STABILIZATION OF γ' PHASE IN $Bi_4V_{2-x}Fe_x^{II}O_{11-1.5x}$ SERIES

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This work reports the room-temperature stabilization of the $Bi_4V_{2-x}Fe_x^{II}O_{11-1.5x}$ γ' phase, a promising ionic conductive material that finds application in solid oxide fuel cell and oxygen sensor devices. The Fe(II) cation proved to be a better stabilizer than Fe(III), which was previously used, since a lower substitution degree of V^{5+} is needed for the former. Powder X-ray diffraction, Fourier-transform infrared spectroscopy and differential scanning calorimetry were used in these experiments.

Keywords: order-disorder transition, solid electrolyte, symmetry

Introduction

$Bi_4V_2O_{11}$ is obtained from the $2Bi_2O_3–xV_2O_5$ solution, where $0.86<x<1.0$ [1]. It presents three polymorphs [1–5]. Although α and β phases present typically isolating performance as ionic conductors, the β↔γ transition, at 600°C, enables a great elevation in ionic conductivity [1, 6], due to atomic position disorder. γ-$Bi_4V_2O_{11}$ presents perovskite-type structure with $(Bi_2O_2)^{2+}$ and $(VO_{3.5})^{2-}$ alternated layers and numerous oxide 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 can be used in solid oxide fuel cell devices and oxygen sensors [8], mainly as a substituting ceramic for stabilized zirconia [9]. In technological aspects superior ionic conductivity is required at lower temperatures [10, 11], and zirconia electrolytes do not fulfil these requirements.

Partial substitution of V^{5+} in the α-$Bi_4V_2O_{11}$ structure by some lower valence cations may stabilize the γ phase, by forming oxide vacancies in the V–O layer of the perovskite structure [1–8, 12–19]. Papers mention compositions applying 10 mol% of Co^{2+} or Cu^{2+} [14–17], however, when Fe^{3+} is used several degree of substitution was determined [18]. For the latter, the γ-like phase was stabilized at x=0.30 (15 mol%). The present work reports on the stabilization of this phase at x=0.20 (10 mol%), using Fe^{2+} as substituting cation.

Experimental

The $Bi_4V_{2-x}Fe_x^{II}O_{11-1.5x}$ $(0.10<x<0.50)$ compounds were obtained from mixing of oxide precursors Bi_2O_3 (Riedel-de Haën, 99.5%), V_2O_5 (Merck, 99.5%) and FeO (Aldrich, 95%) in an agate mortar, using acetone (Merck, P.A.) to promote their homogenization. Each solid mixture was kept 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.

Powder X-ray powder diffraction (PXRD) was performed at room temperature by using a Rigaku Miniflex diffractometer and a Fert – FPM GmbH diffractometer, both with CuK_α radiation and 0.05° per step. Each diffraction pattern was collected in the range $10°<2\theta<50°$. Cell parameters were obtained from diffraction pattern indexing with Dicvol91 program [20].

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.

Differential scanning calorimetry was performed by using a Shimadzu DSC 50 equipment, at a heating rate $10 \ K \ min^{-1}$ under air flow, in the range of 25–650°C. Approximately 90 mg samples were weighted in a platinum crucible.
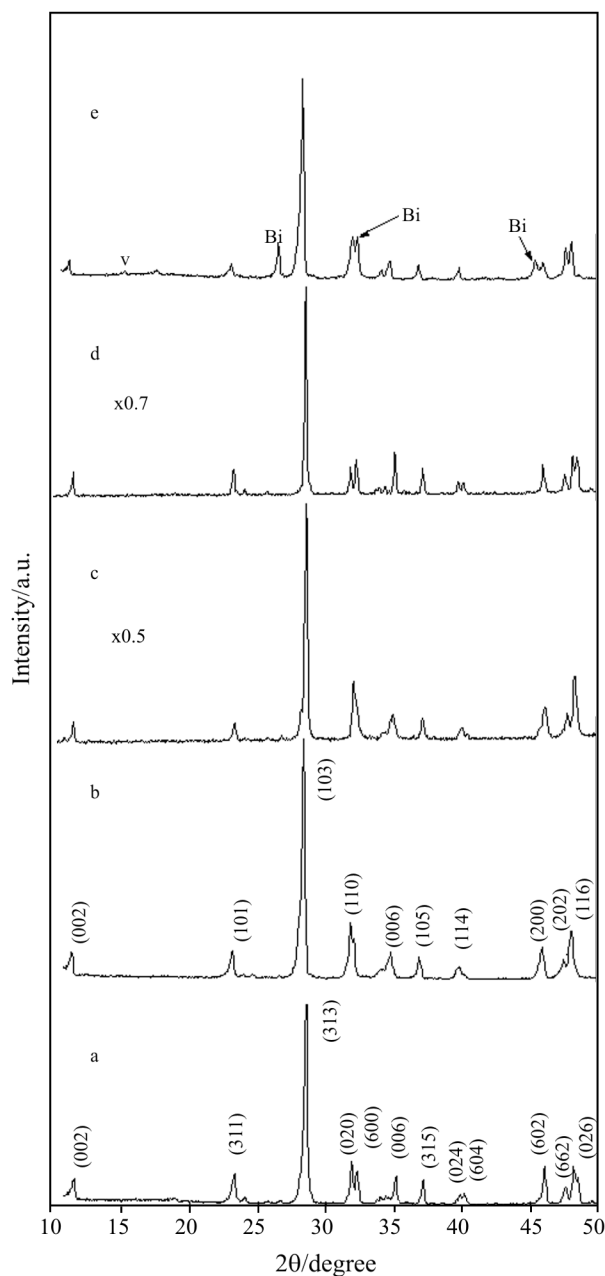
Results and discussion

