On possible Cu doping of Bi_2WO_6

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There has been some controversy over the possibility of doping Bi_2WO_6 with Cu, in which X-ray powder diffraction (XRD) was used to determine the phase purity of materials. By electron probe microanalysis (EPMA), we find that Cu doping does not result in the formation of single phase material and does not enter the structure of Bi_2WO_6. Care is needed in using XRD to assess phase purity of materials, especially solid solution phases and also in cases where partial sample volatilisation may have occurred during synthesis.

Introduction

The high oxide ion conductivity displayed by $Bi_4V_2O_{11}$ and the corresponding BIMEVOX phases obtained by introduction of lower valence cations into V sites has generated a lot of interest in the Aurivillius phases as oxide ion conductors.[1–7] $Bi_4V_2O_{11}$, consisting of $[Bi_2O_2]^{2+}$ sheets interleaved with $[VO_{3.5}\square_{0.5}]^{2-}$ perovskite slabs, where $\square$ represents an oxide ion vacancy, can be considered as the $n=1$ member of the Aurivillius family which has the general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$. The success of doping $Bi_4V_2O_{11}$ has led to interest in the doping of Bi_2WO_6, which is almost isostructural with $Bi_4V_2O_{11}$ but does not contain oxygen vacancies. It was postulated that substitution of W by lower valence cations could lead to an extrinsic oxygen deficiency with enhanced oxide ion conductivity.[8,9] Sharma et al.[8] reported that anion-deficient solid solutions of the general formula $Bi_2W_{1-x}Cu_xO_{6-2x}$ existed for the range $0 < x \leqslant 0.8$. Phases up to $x=0.65$ adopted the orthorhombic Bi_2WO_6 structure while those in the range of $0.7 \leqslant x \leqslant 0.8$ had a tetragonal structure; the $x=0.7$ composition exhibited higher conductivity than the best BIMEVOX phases. Vannier et al.[10] questioned the phase purity of the solid solutions as the XRD patterns reported by Sharma et al. were of rather poor quality. Their experiments on the $x=0.75$ composition showed that instead of a new solid solution, the material was a mixture of $7Bi_2O_3 \cdot 2WO_3$, Bi_2CuO_4 and CuO. Sharma et al.[11] subsequently reported that the solid solution $Bi_2O_3–(1-x)WO_3–xCuO$ existed up to $x=0.7$ and exhibited ferroelectric behaviour similar to Bi_2WO_6.

In most studies, X-ray powder diffraction is used as the standard technique of phase identification. We have found that XRD alone sometimes gives misleading information, especially in materials of variable composition as in the case of K-doped $Bi_4V_2O_{11}$.[12] An additional technique such as EPMA may be required to both confirm the phase purity of materials and to determine accurate compositions of solid solution phases. Here we present results of a study on Cu-doped Bi_2WO_6 using combined XRD and EPMA techniques. As well as limitations in the use of XRD to ascertain phase purity, loss of one or more components by volatilisation at high temperatures can lead to difficulties in the interpretation of results: in the present

materials, significant volatilisation of Bi_2O_3 occurs at melting temperatures.

Experimental

Materials of composition $Bi_2W_{1-x}Cu_xO_{6-2x}$ with x ranging from 0 to 0.75 were prepared by solid state reaction at temperatures just below melting as reported by Sharma et al.[8] Reagents used were Bi_2O_3 (99.9% Aldrich), WO_3 (99.995% Aldrich) and CuO (99.9 Aldrich). Bi_2O_3 and WO_3 were dried at 300 °C while CuO was dried at 700 °C prior to weighing. Mixtures were weighed (ca. 3 g in total), ground with acetone in an agate mortar, dried and fired in Au or Pt foil boats at temperatures ranging from 830 to 1050 °C for 20 h, depending on composition, and then quenched to room temperature. Additional heat treatment experiments at temperatures just below and just above the melting point were carried out on samples of composition $x=0.05$, 0.1, 0.7 and 0.75. For the composition $x=0.1$, the effect of melting at different temperatures and for different durations was studied in detail. All the materials were analysed by XRD using a Shimadzu XRD-6000 diffractometer (Cu Kα radiation) at a scan rate of $2°\ 2\theta\ min^{-1}$. EPMA was carried out on samples with $x=0.1$ and 0.7 using a Cameca SX51 instrument with an incident beam energy of 20 kV and a current of 50 nA. All samples were polished to $<1\ \mu m$ and carbon coated. The standards used were Bi_2CuO_4 for Bi Mα and Cu Kα and WO_3 for W Lα or W Mα. Oxygen contents were calculated by stoichiometry, assuming valence states Bi^{3+}, W^{6+} and Cu^{2+}.

