

Correlated Oxygen Diffusion in BIFEVOX

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Correlation effects in the ionic conductivity of BIFEVOX ($\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-y}$, $0 \leq x \leq 0.9$, $0 \leq y \leq 1$) by impedance spectroscopy measurements have been investigated. The real part of the conductivity shows power-law frequency dependence at high frequencies, and electric modulus plots show asymmetric peaks, as a consequence of correlations in the oxygen ion diffusion. Relaxation functions in the time domain are well-described by stretched exponentials of the form $\phi(t) = \exp(-(t/\tau_0)^\beta)$, with an exponent $\beta = 0.56 \pm 0.03$, which is nearly independent of temperature and Fe content. It is found that the room temperature dc conductivity decreases exponentially when Fe content is increased and the dc conductivity activation energy increases from 0.20 to 0.97 eV. Results are discussed in terms of oxygen vacancy ordering upon Fe substitution in V sites.

Introduction

The fast ionic conducting behavior of $\text{Bi}_4\text{V}_2\text{O}_{11}$ at high temperatures was reported^{1,2} soon after the discovery of this compound.³ The high mobility of oxygen ions in the γ tetragonal phase is known to be responsible for the high ionic conductivity values (0.3 S cm^{-1} at 1000 K). However, on cooling, structural phase transitions $\gamma \leftrightarrow \beta$ and $\beta \leftrightarrow \alpha$ were found to occur at 840 and 680 K, respectively, and a much lower conductivity value is obtained at room temperature.² There have been intensive research efforts since then to stabilize the γ phase at room temperature, looking for optimized conducting properties for potential applications as solid electrolytes. In particular, substitution of vanadium ions by other metallic ions was shown to lead to the so-called BIMEVOX family, with higher conductivity values at room temperature for some compounds.⁴ The structure of these materials consists of alternating $(\text{Bi}_2\text{O}_2)^{2+}$ and $(\text{V}_{2-x}\text{Me}_x\text{O}_y)^{2-}$ perovskite-like blocks in which disordered oxygen vacancies in the metal–oxygen layers are responsible for the ionic conductivity. So far, electrical conductivity studies of the BIMEVOX series have been focused on the determination of dc conductivity values. However, there remain open questions regarding the conduction process. Correlation effects among oxygen vacancies might play an important role in the ionic conducting properties. Moreover, dimensionality effects might also be important because oxygen motion takes place through two-dimensional layers between consecutive $(\text{Bi}_2\text{O}_2)^{2+}$ planes.

In this respect, ac conductivity measurements by impedance spectroscopy have been shown to be a useful technique for investigating ion–ion correlations. Correlated ion motion gives rise to a characteristic power law frequency dependence of the ac conductivity, known as “universal dynamic response”,⁵ described by the Jonscher form,

$$\sigma^*(\omega) = \sigma_{\text{dc}}[1 + (j\omega/\omega_p)^n] \quad (1)$$

where σ_{dc} is the dc conductivity and ω_p is a crossover frequency. The power law frequency dependence of the ionic conductivity appears as a result of a nonrandom hopping conduction mechanism, and n is a fractional exponent related to the degree of correlation among ions which should be zero for random, completely uncorrelated, ionic hops.⁶ The power law dependence of the ac conductivity in the frequency domain reflects in stretched-exponential relaxation functions in the time domain. Time response is obtained from the electric modulus $M^*(\omega) = 1/\epsilon^*(\omega) = j\omega\epsilon_0/\sigma^*(\omega)$, which can be expressed in terms of the time derivative of a relaxation function, $\phi(t)$, according to the expression

$$M^*(\omega) = \frac{1}{\epsilon_\infty} \left[1 - \int_0^\infty \left(-\frac{d\Phi}{dt} \right) e^{-j\omega t} dt \right] \quad (2)$$

ϵ_∞ being the high-frequency value of the dielectric permittivity. It has been previously found⁷ that the relaxation function $\phi(t)$ for ionic conductors is the decay of the electric field at constant displacement vector, which can be well-described by a Kohlrausch–Williams–Watts (KWW) function:⁸

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$$\phi(t) = \exp(-(t/\tau_\sigma)^\beta) \quad (3)$$

