Local structure in BIMEVOX ionic conductors for ME = Mg, Si, Zr, Zn

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Fast oxide ion conductors have found use in devices such as fuel cells, oxygen sensors and gas separation membranes. In last years interest has been focused on a family of oxide ion conductors based on bismuth vanadate, Bi$_4$V$_2$O$_{11}$, which have high conductivities at relatively low temperatures (ca. $10^{-3}$ S cm$^{-1}$ at 500°C). The structure of the parent compound, Bi$_4$V$_2$O$_{11}$ consists of alternating layers of [Bi$_2$O$_2$]$_2$ and [VO$_{3.5}$]$_2$. Substitutional doping of vanadium by lower valency cations (in most cases divalent metals) leads to a stabilisation of the $\gamma$-phase having a high ion conductivity at room temperature. This family of solid electrolytes has become known as the BIMEVOX system [1,2]. Till now, two papers on EXAFS studies in BIMEVOX system concerning only a few compositions have been published [3,4].

In this work we studied X-ray absorption fine structure in BIMEVOX materials with bivalent and tetravalent dopants. BIMEVOX samples with ME = Si, Mg, Zr, Zn have been prepared from high-purity oxides by conventional solid state interdiffusion procedures. XAFS measurements have been carried out at the A1 station by the transmission method.

Fig.1 presents the normalised XANES spectra for BIZNVOX with different zinc content. It shows abrupt change of the spectra between two compositions with 22 % and 40 % of zinc. This corresponds to crossing the zinc solubility limit and formation of polyphasic system. In this study only the single $\gamma$-phase compositions have been examined. It corresponds to a dopant content well below 30% for all studied BIMEVOX materials. The distinct pre-edge peak has practically the same position for all studied BIMEVOX’es (Fig.2). A comparison with V$_2$O$_5$ standard indicates that vanadium is almost exclusively in 5+ charge state [5]. The strength of the pre-edge feature indicates highly non-centrosymmetric position of vanadium atoms. As has been shown for V$_2$O$_5$ [6], the strength of this peak comes about almost exclusively from the short V-O bond and its asymmetry to the opposite bond. This suggests that “apical” oxygens in BIMEVOX materials are far from ideal octahedral positions. When two oxygen vacancies are present in equatorial positions, local environment of vanadium atom is effectively tetrahedral-like for which a strong pre-edge feature is usually observed.

![Fig.1. XANES for BIZNVOX for different Zn content.](image1.jpg)

![Fig.2. Pre-edge peak for BIMEVOX with different ME dopants.](image2.jpg)
EXAFS has been measured at the vanadium K edge for all studied BIMEVOX’es and for the zinc K edge. The range of the useful data is limited to the nearest neighbour shell, because of disorder in higher shells. The data has been analysed, taking into account results of the combined X-ray and neutron powder diffraction [7,8]. In particular they have revealed two main types of vanadium/dopant coordination viz. distorted octahedral and distorted tetrahedral. EXAFS results indicate, shorter vanadium bonds with 1 or 2 oxygen atoms and longer bonds with 2 or 3 oxygen atoms. Analysis of zinc K edge EXAFS indicates, that the Zn-O distances are shorter than the V-O distances. The shorter bonds have 1.5 Å length and longer 1.95Å. The total coordination number is for zinc closer to 4, what is expected in the equatorial vacancy model [2].

In conclusion, vanadium K-edge XANES appears to be a sensitive probe of the crystallographic phase of the studied BIMEVOX materials. The high intensity of the pre-edge peak is associated with a strongly non-centrosymmetric environment of V atoms. Position of the pre-edge peak in the XANES spectra of vanadium indicates its valence state close to 5+ in all studied BIMEVOX’es. Vanadium coordination, as inferred from EXAFS data, shows also similarity for all BIMEVOX’es with two V-O bond lengths. It is, however difficult to determine exact occupation numbers for oxygen atoms from our data and to judge dominant location of oxygen vacancies (apical or equatorial positions). Zinc coordination number in BIZNVOX is close to 4, the interatomic distances to oxygen atoms are shorter than for vanadium.

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References