Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 883–886

THERMAL ANALYSIS AND STRUCTURAL CHARACTERIZATION OF $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ ($0.02 \le x \le 0.50$)

L. F. Brum Malta and Marta Eloisa Medeiros[*]

Department of Inorganic Chemistry, Institute of Chemistry, UFRJ, Cidade Universitária CT Bloco A-Lab. 638
Rio de Janeiro 21945-970, RJ, Brazil

This work reports the study of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ ($0.02 \le x \le 0.50$) series, which is a potential source of solid electrolytes to apply in oxygen sensors. X-ray powder diffraction was used to point out the formation of major ionic conductive phases and minor ones. The modifications of vanadate substructure were probed, at short range, by Fourier-transform infrared spectroscopy. Differential scanning calorimetry evidenced the formation of tetragonal γ phase, which can be ionic conductive, for $x=0.14$.

Keywords: *BIMEVOX, order–disorder transition, solid electrolyte*

Introduction

$Bi_4V_2O_{11}$ is obtained from the $2Bi_2O_3$–xV_2O_5 solid solution, where $0.86 \le x \le 1.0$ [1]. It presents three polymorphs [1–5]: the α-$Bi_4V_2O_{11}$ phase is the stable polymorph at room temperature. It has orthorhombic unit cell, which is a superstructure with tripled *a* parameter and $a=5.53$ Å, $b=5.61$ Å and $c=15.28$ Å [1–4]. The β phase is only stable in the 450–580°C interval; it has a tetragonal unit cell, with duplicated *a* parameter and $a=b=11.29$ Å and $c=15.40$ Å [1–5]. Finally, the γ polymorph also has a tetragonal unit cell, with $a=b=4.00$ Å and $c=15.49$ Å. Its stability occurs above 580°C [1–5].

Although α and β phases present weak performance as ionic conductors, the β↔γ transition, at 600°C, enables a great increase of ionic conductivity [1, 6], due to the disorder in the anion sublattice. γ-$Bi_4V_2O_{11}$ presents perovskite-type structure with $(Bi_2O_2)^{2+}$ and $(VO_{3.5})^{2-}$ alternated layers and numerous oxygen vacancies in the V–O layer [1–5]. The γ' polymorph, with the same crystalline system (tetragonal) and cell parameters of the γ phase, is described as a result of ordered sites in a vitreous matrix [7].

Hence, γ-$Bi_4V_2O_{11}$ is a promising oxygen-conducting solid electrolyte. It finds application in oxygen sensors [8], mainly as a substituting ceramic for stabilized zirconia [9]. Technologically, there is a need for superior ionic conductivities at lower temperatures [10, 11], and zirconia electrolytes cannot match these requirements.

Partial substitution of V^{5+} in the α-$Bi_4V_2O_{11}$ structure by some lower valence cations stabilizes the γ phase, by forming oxygen vacancies in the V–O layer of the perovskite structure [1–8, 12–19]. Previous reports described compositions applying 10 mol% of Co^{2+}or Cu^{2+} [14–17], while when using Fe^{3+} [18] and Fe^{2+} [19], several substitution degrees were evaluated. For Fe^{2+}-substituted bismuth vanadate, the γ-like phase was stabilized at $x=0.20$ (10 mol% of substitution degree) using a lower dopant content than that for Fe^{3+}-substituted ceramics [18]. The present work proposes the study of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ ($0.02 \le x \le 0.50$) series by means of structural characterization, using Fourier-transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRPD) as short-range and long-range analysis, respectively. Differential scanning calorimetry (DSC) was performed in order to sustain the former results.

Experimental

The $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ compounds were obtained from oxide mixing of precursors Bi_2O_3 (Riedel-de Haën, 99.5%), V_2O_5 (Merck, 99.5%) and BaO (Aldrich, 99%) in an agate mortar, using acetone (Merck) to aid the homogenization process. Each solid mixture was heated at 100°C for 24 h to activate the precursors, then calcined at 800°C in a platinum crucible and quenched to room temperature after 16 h of reaction.

XRPD was performed at room temperature by using a Shimadzu diffractometer, with CuK_α radiation and 0.05° per step. Each diffraction pattern was collected in the range $10° \le 2\theta \le 50°$. Identification of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ polymorphs from diffraction pat-

---

[*] Author for correspondence: martam@iq.ufrj.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Unit cell parameters and crystalline system determined for each composition of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ series

Composition	Unit cell parameters/Å			Crystalline system
	a	*b*	*c*	
x=0.00	16.616±0.006	5.611±0.002	15.305±0.006	orthorhombic
x=0.02	16.61±0.02	5.617±0.007	15.33±0.02	orthorhombic
x=0.06	16.632±0.005	5.604±0.002	15.330±0.005	orthorhombic
x=0.10	16.65±0.02	5.604±0.007	15.33±0.02	orthorhombic
x=0.14	3.94±0.01	3.94±0.01	15.41±0.06	tetragonal

terns was done with help of literature data [2] by using a least-squares program.