Results and discussion

A partial phase diagram of the $Bi_2O_3–CuO–WO_3$ system, determined from the results of heat treatment experiments at subsolidus temperatures, is shown in Fig. 1. The hypothetical solid solution of formula $Bi_2W_{1-x}Cu_xO_{6-2x}$, shown by a dashed line, passes through two three-phase triangles consisting of $Bi_2WO_6–CuO–Bi_{14}W_2O_{27}$ and $Bi_{14}W_2O_{27}–CuO–Bi_2CuO_4$, respectively, with a cross-over at the composition $x=0.71$. As discussed later, by combined XRD and EPMA,

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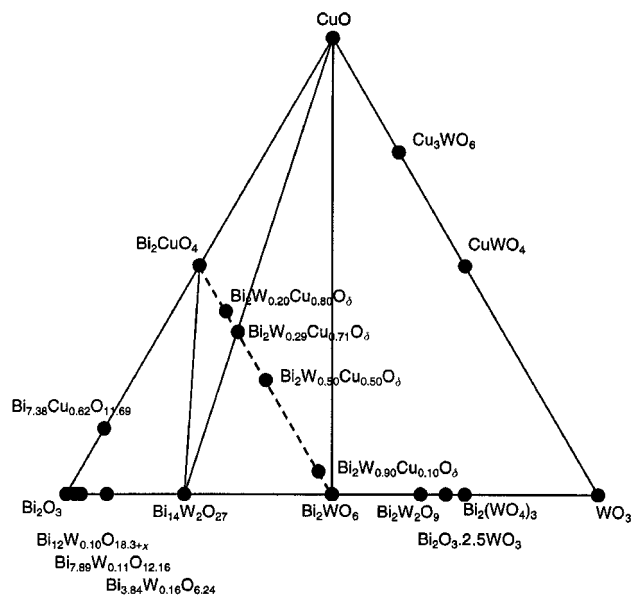
Fig. 1 Partial phase diagram of the Bi_2O_3–CuO–WO_3 system.

Temperature/°C	Duration/h	Weight loss(%)	XRD pattern
940	10	0	Mixture
1000	24	1.2	Mixture
1050	24	4.7	Mixture
1070	24	11.8	Single phase

there was no evidence that Cu could enter the structure of Bi_2WO_6 to form a solid solution.

Samples prepared at temperatures just below or just above melting showed no difference in their XRD patterns. For the composition $x = 0.1$, which commenced melting at 1040 °C, the XRD pattern of the sample heated at 1050 °C for 24 h, Fig. 2c, shows a small peak next to the most intense peak at $2\theta \approx 28°$ in the pattern of Bi_2WO_6, Fig. 2a, and is attributed to $Bi_{14}W_2O_{27}$. However, upon heating at 1070 °C for 24 h, the pattern appears to be that of pure Bi_2WO_6, Fig. 2b. This was accompanied by a weight loss of *ca.* 12%, Table 1. It thus appears that
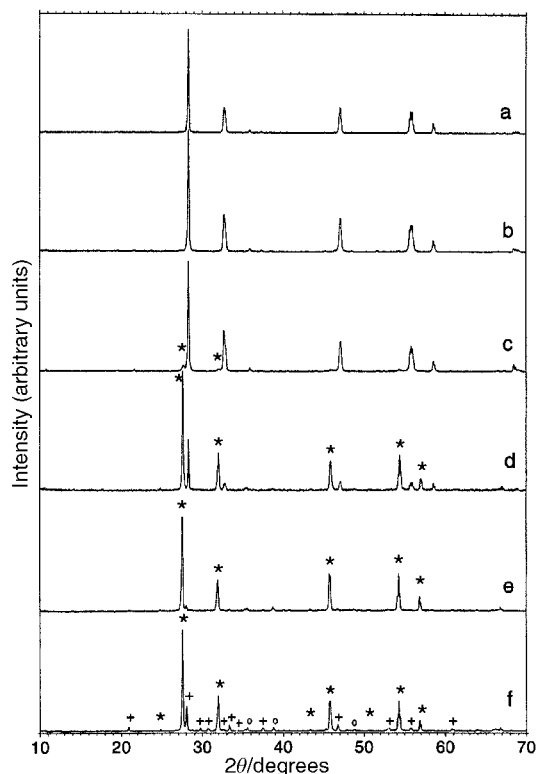
volatilisation of Bi_2O_3 occurs upon prolonged heating at temperatures above melting, giving rise to misleading information regarding the phase(s) that should exist.