The characteristic relaxation time τ_σ is found to be approximately the inverse of the crossover frequency ω_p in eq 1, $\tau_\sigma \approx 1/\omega_p$, and therefore thermally activated with the same activation energy as the dc conductivity. The exponent β has been also related to the degree of correlation in the ion transport,⁹ and one would expect β to be close to 0 for strongly correlated systems and 1 for random Debye-like hops. The electric modulus representation has been widely used in the analysis of correlated ion motion in ionic conductors because of its relative insensitivity to blocking phenomena. Moreover, it has been recently shown that the relaxation function obtained from the electric modulus representation of experimental data is directly related to the microscopic dynamics of ion hopping.¹⁰

In this paper we present electrical conductivity measurements in the BIFEVOX system $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-y}$ ($0 \leq x \leq 0.9$, $0 \leq y \leq 1$) in which V ions have been systematically substituted by Fe ions up to a content of 0.9 per formula. In a previous paper,¹¹ some of us have presented a microstructural study of the BIFEVOX series by TEM. It turns out that an increase of Fe content results in a decrease of the oxygen content and in the appearance of two different structural domains that differ in the V(Fe)-O layers ordering range. Both types of domains intergrow in variable ratio as a function of the iron content, but they appear to contain vanadium and iron in a random distribution. The effect of Fe substitution is a systematic reduction of the room temperature dc conductivity together with an increase of the activation energy. In this scenario ion-ion correlations are examined upon Fe substitution, and interestingly we have found that the correlation exponent β remains almost constant, independent of temperature and Fe content, although the dc conductivity changes by more than 5 orders of magnitude at room temperature. Results are discussed in terms of oxygen vacancy ordering effects upon Fe substitution in V sites.

Experimental Section

Samples of composition $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-y}$ ($0 \leq x \leq 0.9$, $0 \leq y \leq 1$) were prepared by the solid state reaction of the previously dried stoichiometric amounts of Bi_2O_3 (Merck, 99.9%), V_2O_5 (Merck, 99.9%), and Fe_2O_3 (Merck, 99.9%). For further details concerning synthesis as well as chemical and microstructural characterization, see ref 11.

Impedance spectroscopy measurements have been performed using automatically controlled HP4284A and HP4285A precision LCR meters in the frequency range 20 Hz to 5 MHz and for temperatures ranging from 143 to 497 K. Samples were cylindrical pellets 8 mm in diameter and about 1–1.5-mm thick on whose faces silver electrodes were deposited. Measurements were conducted under a N_2 flow to ensure an inert atmosphere.

Results and Discussion

Figure 1 shows the frequency dependence of the real part of the conductivity of $\text{Bi}_4\text{V}_{1.8}\text{Fe}_{0.2}\text{O}_{10.8}$ for a number

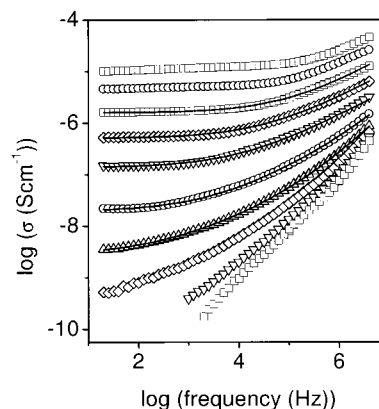


Figure 1. Real part of the conductivity vs frequency of $\text{Bi}_4\text{V}_{1.8}\text{Fe}_{0.2}\text{O}_{10.8}$ for several temperatures (from top to bottom in the figure: 497, 467, 437, 407, 377, 338, 308, 278, 243, and 213 K). Note the low-frequency dc plateau and the power law frequency dependence at high frequencies.

of temperatures between 213 and 497 K. We have chosen this sample as representative of the whole BIFEVOX ($0 \leq x \leq 0.9$) series because all the samples analyzed present the same features. At the highest temperatures a dc conductivity plateau is observed at low frequencies and a power law dependence of the conductivity at frequencies higher than the crossover frequency ω_p . Lines in the figure are fits to eq 1, which allows obtaining the values of σ_{dc} and ω_p as a function of temperature. Both σ_{dc} and ω_p were found to be thermally activated with the same energy, E_σ , pointing to a common origin of the dc conductivity and the power law contribution in ionic hopping.¹² With decreasing temperature, the onset of the power law shifts to lower frequencies, and the dc conductivity decreases according to the activated temperature dependence (Figure 1). At the lowest temperatures a dc plateau is not observed, even at the lowest frequencies, and the power law term of the ac conductivity changes into an almost linear frequency-dependent contribution due to the onset of another regime. This contribution to the conductivity consists of an almost frequency-independent dielectric loss $\epsilon'' \sim A$, which is known as “nearly constant loss”, and dominates ac conductivity of ionic conductors at enough low temperatures or high frequencies. This nearly constant loss occurs in crystalline and glassy ionic conductors,¹³ although it has been reported to be absent in some dilute crystalline systems with low concentration of mobile ions.¹⁴ One of its major properties is a weak temperature dependence,¹⁵ opposed to the activated temperature dependence of σ_{dc} and ω_p , that points to a different origin than ionic hopping.¹⁶ The slower temperature dependence of the nearly constant loss can be observed in Figure 1 at the lowest temperatures, with data nearly collapsing for different temperatures at the highest frequencies.