Fourier-transform infrared spectra were obtained in the 4000–400 cm^{-1} range by a Nicolet Magna spectrometer, with 4 cm^{-1} resolution. Samples were prepared using the KBr pellet technique.

DSC curves were acquired by using a Mettler TC 11 equipment, coupled to a DSC 25 calorimeter, with 5°C min^{-1} step under an N_2 flow, in the range of 25–500°C. Approximately 7 mg of each sample were weighed in an aluminum cell for curve acquisition.

Results and discussion

According to the polymorph identification procedure described in the X-ray diffraction experimental section, orthorhombic unit cell of α–$Bi_4V_2O_{11}$ [2] is obtained in the $0.02 \leq x \leq 0.10$ interval (Fig. 1, Table 1). A closer look at these diffraction patterns evidences that the increase of barium content leads to the exchange of peak intensity between the reflections at 31.62 and 32.04° in the cited composition interval. Also the peaks at 47.92 and 48.22° indicate the complete coalescence at *x*=0.10. These long-range structural modifications are consequences of Bi_2O_3–V_2O_5–BaO solid solution formation.

On the other hand, the *x*=0.14 diffraction pattern (Fig. 1) gives characteristic tetragonal unit cell of γ-$Bi_4V_2O_{11}$ (Table 1) [2] in addition to the peaks at 10.90 and 28.10°. These correspond to a minor phase which is detected in the reacted mixture until *x*=0.30.

The increase of barium content above *x*=0.14 leads to the deterioration of γ-$Bi_4V_2O_{11}$ alike phase, since the characteristic peaks at 11.5 and 23.3° progressively vanish until *x*=0.50. Simultaneously, a new phase begins to form at *x*=0.20, relative to 26.70 and 32.50° reflections, with completion at *x*=0.50. These modifications above *x*=0.10 point out the end of compositional domain of Bi_2O_3–V_2O_5–BaO solid solution.

FTIR spectrum of $Bi_4V_2O_{11}$ (Fig. 2) shows the broad band of VO_y group centred at 760 cm^{-1}. Table 2 presents the assignment of the vibrations modes for the compounds in the $0.00 \leq x \leq 0.14$ interval. Previous reports [5, 12] have stated four different geometries for VO_y polyedra in α phase (two distorted octahedral and two distorted tetrahedral [5]). The band at 812 cm^{-1} is relative to the asymmetric stretching mode of VO_4^{3-} [20], while the modes at 765, 717 and 615 cm^{-1} are relative to the V–O stretching in octahedral units. These bands also appear for *x*=0.02 and 0.06. For the former, the presence of shoulders at 1053 and 928 cm^{-1} which are relative to the stretching of V=O bonds, signals the formation of vanadium

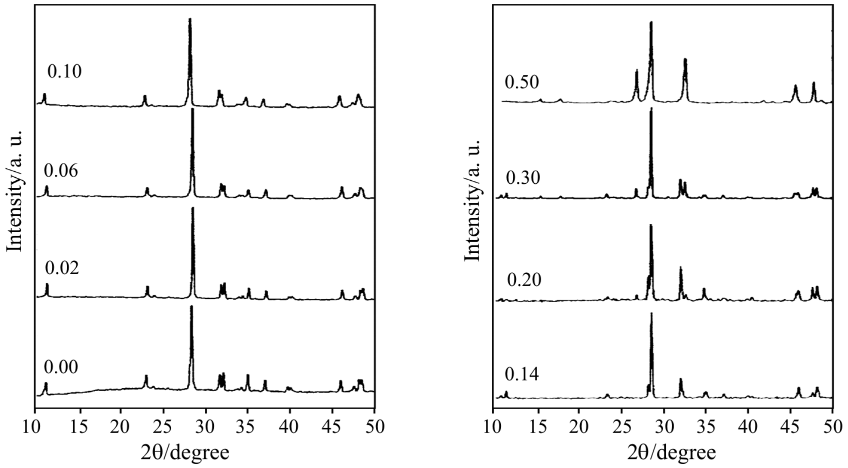

Fig. 1 XRPD patterns of nominal compositions having the general formula $Bi_4V_{2-x}Ba_xO_{11-1.5x}$, where *x* values are indicated

Table 2 IR assignments of $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ compounds in the 1200–600 cm^{-1} range

