High-Throughput Synthesis and Characterization of BiMoVOX Materials

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Abstract. The high throughput synthesis and characterization of a particular family of ceramic materials, bismuth molybdenum vanadium oxides (BiMoVOX), suitable as inorganic yellow pigments and low temperature oxidation catalysts, is described. Samples, synthesized by calcination and peroxo sol-gel methods, are characterized by X-ray powder diffraction, UV-visible and XAFS spectroscopy. A combined high-throughput XRD/XAFS study of a 54 samples array, with simultaneous refinement of data of both techniques, has been performed. Molybdenum doping of bismuth vanadate results in a phase transition from monoclinic $BiVO_4$ to tetragonal $Bi(V,Mo)O_4$, both of scheelite type. Both central metals, V^{5+} and Mo^{6+}, remain in a tetrahedral coordination. UV/visible spectroscopy identifies a linear blue shift as a function of Mo^{6+} amount.

Keywords: High-Throughput, XAFS, BiMoVOX, pigments, combined XAFS/XRD analysis.
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INTRODUCTION

High throughput and combinatorial techniques have been used in the pharmaceutical industry for many years. Parallel synthesis and screening for biological activity have resulted in the discovery of numerous new potential drug molecules. This approach has more recently been adapted for inorganic synthesis with the aim of discovering novel materials [1]. X-ray diffraction (XRD) methods are currently one of the most widely explored methods for the high throughput screening of structures, but their application is intrinsically limited to crystalline samples with sufficient long-range order. In this project we have developed high-throughput characterization techniques, including X-ray absorption fine structure (XAFS) spectroscopy to allow in situ characterization of materials without long-range ordering.

This study describes the synthesis and characterization of a particular family of ceramic materials, bismuth molybdenum vanadium oxides, BiMoVOX, suitable as inorganic pigment [2] and low temperature heterogeneous oxidation catalysts [3].

EXPERIMENTAL

Two different method of synthesis have been utilized to obtain BiMoVOX ($Bi_{1-x/3}V_{1-x}Mo_xO_4$, with $0.05 < x < 0.45$) materials: (1) calcination and (2) peroxo sol-gel route suitable in high throughput techniques.

In order to carry out numerous reactions in parallel on an alumina substrate we used a reusable mask system, with a 6x9 grid of 5-mm holes.

Arrays of BiMoVOX series were prepared by peroxo sol-gel route, from solutions of the metal nitrates or ammoniates (about 0.5 M) in diluted nitric acid or hydrogen peroxide. These were dispensed into a standard 54 well plate in the appropriate ratios and mixed using a Packard Multiprobe II robot. Solvent was evaporated at 60°C overnight in air before the tiles were fired at 700°C in oxygen atmosphere for 10 hours.

Colour measurements of bulk samples were performed using a Perkin Elmer Lambda 35 UV/vis spectrometer. Diffraction patterns were measured using a Siemens D5000 (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å) for bulk series, and a Bruker D8 Discover with General Area Detector Diffraction System (GADDS) for combinatorial screening; the high throughput XRD scan time was two minutes, allowing data for each 54

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member array to be collected in under two hours. Phases present were identified by comparison with the PDF2 database. Data refinements of bulk materials were performed using GSAS program [4].

High throughput XAFS analysis was performed using a XYZ translation stage (Parker) for sample positioning. An array was aligned at 45° towards the beam in order to maximize the solid angle of the detector, which was positioned approximately 5 cm above the well plate. Data acquisition and automatic movement of the XYZ stage as well as synchronization with the station main computer through the TCP/IP protocol were achieved using LabVIEW software [5]. XAFS spectra were collected at the Daresbury Laboratory SRS on Station 9.3 in fluorescence mode. A double crystal monochromator, Si(111), together with a 9 element Ge solid state fluorescence detector were used for XAFS measurement in the energy range, 20 KeV, of Molybdenum K-edge. EXAFS data analysis relative to the bulk series was performed using the *PAXAS* [6] and *Excurve98* [7] programs.

