OPTICAL PROPERTIES OF CALCIUM DOPED $BiVO_4$ DIRECT WIDE BAND SEMICONDUCTORS

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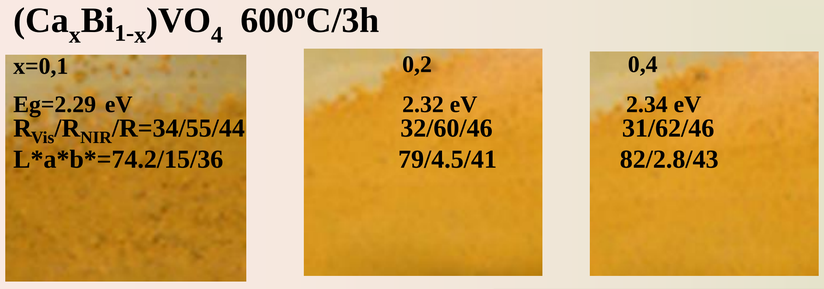
INTRODUCTION

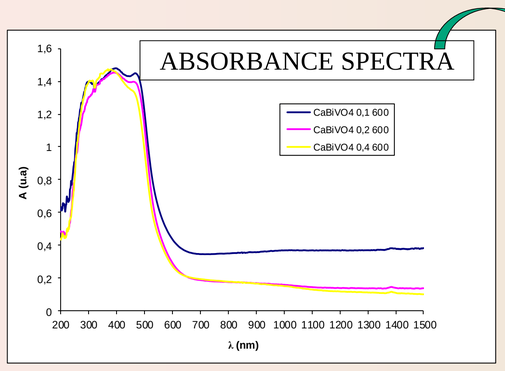
$BiVO_4$ exists in four polymorphs: orthorhombic, zircon-tetragonal, monoclinic, and scheelite-tetragonal structure. Although orthorhombic is the most common phase in nature, (mineral pucherite), they have not been synthesized in the laboratory. The low temperature synthesis of $BiVO_4$ produces the zircon-tetragonal phase with bandgap 2.9 eV that at 528 K, transforms into the monoclinic phase, reversible to tetragonal by adjusting the temperature. In these crystal structures, four O atoms in tetrahedral coordination coordinate V and each Bi is coordinated to eight O atoms from eight different VO_4 tetrahedral units. Monoclinic $BiVO_4$ (*I2/b*) has garnered interest for PEC application from seawater which is much more difficult due to the presence of contaminating ions and a more harsh corrosive environment (1). $BiVO_4$ had a photocurrent density of 2.16 mA cm^{-2} at 1.0 V_{RHE} in natural seawater under AM 1.5G sunlight (1000 W m^{-2}), and exhibited the highest incident photon conversion efficiency IPCE at 1.0 V_{RHE} in the visible light region of 440–480 nm among all known oxide photoanodes (2).

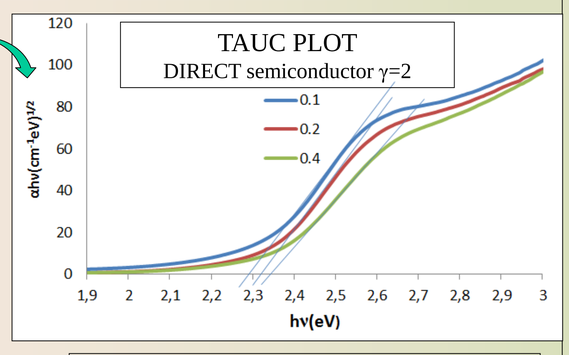
AIMS

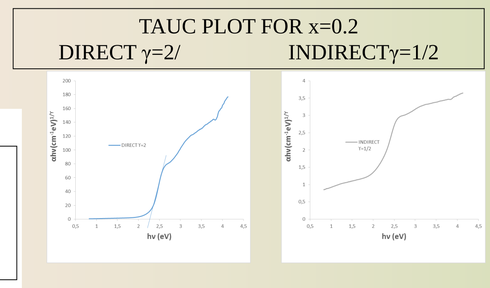
In this communication aliovalent $Ca_xBi_{1-x}VO_4$ x=0.05, 0.1, 0.2, 0.4 solid solutions have synthesized by solid state reaction method using m-Bi_2O_3, $CaCO_3$ and NH_4VO_3 as raw precursors that were fired at 600 and 1000ºC with soaking time of 3 h. The samples were characterized by XRD, UV-Vis-NIR, CIEL*a*b* and Tauc analysis (3) in order to measure the the evolution of the bandgap, NIR reflectance and the stability of the semiconductor with temperature (4).