IR assignment	Composition				
	0.00	0.02	0.06	0.10	0.14
$\nu_{S(V-O)}$	765 s 615 w	870 w 768 s 623 w	771 s	758 s	–
$\nu_{AS(V-O)}$	812 s 717 s	831 s 723 s	827 s 723 s	820 m 715 s	820 m 710 s
$\nu_{(V=O)}$	–	1053 w 928 w	–	–	–

s – strong, m – medium, w – weak, ν_S – symmetric stretching mode, ν_{AS} – asymmetric stretching mode

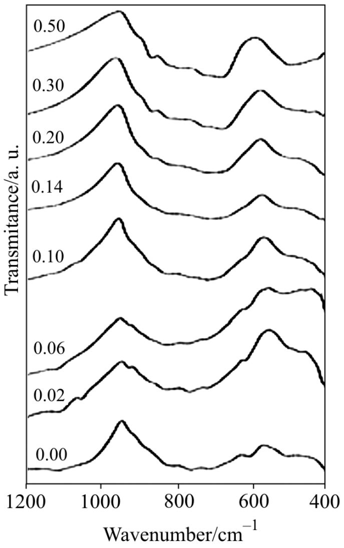

Fig. 2 FTIR spectra of nominal compositions having the general formula $Bi_4V_{2-x}Ba_xO_{11-1.5x}$, where x values are indicated

polyoxyanions [21]. This result sustains the formation of solid solution between the reactants for these compositions. These vibration modes vanish in x=0.10 spectrum, in which the intensity maximum of VO_y band dislocates from 760 (x=0.00) to 715 cm^{-1}. This short-range structural modification is supported by a unique, octahedral geometry for vanadium in the tetragonal $Bi_4V_2O_{11}$ compound [12] since there is an increase of the reduced mass of VO_y polyhedra. However, one IR band, assigned as T_1u triply degenerate asymmetric stretching, would be observed if only octahedral units were present. Table 3 shows that the decrease in symmetry from Oh to D_4h and D_2h point groups produces an increase of the band number in IR spectrum. Two intense bands at 819 and 715 cm^{-1} are observed for x=0.10 and 0.14 compositions, Fig. 2, which means that vanadate units have vacancies in the oxygen sublattice. The main effect here is the lowering of the group symmetry. These vacancies are generated by cationic substitution, according to the process expressed by the following equation:

$$2BaO \xrightarrow{(Bi_4V_2O_{11})} 2Ba_V''' + 2O_O + 3\square_O^{\bullet\bullet} \tag{1}$$

where Ba_V''' is the impurity center with triply negative charge, which is formed by the aliovalent substitution of V^{5+} by Ba^{2+}; O_O represents the partial filling of sites in the oxygen sublattice; $\square_O^{\bullet\bullet}$ is the double-ionized anionic vacancy with effective positive charge in the oxygen sublattice. FTIR results let one conclude that, at short distance, tetragonal phase is formed earlier (x=0.10 composition) than expected by XRPD results. For x>0.14, the number of IR bands increases due to the formation of a new compound, as showed by the XRPD data.

DSC curves, Fig. 3, show the orthorhombic↔tetragonal transition at 430°C in the $0.02 \leq x \leq 0.10$ interval. For x=0.14, two thermal events are observed. As a minor phase is formed simultaneously with the tetragonal phase, it may correspond to at least one of

Table 3 Correlation between IR vibrational activity and point groups for the V–O asymmetric stretching in vanadate group

Point group	IR vibrational activity	Number of IR bands
Oh	T_1u	1
D_4h	A_2u+Eu	2
D_2h	B_1u+B_2u+B_3u	3

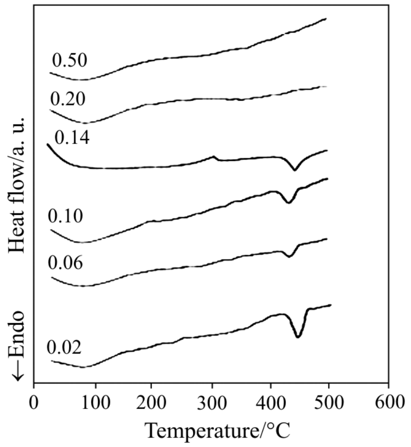

Fig. 3 DSC curves of nominal compositions having the general formula $Bi_4V_{2-x}Ba_xO_{11-1.5x}$, where x are indicated

these events. However, as XRPD data showed, this minor phase is also formed for x=0.20, but the DSC curve for this composition presents no peaks. Hence, these thermal transitions are related to the tetragonal phase formed at x=0.14. The exothermic peak at 300°C corresponds to a disorder–order transition, as the tetragonal↔orthorhombic one. This is coherent with the fact that numerous oxygen vacancies are present in the tetragonal γ phase while α polymorph has ordered domains. As expected, vacancy extinction is exothermic and this is the case of the disorder–order transition. The contrary process, vacancy formation, is endothermic, hence the peak at 430°C is generated by the orthorhombic↔tetragonal transition, as those observed in the $0.02\leq x\leq 0.10$ interval. No thermal events are verified for x=0.50 composition.

