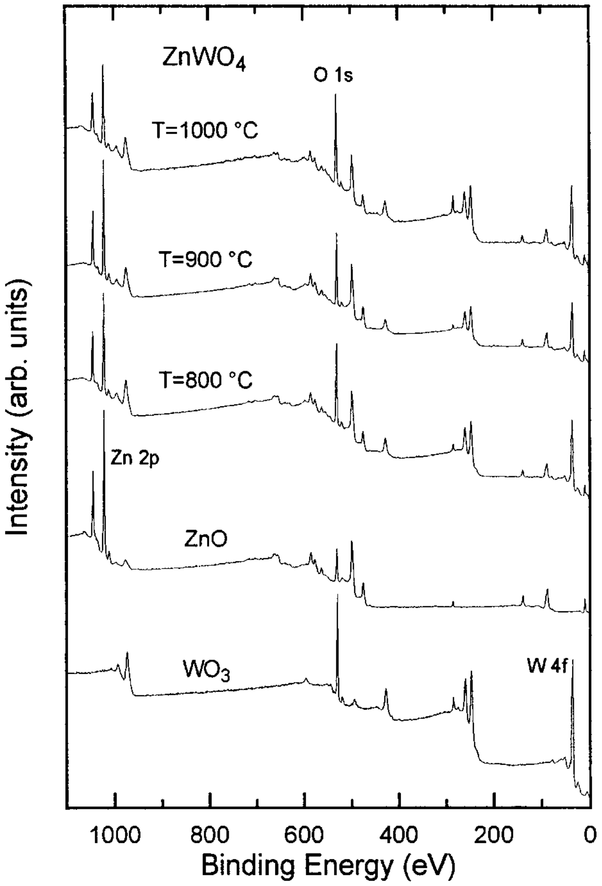

Figure 7 X-ray photoelectron spectroscopy survey scan of bulk ZnO, WO_3 and $ZnWO_4$ measured at different temperatures.

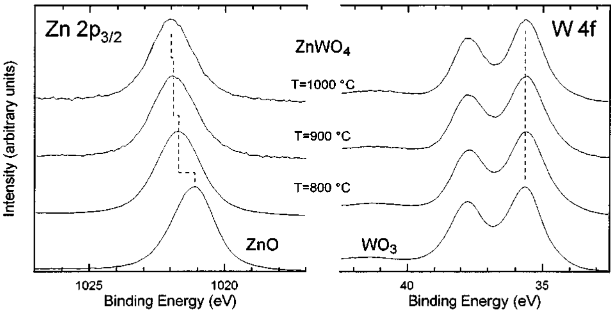

Figure 8 Detailed XPS spectra of W 4f and Zn $2p_{3/2}$ of bulk WO_3, ZnO and $ZnWO_4$ measured at different temperatures.

environment of Zn that changes on going from ZnO to $ZnWO_4$. Furthermore, the Zn 2p peak shifts towards higher binding energies as the sintering temperature increases from 800 °C to 1000 °C. This behaviour can also be explained by the XRD results, where we have observed a nearly completed formation of $ZnWO_4$ at 800 and 900 °C compared to 1000 °C sintered samples. To our knowledge, these are the first XPS measurements on the $ZnWO_4$ compound.

4. Conclusions

In conclusion, we have synthesised high purity bulk single phase $ZnWO_4$ from the equimolar mixtures of ZnO and WO_3. The formation of this single phase has been confirmed by X-ray diffraction for the sample sintered at 1000 °C for 24 h. The purity of the compound is confirmed by energy dispersive X-ray analysis as well as X-ray photoelectron spectroscopy studies indicating the absence of foreign ions and the exact percentages of composition, 16% of Zn, 16% of W and 68% of O in the bulk $ZnWO_4$. Scanning electron microscopy pictures of $ZnWO_4$ powders sintered at 1000 °C for 24 h reveals the uniform rock like structures.

References

1. T. OI, K. TAKAGI and T. FUKAZAWA, *Appl. Phys. Letts.* **36** (1980) 278.
2. B. C. GRABMAIER, *IEEE Trans. Nuc. Sci.* **NS-31** (1984) 372.
3. W. KOLBE, K. PETERMANN and G. HUBER, *IEEE. J. Quant.Electron.* **QE-21** (1985) 1596.
4. Y. V. PISAREVSKII, I. M. SILVETROVA, R. VOSZKA and A. PÈTER. *Physical Review B* **43** (1990) 10356.
5. H. WANG, F. D. MEDINA, Y. D. ZHOU and Q. N. ZHANG, *ibid.* **45** (1992) 10356.
6. O. S. FILIPSENKO, E. A. POBEDIMSKAYA, V. I. PONOMAREV and N. V. BELOV, *Kristallografia* **13** (1968) 1073.
7. Handbook of X-ray Photolectron Spectroscopy, edited by J. Chastain (Perkin Elmer Corporation, Eden Prairie, Minnesota, USA 1992).

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