Figure 2 shows the frequency dependence of the imaginary part of the electric modulus, $M''(\omega)$, for

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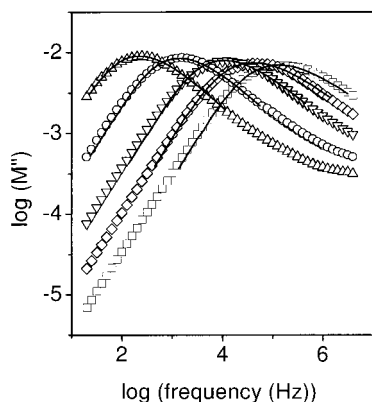


Figure 2. Imaginary part of the electric modulus vs frequency of $\text{Bi}_4\text{V}_{1.8}\text{Fe}_{0.2}\text{O}_{10.8}$ presented in a double-logarithmic scale for several temperatures (437 K (\square), 407 K (\diamond), 377 K (∇), 338 K (\circ), and 308 K (\triangle)). Solid lines are fits to expressions (2) and (3) in the text, showing KWW relaxation functions in the time domain.

various temperatures. Solid lines are fits to expressions (2) and (3). In the temperature range (308–437 K) where a peak is observed in the electric modulus, values close to 0.56 were obtained for the exponent β , showing a slight increase with temperature between 0.54 and 0.58. Similar values of $\beta = 0.56 \pm 0.03$ were obtained for samples with other Fe contents. At the lowest temperatures the high-frequency side of the maximum turns into a plateau at the highest frequencies due to the “nearly constant loss” contribution. It is worth pointing out that the modulus peak frequency was thermally activated with the same activation energy of the dc conductivity obtained from Figure 1. This supports the fact that our results are essentially not affected by blocking at grain boundaries. The use of the modulus formalism to analyze ion dynamics has been recently criticized,¹⁷ the argument being that the shape of modulus peaks might be influenced by the value of the high-frequency permittivity, ϵ_∞ , not involved in ion dynamics. This point of view remains a subject of debate.^{10,18} Moreover, it is not relevant in the analysis presented here because we found similar values of the high-frequency permittivity in all samples, $\epsilon_\infty = 30 \pm 5$, almost independent of Fe content.

Figure 3 displays the temperature dependence of the dc conductivity data in Arrhenius plots for several Fe contents in the $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-y}$ ($0 \leq x \leq 0.9$, $0 \leq y \leq 1$) series. It is observed that the activation energy of the ionic conduction process increases with Fe content from 0.20 to 0.97 eV. The steep increase in the activation energy results in an exponential decrease of the dc conductivity at a given temperature upon Fe substitution (see Figure 4). Moreover, we have found that the dc conductivity activation energy increases linearly with Fe content, as shown in the inset of Figure 4. This behavior cannot be simply understood in terms of the change in the charge carrier concentration resulting from Fe substitution, and its explanation requires a close inspection of the microstructural changes taking place. The substitution of V(V) ions by Fe(III) in

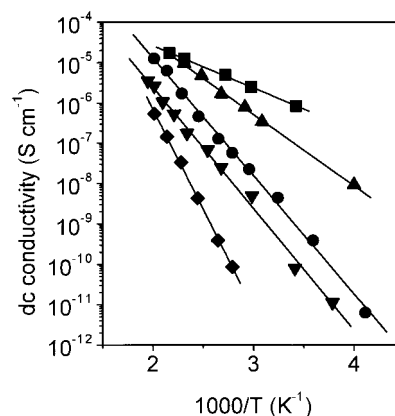


Figure 3. Arrhenius plot of dc conductivity data for several Fe contents in the BIFEVOX series $\text{Bi}_4\text{V}_{2-x}\text{Fe}_x\text{O}_{11-y}$. The activation energies are $E_\sigma = 0.20$ eV for $x = 0$ (\blacksquare), $E_\sigma = 0.35$ eV for $x = 0.1$ (\blacktriangle), $E_\sigma = 0.56$ eV for $x = 0.2$ (\bullet), $E_\sigma = 0.60$ eV for $x = 0.5$ (\blacktriangledown), and $E_\sigma = 0.97$ eV for $x = 0.9$ (\blacklozenge).