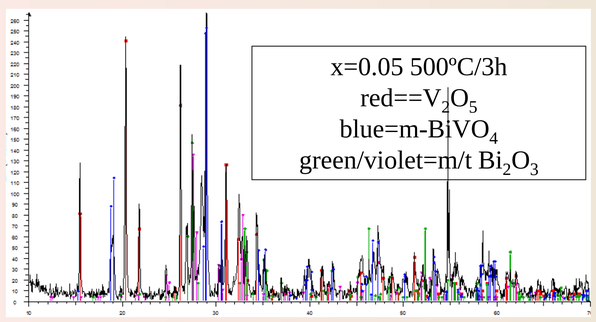
$(Ca_xBi_{1-x})VO_4$ 600ºC/3h

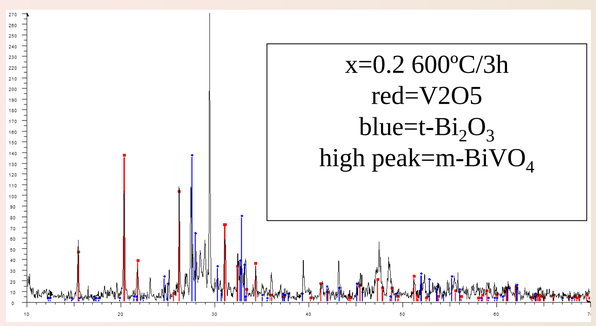


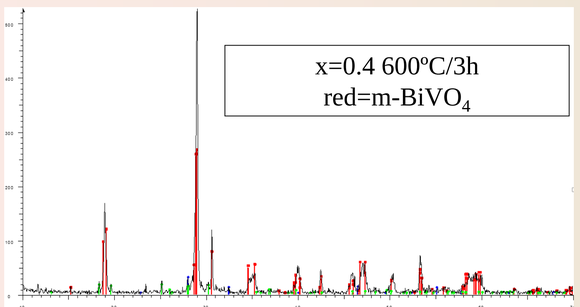


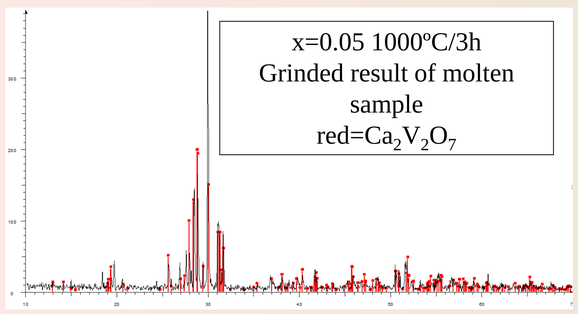


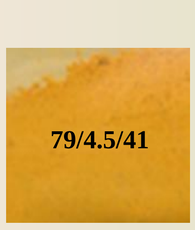


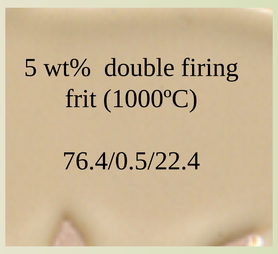


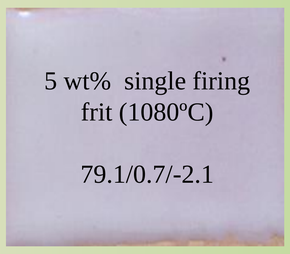


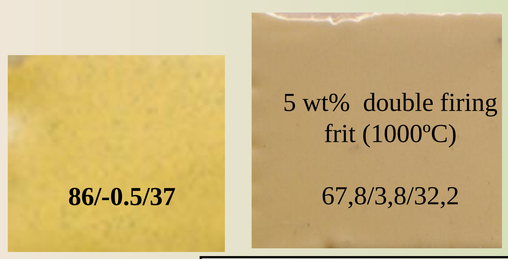












EXPERIMENTAL

X-Ray Diffraction (XRD) on a Siemens D5000 diffractometer using Cu K_α radiation (10-70 º2θ range, scan rate 0.02 º2θ/s, 4 s per step and 40 kV and 20 mA conditions).