Conclusions

The $Bi_4V_{2-x}Ba_xO_{11-1.5x}$ series was studied in the $0.02\leq x\leq 0.50$ interval. XRPD data pointed out the compositional domain of the Bi_2O_3–V_2O_5–BaO solid solution in the range $0.02\leq x\leq 0.10$. At x=0.14, a minor phase was obtained simultaneously with γ phase; above this composition, a new phase began to form, with completion at x=0.50.

FTIR analysis signaled, at short-range, the formation of γ phase at x=0.10. Vacancies in the oxygen sublattice lowered VO_y symmetry, hence more bands than expected for vanadate octahedral geometry were observed in x=0.10 and x=0.14 spectra.

DSC curves showed disorder–order and order-disorder transitions at 300 and 430°C, respectively. The former was only verified for x=0.14 composition, hence it was associated with γ phase.

The present report sustains the use of thermal analysis to evidence the polymorphism of bismuth vanadates. It represents a part of our continuous work on obtaining inorganic electrolytes to apply in solid-state devices as oxygen sensors.

Acknowledgements

The authors would like to thank PIBIC-CNPq and CNPq for financial support; IQ-UNICAMP for XRPD analysis and PEMM-COPPE-UFRJ for DSC analysis.

References

1 F. Abraham, J. C. Boivin, G. Mairesse and G. Nowogrocki, Solid State Ionics, 40–41 (1990) 934.
2 F. Abraham, M. F. Debreuillegresse, G. Mairesse and G. Nowogrocki, Solid State Ionics, 28–30 (1988) 529.
3 A. A. Bush, V.G. Koshelayeva and Yu. N. Venevtsev, J. Appl. Phys., 24 (1985) 625.
4 C. Sant and J. P. Contour, J. Crystal Growth, 153 (1995) 63.
5 O. Joubert, A. Jouanneaux and M. Ganne, Mater. Res. Bull., 29 (1994) 175.
6 C. K. Lee, D. C. Sinclair and A. R. West, Solid State Ionics, 62 (1993) 193.
7 G. Mairesse, C. R. Acad. Sci. Séries II, 2 (1999) 651.
8 R. N. Vannier, G. Mairesse, G. Nowogrocki, F. Abraham and J. C. Boivin, Solid State Ionics, 53–56 (1992) 713.
9 G. Dell'Agli, G. Mascolo, M. C. Mascolo and C. Pagliuca, J. Therm. Anal. Cal., 80 (2005) 721.
10 K. Huang, M. Feng and J. B. Goodenough, J. Am. Ceram. Soc., 81 (1998) 357.
11 L. F. Brum Malta, V. da Rocha Caffarena, M. E. Medeiros and T. Ogasawara, J. Therm. Anal. Cal., 75 (2004) 901.
12 M. Anne, M. Bacmann, E. Pernot, F. Abraham, G. Mairesse and P. Strobel, Physica B, 180–181 (1992) 621.
13 T. Iharada, A. Hammouche, J. Fouletier, M. Kleitz, J. C. Boivin and G. Mairesse, Solid State Ionics, 48 (1991) 257.
14 M. H. Paydar, A. M. Hadian, K. Shimanoe and N. Yamazoe, J. Mater. Sci., 37 (2002) 2273.
15 M. Guillodo, J. Fouletier, L. Dessemond and P. Del Gallo, Electrochim. Acta, 47 (2002) 2809.
16 V. N. Tikhonovich, E. N. Naumovich, V. V. Kharton, A. A. Yaremchenko, A. V. Kovalevsky, A. A. Vecher, Electrochim. Acta, 47 (2002) 3957.
17 A. Watanabe and K. Das, J. Solid State Chem., 163 (2002) 224.
18 E. García-González, M. Arribas and J. M. González-Calbet, Chem. Mater., 13 (2001) 96.
19 L. F. B. Malta and M. E. Medeiros, J. Therm. Anal. Cal., 81 (2005) 149.
20 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Ed., John Wiley & Sons, New York 1986.
21 L. V. Kristallov, O. V. Koryakova and L. A. Perelyaev, Russ. J. Inorg. Chem., 32 (1987) 1073.

Received: September 21, 2006
Accepted: December 28, 2006

DOI: 10.1007/s10973-006-8203-0