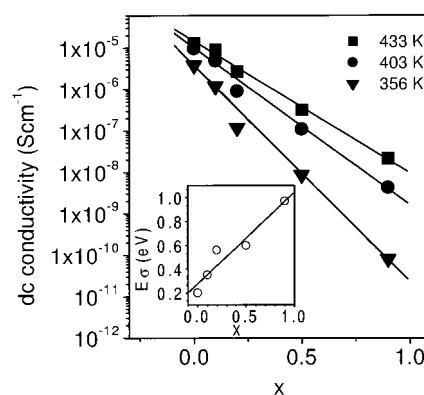


Figure 4. dc conductivity vs Fe content for fixed temperatures: 356 K (\blacktriangledown), 403 K (\bullet), and 433 K (\blacksquare). There is an exponential decrease of the dc conductivity as Fe content is increased. The inset shows that the dc conductivity activation energy increases with Fe content, the solid line being the linear fit.

$\text{Bi}_4\text{V}_2\text{O}_{11}$ introduces oxygen vacancies, which are accommodated in domains with different oxygen stoichiometry. In addition to the host matrix $\text{Bi}_4\text{V}_2\text{O}_{11}$ with disordered oxygen vacancies, two structural domains appear which have been shown to present the anionic stoichiometries $\text{O}_{10.66}$ and O_{10} labeled ① and ②, respectively, in Figure 4 of ref 11. Both types of domains increase in size with increases in the iron content at the expense of the highly conducting host matrix. The domain with anionic stoichiometry $\text{O}_{10.66}$ is characterized by an ordering of the oxygen vacancies, giving rise to the 3-fold commensurate modulation along the b axis. The ordered distribution of two square pyramids and one octahedron along $[010]$, that is, the oxygen vacancies ordering, imposes an important constrain to oxygen diffusion, which reflects in the increase of the dc activation energy. In the O_{10} domains, the perovskite layers are now formed by squared-based pyramids¹⁹ as in the $\text{Bi}_4\text{V}_2\text{O}_{10}$ compound, and the oxygen positions that were previously vacant positions became unoccupied sites. For the oxygen ions hopping, this is the situation equivalent to having all metallic atoms in octahedral coordination, that is, without anionic vacancies as in Bi_2 -

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MoO₁₂.²⁰ Thus, the ionic conductivity is expected to be highly restricted in these domains, contributing less to the conducting mechanism.

The existence of domains with very different conductivity suggests a complicated scenario in which oxygen vacancies diffuse through the O_{10.66} domains such as in a percolation-limited system. The increase in size of the O₁₀ domain, with a small contribution to the conductivity, and the O_{10.66} domain, with a reduced oxygen mobility, results in an increase of the activation energy for the dc conductivity. For the sample with $x = 0.9$ the material has oxygen stoichiometry close to O₁₀, and the oxygen vacancies turn into unavailable positions for the oxygen atoms.¹⁹ As a result, it shows a high activation energy of 0.97 eV and a low value of the dc conductivity, below 10⁻¹² Scm⁻¹, at room temperature.

Conclusions

In summary, we have presented a study of oxygen ionic conductivity in the BIFEVOX series. An analysis

of the ac conductivity and the electric modulus has been conducted by impedance spectroscopy, showing power law dependencies in the frequency domain. Stretched exponentials of the form $\phi(t) = \exp(-(t/\tau_o)^\beta)$ have been shown to describe the correlation function for the electrical conductivity relaxation in the time domain, with an exponent β different from 1, as a consequence of correlation effects in the oxygen ion diffusion. It has also been found that the room temperature dc conductivity decreases exponentially with Fe content and the dc conductivity activation energy largely increases. These results have been discussed in terms of oxygen vacancy ordering due to the appearance of two additional domains with different oxygen stoichiometries in the microstructure, upon substitution of V ions by Fe ions. In these domains of less oxygen stoichiometry, whose relative size increases with Fe content of the samples, the oxygen mobility is expected to be more restricted from microstructural considerations.

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