High throughput combined XAFS/XRD analysis was executed using *X-Mult* and *P* programs [8]. Both programs are in development to process and analyze arrays of EXAFS and XRD data in a more efficient manner. X-Mult allows automatic background subtraction of a large number of XAFS spectra, while P refines multiple EXAFS and XRD results simultaneously. A representative example of combined XRD/EXAFS refinement data obtained by P is shown in Fig. 4.

RESULTS

Doping of monoclinic $BiVO_4$ with Mo leads to a phase transition from monoclinic to a tetragonal scheelite structure [9], as displayed by XRD in Fig. 1 for the sol-gel series, (samples have the same colour in all XRD/XAFS/UV-vis graphics). With increasing Mo concentration, the XRD peak positions shift, reflecting the changes in d-spacing and consequent volume cell growth by incorporation of the molybdenum ions into the $BiVO_4$ structure [10].

Mo K-edge XANES spectra are presented in Fig. 2. The pre-edge feature at ~ 20013 eV originates from a 1s to 4d electronic transition. This transition is dipole-forbidden in centrosymmetric structures, indicating that the Mo^{6+} centers adopt tetrahedral symmetry with the result of p-d orbital mixing. Literature reports Mo^{6+} ions directly replace V^{5+} while keeping a tetrahedral coordination [11]. EXAFS data analysis indicates Mo^{6+} ions are bonded to four oxygens.

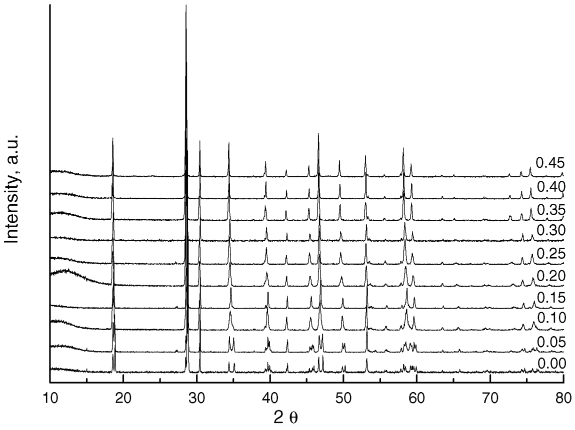

FIGURE 1. XRD diffraction pattern of BiMoVOX bulk series made by the peroxo sol-gel reaction.

A linear increase in Mo-O bondlength as a function of Mo is observed, Table 1. The materials synthesised by the calcination method do not display this trend probably because this synthesis procedure leads to inhomogeneous materials.

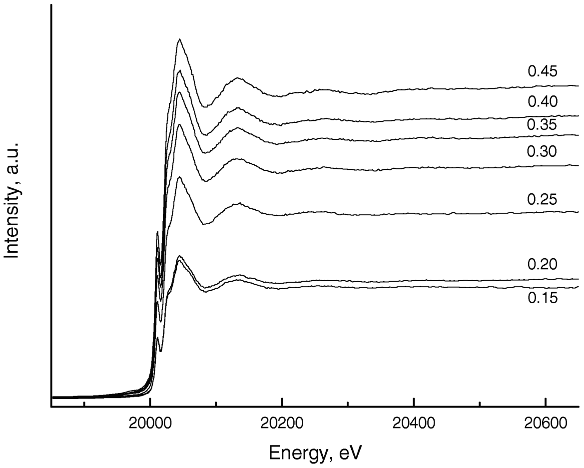

FIGURE 2. XAFS analysis of BiMoVOX bulk series made by peroxo sol-gel reaction.

TABLE 1. Mo-O bond-length.