At $x = 0.5$, the relative intensity of peaks due to Bi_2WO_6 and $Bi_{14}W_2O_{27}$ is reversed, Fig. 2d, and the pattern is clearly that of a mixture of Bi_2WO_6, $Bi_{14}W_2O_{27}$ and a third phase, probably CuO. At $x = 0.7$, Fig. 2e, the pattern is predominantly that of $Bi_{14}W_2O_{27}$, with a few minor peaks. At $x = 0.75$, Fig. 2f, the peaks can be assigned to a mixture of $7Bi_2O_3 \cdot 2WO_3$, Bi_2CuO_4 and CuO, as suggested by Vannier *et al.*[10]

The EPMA back scattered electron (BSE) image of the material with composition $x = 0.1$, prepared at 1050 °C, showed the presence of two minor phases in addition to the main phase, Fig. 3a. Elemental analysis of the main phase showed no Cu but gave atomic percentages of Bi and W that agreed well with calculated values in Bi_2WO_6 (Table 2). Cu appeared to be present in the minor phases, as seen in the false-colour element map, Fig. 3b. However, it was not possible to obtain accurate microprobe data of the minor phase(s) as they occurred at grain boundaries or along cracks with very small grain sizes. This combination of the elemental analyses, Table 2 and the
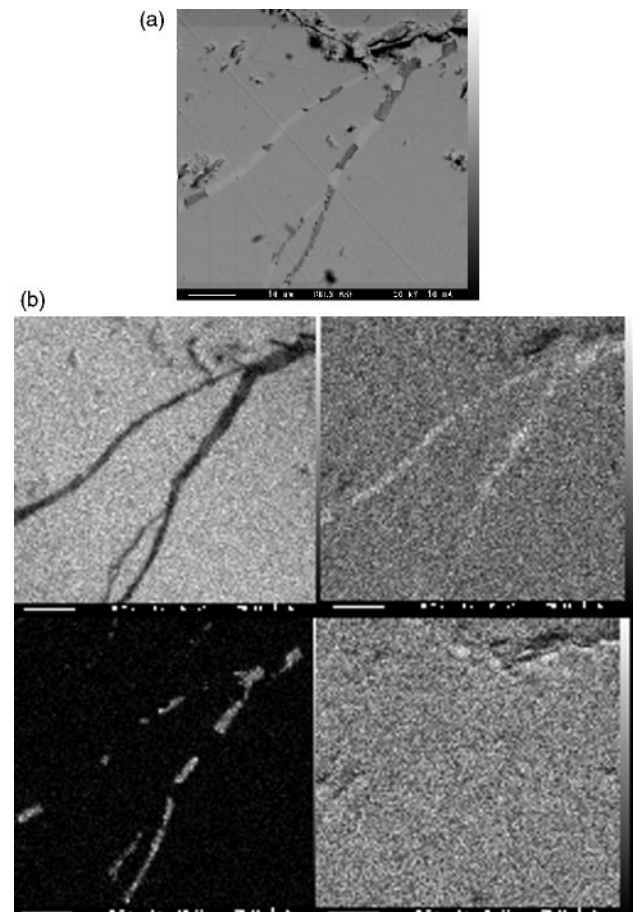

Fig. 2 X-Ray powder diffraction patterns of $Bi_2Cu_xW_{1-x}O_{6-2x}$ phases: (a) $x = 0$; (b) $x = 0.1$, synthesized at 1070 °C for 24 h; (c) $x = 0.1$, synthesized at 1050 °C for 24 h; (d) $x = 0.5$; (e) $x = 0.7$; (f) $x = 0.75$; (*) $7Bi_2O_32WO_3$, (+) Bi_2CuO_4, (o) CuO.