Long-range structural characterization was determined by the PXRD technique.

According to the procedure described in the X-ray diffraction experimental section, orthorhombic


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Table 1 Cell parameters and crystalline system obtained for each compound of $Bi_4V_{2-x}Fe_x^{II}O_{11-1.5x}$ series

Composition	Cell parameters/Å	Crystalline system
$X=0.10$	$a=5.53(6)$; $b=5.60(2)$; $c=15.30(0)$	Orthorhombic
$X=0.20$	$a=b=3.93(3)$; $c=15.3(4)$	Tetragonal
$X=0.30$	$a=b=3.94(5)$; $c=15.4(2)$	Tetragonal
$X=0.40$	$a=5.52(8)$; $b=5.60(2)$; $c=15.2(9)$	Orthorhombic
$X=0.50$	$a=b=3.94(0)$; $c=15.4(5)$	Tetragonal

unit cell for the $x=0.10$ compound. Its cell parameters (Table 1) and PXRD pattern (Fig. 1a) are typical of α-$Bi_4V_2O_{11}$ [2], which is orthorhombic. On the other hand, tetragonal unit cells were obtained for the $x=0.20$ and 0.30 compositions (Table 1 and Figs 1b,

Fig. 1 PXRD patterns of nominal compositions having the general formula $Bi_4V_{2-x}Fe^{(II)}_xO_{11-1.5x}$, where x=(a) 0.10; (b) 0.20; (c) 0.30; (d) 0.40 and (e) 0.50. For the $x=0.50$ composition, V means V_2O_5 and Bi means Bi_2O_3
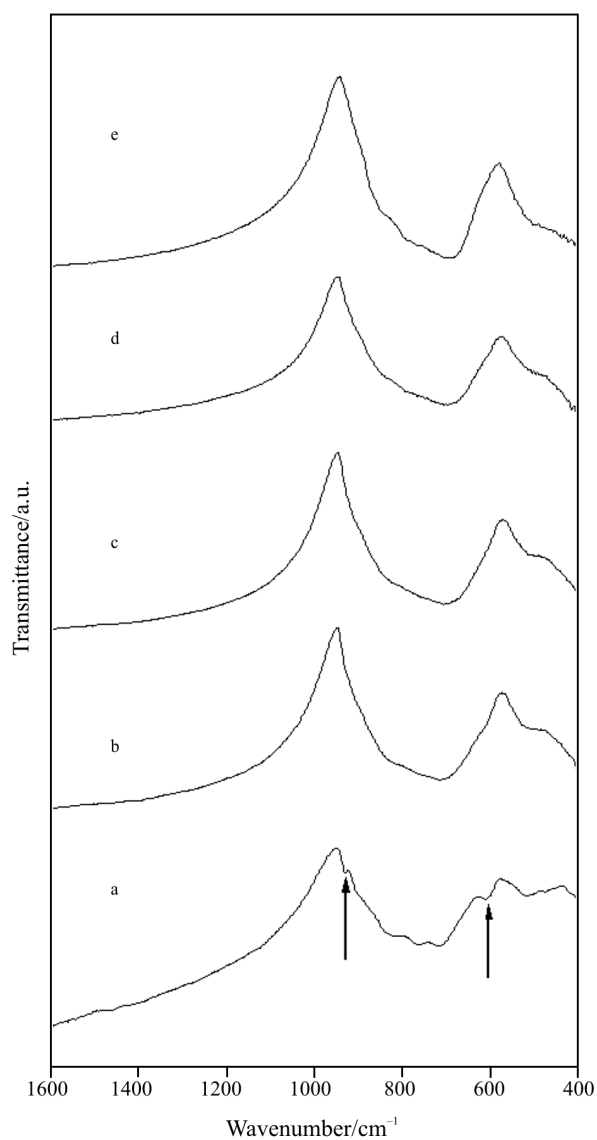
Fig. 2 FTIR spectra of nominal compositions having the general formula $Bi_4V_{2-x}Fe^{(II)}_xO_{11-1.5x}$, where x=(a) 0.10; (b) 0.20; (c) 0.30; (d) 0.40 and (e) 0.50. Vibrational modes at 930 and 609 cm^{-1} are indicated
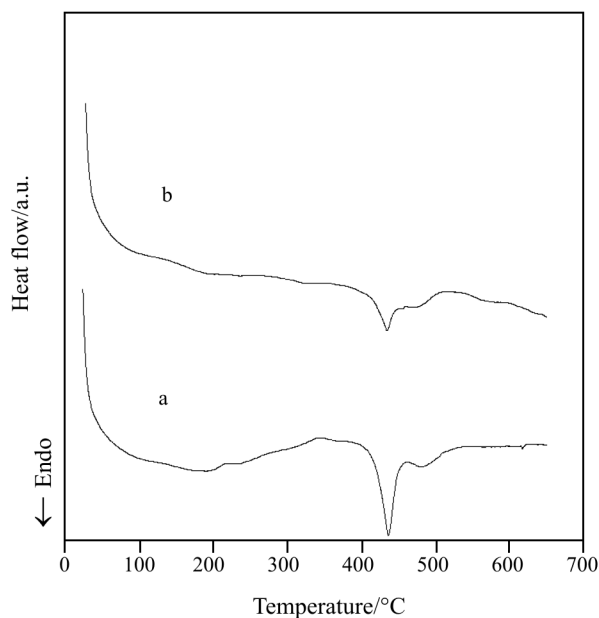
Fig. 3 DSC curves of $Bi_4V_{2-x}Fe^{(II)}_xO_{11-1.5x}$, where x=(a) 0.20 and (b) 0.30

c). By their characteristic cell parameters (Table 1) it can be concluded that these correspond to γ-$Bi_4V_2O_{11}$ alike compounds [2]. For x=0.40 (Fig. 1d), an orthorhombic α-alike phase was obtained (Table 1), which has already been described as a metastable compound [21]. Finally, for x=0.50, the presence of V_2O_5 and Bi_2O_3 was identified, and a characteristic tetragonal γ-$Bi_4V_2O_{11}$ pattern (Table 1 and Fig. 1e). Hence, stabilization of γ alike phase is achieved for 10 mol% of substitution (x=0.20).