$Bi_{1-x/3}V_{1-x}Mo_xO_4$	Mo-O, Å Calcin. (bulk)	Mo-O, Å Sol gel (bulk)	Mo-O, Å Sol gel (array)
X = 0.15	1.756(8)	1.755(8)	1.757(9)
X = 0.20	1.752(8)	1.732(11)	1.783(10)
X = 0.25	1.750(9)	1.734(12)	1.740(14)
X = 0.30	1.757(9)	1.751(9)	1.767(7)
X = 0.35	1.759(9)	1.756(10)	1.761(5)
X = 0.40	1.759(10)	1.759(10)	1.751(8)
X = 0.45	1.758(11)	1.767(10)	1.750(7)

The colour of both $BiVO_4$ and BiMoVOX materials arises from a ligand O^{2-} to metal (V^{5+} or Mo^{6+}) charge-transfer transition. Colour curves of sol-gel BiMoVOX series show (for $x > 0.20$) a linear increasing blue shift of the optical band edge with the amount of Mo^{6+}. The band gaps of the BiMoVOX series were estimated to be 2.35 – 2.41 eV from the onsets of the absorption edges, when x increase from 0.05 to 0.45, Fig. 3. Materials synthesized with calcination reactions show higher band edges values for all samples. This difference is most likely related to the synthesis method since colour and colour intensity depend on many factors including phase composition, stoichiometry, particle size and morphology. Therefore it has proven very difficult to control the pigmentary colours of bismuth vanadate and BiMoVOX materials.

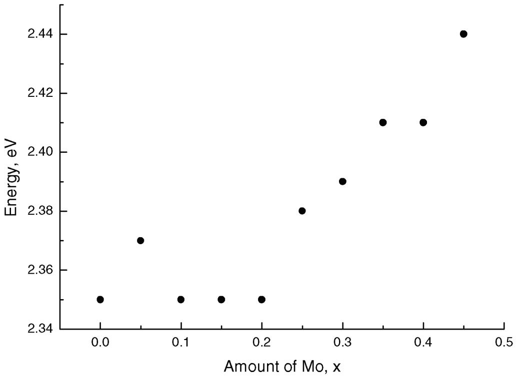

FIGURE 3. Band gap of BiMoVOX bulk series made by peroxo sol-gel reaction.

Experimental data obtained for BiMoVOX materials deposited onto the HTP array and analysed with the new programs show similar XRD refinement results as for the bulk series. A phase transition from monoclinic $BiVO_4$ to a tetragonal scheelite structure is observed, with an increase in cell volume. The first shell EXAFS results for the array series are shown in Table 1. Mo-O bond length values comparable to the bulk series are obtained, however, no linear trend between bond length and Mo doping is observed. This is most likely due to less homogeneous samples compared to the materials prepared in bulk.

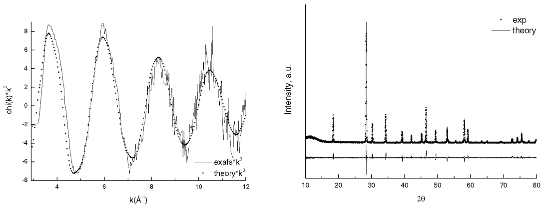

FIGURE 4. Combined XAFS/XRD Analysis of BiMoVOX bulk sol-gel sample made by "P" program.

DISCUSSION AND CONCLUSION

Introduction of synchrotron-based XAFS spectroscopy in high-throughput methodology has been achieved. Arrays of BiMoVOX compounds are prepared in a high throughput manner, with the peroxo sol-gel route using robotic methodologies. Automatic acquisition of XAFS and XRD data for large arrays of samples is performed. Further optimisation of the process is required, however, with the current synthesis and analysis system an array of 54 samples can be prepared and characterised in about 2 days. This presents a significant improvement on the standard one-at-a-time approach. The main challenge of high throughput experimentation is the analysis and interpretation of the large amounts of data created. Improvements in data handling using specific software developed for combined XAFS/XRD high-throughput data analysis should reduces this problem and will allow more complex pigment systems to be studied efficiently. Vanadium K-edge XAFS data will be collected to complete the BiMoVOX material characterization.

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