Fig. 3 EPMA results of sample with $x = 0.1$ in $Bi_2Cu_xW_{1-x}O_{6-2x}$: (a) back scattered image (BSE); (b) elemental map, clockwise from top left: (i) W Mα, (ii) Bi Mα, (iii) O Kα, (iv) Cu Kα; elemental concentration proportional to lightness.

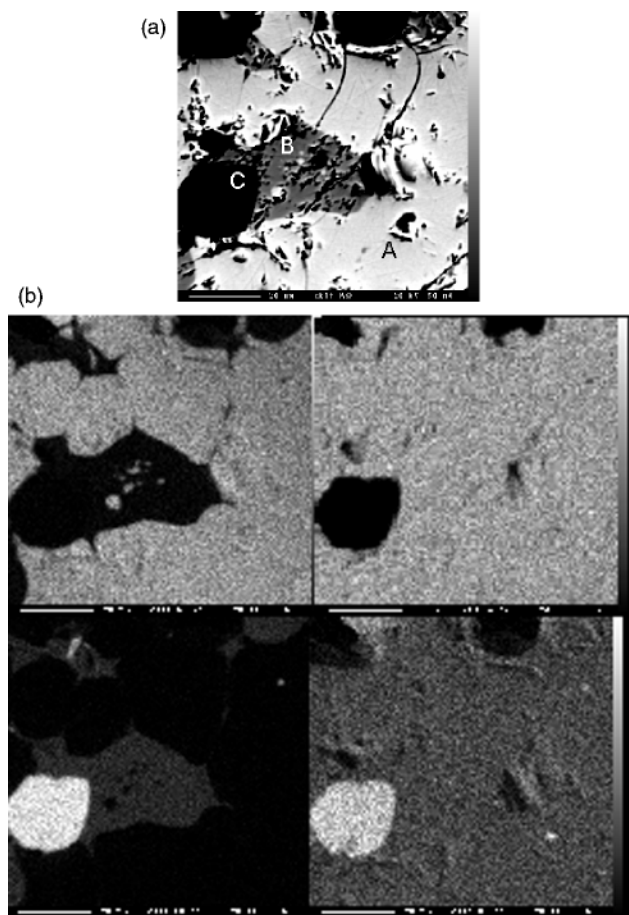**Fig. 4** EPMA results of sample with $x = 0.7$ in $Bi_2Cu_xW_{1-x}O_{6-2x}$: (a) back scattered electron image; (b) elemental map, clockwise from top left: (i) W Lα, (ii) Bi Mα, (iii) O Kα, (iv) Cu Lα; elemental concentration proportional to lightness.

false colour map, Fig. 3b, shows clearly that Bi_2WO_6 does not accept Cu as a dopant.

Although the XRD pattern of the material with composition $x = 0.7$ was almost phase pure, EPMA showed clearly the presence of three phases, labelled as phases A (main phase), B and C in the BSE image, Fig. 4a. Elemental analysis showed that phase C was CuO, while phases A and B had compositions that agreed with expected values for $Bi_{14}W_2O_{27}$ or $7Bi_2O_3 \cdot 2WO_3$ and Bi_2CuO_4 respectively, Table 2. The distribution of these elements in the three phases is seen clearly in the false colour elemental map, Fig. 4b. This shows, in fact, that composition $x = 0.7$ has $x \geqslant 0.71$ and has thus crossed over the $Bi_{14}W_2O_{27}$–CuO join into the triangle $Bi_{14}W_2O_{27}$–Bi_2CuO_4–CuO.

EPMA is exceptionally valuable for obtaining microanalytical data on multiphase samples, such as the present Cu-containing materials. To obtain macroanalytical data on the whole sample, other techniques are required, however, unless the volume fractions of the various phases present could be determined. In the present study, we have not attempted image analysis to estimate the volume fractions of the different phases.

There are a number of possible reasons why identification of secondary phases by XRD may be difficult. These include: (1) overlapping of the strongest peaks with those of the main phases; (2) absorption of X-rays diffracted from the secondary phase if the main phase contains elements of high atomic number; (3) a general decrease in intensity of XRD lines of the secondary phase if it is of lower symmetry than the main phase (due to the reduction in multiplicities and, therefore, increase in the number of lines); (4) poorer quality of the XRD pattern of the secondary phase if, at the temperature of reaction, it forms a liquid that subsequently crystallizes rapidly upon cooling; and (5) instrumental problems associated with the XRD such as overall sample size, low instrumental sensitivity setting or high background due to fluorescence. Each of these problems can be overcome once they are recognized; the difficulty is to recognize that the problems may exist at the outset.