L*a*b* color parameters of samples measured following the CIE-L*a*b* (Commission Internationale de l'Éclairage) colorimetric method using a X-Rite SP60 spectrometer, with standard lighting D65 and 10º observer. On this method, L* is a measure of lightness (100=white, 0=black) and a* and b* of color parameters (-a*=green, +a*=red, -b*=blue, +b*=yellow).

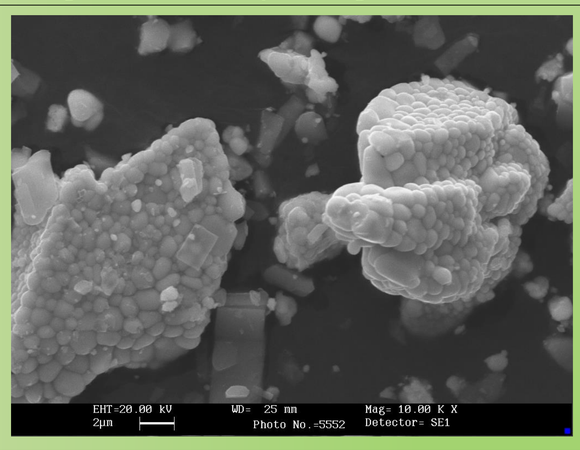
UV-Vis-NIR spectra of samples and also of the applications of the pigments samples were collected using a Jasco V670 spectrometer through diffuse reflectance technique, which gives data in absorbance using arbitrary units (A) or in reflectance units (R(%)). Band gap energy of semiconductors was calculated by Tauc plot using the UV-Vis-NIR spectra of Kubelka-Munk model.

Total solar reflectance R and solar reflectance in the NIR range R_{NIR} evaluated from UV-Vis-NIR spectra through diffuse reflectance technique as the integral of the measured spectral reflectance and the solar irradiance divided by the integral of the solar irradiance in the range of 350 to 2500 nm for R, 700 to 2500 nm for R_{NIR} or 350-700 nm for R_{Vis} as in:

$$R = \frac{3\int_{502}^{500}(\lambda)i(\lambda)d\lambda}{3\int_{502}^{500}(\lambda)d\lambda}$$

Where, (λ) is the spectral reflectance (Wm^{-2}) measured from UV-Vis-NIR spectroscopy and ***i*** (λ) is the standard solar irradiation ($Wm^{-2}nm^{-1}$) according to the American Society for Testing and Materials(ASTM) Standard G173-03.

SEM-EDX : samples show agglomerates of fine particles of 1 µm of particle size



CIEL*a*b*COLOR AND R_{NIR} PARMETERS

Compared with yellow-green precursor m-Bi_2O_3 (L*a*b*=89.7/-2.5/21) and the dark orange-yellow of commercial yellow $PbCrO_4$ (74.6/22.2/61) the Ca-BiVO4 solid solutions shows an intermediate shade (e.g. 79/4.5/41 for x=0.4). The solid solutions give brigh tellow shade (b*=22-32) in double firing glaze at 1000ºC but appeears colorless in high temperature single fire glazes. R_{NIR} increase with x associated to a better yellow performance.

CONCLUSIONS

An increase in NIR reflectance, associated to a decrease of the band gap, was detected with x. At 1000ºC samples melt and a yellow glass-ceramic showing $Ca_2V_2O_7$ devitrifications is observed that 5 wt% glazed in a double firing frit (1000ºC) shows a yellow color (L*a*b*=67.8/3.8/32.2) but is colorless in higher temperature single fire glazes.

Acknowledgement

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