The FTIR spectra (Fig. 2) show a short-range symmetry modification for VO_y polyedra, with a band centered at 760 cm^{-1}. This is marked with arrows at 930 and 609 cm^{-1} for x=0.20 (Fig. 2). This short-range symmetry increase is supported by previous reports [5, 12] which stated four different geometries for VO_y polyedra in α-phase (one distorted octahedral, one distorted tetrahedral and two distorted trigonal pyramids [5]) and a unique, octahedral geometry for vanadium in the γ phase [12]. For the x=0.50 composition (Fig. 2e), it can be observed that the bands of V_2O_5, do not appear. It can be due to their low intensity and also can be covered by the vanadate band in this wavenumber region (1000–600 cm^{-1}). In general the short-range symmetry increase of VO_y polyedra supports the long-range structural modifications verified before.

Finally, DSC measurements were carried out to identify which tetragonal phase forms at x=0.20 and 0.30 compositions (Fig. 3). According to the characteristic $Bi_4V_2O_{11}$ thermal transitions described in the literature [17, 22], the endothermic peak at 435°C, observed in each DSC curves, can be assigned to an order-disorder γ'$\rightarrow\gamma$ transition. Hence, when Fe^{2+} to substitute V^{5+} tetragonal γ` phase is stabilized at room temperature.

Conclusions

The results showed that Fe^{2+} stabilizes the tetragonal γ' phase at 10 mol% degree of substitution. This is lower than the required molar fraction of Fe^{3+} (15 mol%) for the same purpose [18], which arises from the greater discrepancy between the valence state of Fe(II) and V(V), generating a larger number of oxide vacancies in the V–O layer.

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