We may now comment on the discrepancy between the results of Sharma et al.[11] and Vannier et al.[10] Sharma et al. found that, by XRD, samples heated at 1070 °C gave phase-pure Bi_2WO_6 solid solutions. We find that, at this temperature, significant volatilisation of Bi_2O_3 occurs and, therefore, compositions that initially fall within the three-phase triangle Bi_2WO_6–$Bi_{14}W_2O_{27}$–CuO gradually show a reduction in $Bi_{14}W_2O_{27}$ content until, eventually, they should contain mixtures of Bi_2WO_6 and CuO. Since it is difficult to detect CuO in the presence of main phase Bi_2WO_6 by XRD, this may be the reason why the existence of a Bi_2WO_6–CuO solid solution was claimed.

Conclusion

EPMA is an invaluable technique in the study of the phase purity of materials. It complements powder XRD, especially in cases where the main phase is of variable composition and the properties of interest are sensitive to compositional variations or the presence of dopants. By using combined XRD and EPMA techniques, it has been shown clearly that Cu doping of Bi_2WO_6 does not result in the formation of solid solutions at temperatures close to melting. This is consistent with the results of computational studies showing a relatively unfavourable energy of dissolution of Cu in Bi_2WO_6.[13]

Acknowledgements

Table 2 EPMA results for $Bi_2Cu_xW_{1-x}O_{6-2x}$ (esds in parentheses)

x	Bi (atom%)		W (atom%)		Cu (atom%)	
	EPMA	Calculated value	EPMA	Calculated value	EPMA	Calculated value
0.1	22.30(13)	22.22[a]	11.05(9)	11.11[a]	0.03(2)	0
0.7						
Phase A	31.91(18)	32.56[b]	4.94(7)	4.65[b]	0.22(15)	0
Phase B	28.61(8)	28.57[c]	0.05(6)	0	14.14(13)	14.29[c]
Phase C	0.19(7)	0	0.02(1)	0	49.73(11)	50.0[d]

[a]Calculated value for Bi_2WO_6. [b]Calculated value for $Bi_{14}W_2O_{27}$. [c]Calculated value for Bi_2CuO_4. [d]Calculated value for CuO.

References

1. F. Abraham, J. C. Boivin, G. Mairesse and G. Nowogrocki, *Solid State Ionics*, 1992, **40/41**, 934.
2. J. B. Goodenough, A. Manthiram, M. Paranthaman and Y. S. Zhen, *Mater. Sci. Eng. B*, 1992, **12**, 357.
3. E. Pernot, M. Anne, M. Bacmann, P. Strobel, J. Fouletier, R. N. Vannier, G. Mairesse, F. Abraham and G. Nowogrocki, *Solid State Ionics*, 1994, **70/71**, 259.
4. V. Sharma, A. K. Shukla and J. Gopalakrishnan, *Solid State Ionics*, 1992, **58**, 359.
5. O. Joubert, A. Jouanneaux, M. Ganne, R. N. Vannier and G. Mairesse, *Solid State Ionics*, 1994, **73**, 309.
6. C. K. Lee, B. H. Bay and A. R. West, *J. Mater. Chem.*, 1996, **6**, 331.
7. C. J. Watson, A. Coats and D. C. Sinclair, *J. Mater. Chem.*, 1997, **7**, 2091.
8. V. Sharma, A. K. Shukla and J. Gopalakrishnan, *J. Mater. Chem.*, 1994, **4**, 703.
9. N. Baux, R. N. Vannier, G. Mairesse and G. Nowogrocki, *Solid State Ionics*, 1996, **91**, 243.
10. R. N. Vannier, G. Nowogrocki and G. Mairesse, *J. Mater. Chem.*, 1995, **5**, 361.
11. V. Sharma, K. B. R. Varma and A. K. Shukla, *Bull. Mater. Sci.*, 1995, **18**, 631.
12. C. K. Lee, A. M. Coats and A. R. West, *Powder Diffr.*, 1997, **12**, 245.
13. M. S. Islam, S. Lazure, R. N. Vannier, G. Nowogrocki and G. Mairesse, *J. Mater. Chem.*, 1998, **8**, 655.