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Compressed Cu^{2+} Ions in a $Bi_4V_2O_{11}$ Oxide Matrix. 1. EPR and UV–Visible Study

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BICUVOX.x ($Bi_2V_{1-x}Cu_xO_{5.5-1.5x}$) prepared with different atomic ratios Cu/V and calcined under a dry air at 1093 K have been characterized by electron paramagnetic resonance (EPR). The inverted g anisotropy values of the copper(II) ions EPR signal ($g_\perp > g_\parallel$) can be interpreted by an octahedral symmetry strongly distorted with a compression of oxygen atoms along the apical direction. These results have been confirmed by UV–visible spectroscopy.

Introduction

The compounds obtained by partial substitution for vanadium with other elements in $Bi_4V_2O_{11}$ are designated by BIMEVOX and constitute a new family of attractive materials owing to their high oxide ion conductivity.[1]

$Bi_4V_2O_{11}$, the parent compound, exhibits three different polymorphs α, β, and γ and undergoes two successive phase transitions $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ at about 720 and 840 K on heating, respectively.[2]

The high-temperature γ-type phase can be stabilized at room temperature by chemical substitution. For instance, substitution for vanadium with copper gives rise to the BICUVOX family. Generally, BICUVOX.x represents the solid solution $Bi_2V_{1-x}Cu_xO_{5.5-1.5x}$ if Bi(3+), V(5+), and Cu(2+) are the oxidation states and x is the percent of the vanadium replaced by copper.[3] When $x < 7$, the compound is orthorhombic with an α-type incommensurately modulated structure. In the range $7 < x < 12$, the room-temperature unit cell becomes tetragonal with a γ-type structure.[3,4] Studies of conductivity and electrochemical characterization of BICUVOX.10 samples have already been described.[3–7]

From a structural point of view all these phases are related to the Aurivillius ones: Bi_2O_2 sheets alternate with (V,Me)O perovskite-like corner-sharing octahedra, the perovskite slabs being oxygen deficient. A first structural approach has already been carried out on BICUVOX.10 from single-crystal X-ray diffraction data,[3] and from neutron powder diffraction data.[8] Satellite incommensurate reflections were not taken into account, and the structure determined was therefore an "average structure".

Electron paramagnetic resonance (EPR) and UV–visible spectroscopy seem to be the best techniques to study the valence states of copper and their symmetry when they are present in solids either in substitutional sites or on the surface in form of isolated ions or clusters. The intensity and the EPR parameters of the signal from isolated Cu^{2+} ions may be regarded as a measure of the oxidation degree and of the number of coordinated ligands or vacancies surrounding copper.[9,10] The wavelength of the absorption band of the cupric ions in the UV–visible spectra gives more information on the environment of these species. When this parameter increases, in general from 300 to 1500 nm, the Cu^{2+} ions change from octahedral to tetrahedral symmetry or the number of coordination decreases.[11]

In this work, we report EPR and UV–visible investigations to characterize the symmetry and the nature of copper(II) ions in BICUVOX.x.

Experiment

Polycrystalline samples at different atomic ratios Cu/V were prepared by heating appropriate compositions of Bi_2O_3, V_2O_5, and CuO oxides at 1093 K for 20 h in gold crucibles in air and were characterized by their X-ray diffraction patterns obtained with a Guinier–De Wolff camera (Cu Kα radiation).

The electron paramagnetic resonance (EPR) spectra were recorded on a Varian E 109 spectrometer at 9.3 GHz (X band) with a rectangular dual cavity. Modulations at 100 and 10 kHz were used in both channels with modulation amplitudes of 10 G for the solids and 1 G for the standard sample (strong pitch Varian, $g = 2.0028$). The hyperfrequency power was chosen small enough to prevent any saturation. The spectra were systematically recorded at room temperature and 77 K.

UV–visible spectra were recorded at room temperature in the range 200–800 nm with a Kontron-Uvikon 860 equipped with an integrating cell and barium sulfate as reference.

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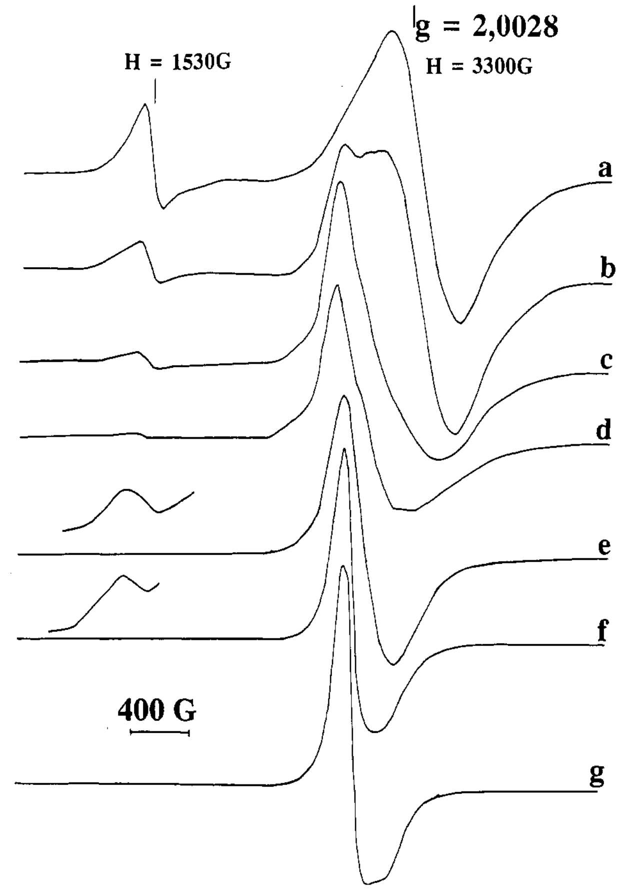

Figure 1. EPR spectra recorded at room temperature of BICUVOX.*x* calcined under dried air at 1093 at various Cu/V atomic ratios: (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.5$; (d) $x = 1$; (e) $x = 5$; (f) $x = 10$, and (g) $x = 15$.

Table I. g Values of Cu^{2+} Ions in BICUVOX.x Solids at Different Atomic Ratios Cu/V

	BICUVOX.x (%)						
	0.1	0.5	1	2	5	10	15
$g_\parallel$	2.051	2.052	2.057	2.063	2.060	2.132	2.078
$g_\perp$	2.326	2.343	2.348	2.335	2.296	2.295	2.279

Results and Discussions

EPR Spectroscopy. Figure 1 shows the EPR spectra obtained on BICUVOX.x samples containing different copper concentrations ($0 < x < 15$).

The first spectrum (Figure 1a), obtained on $Bi_4V_2O_{11}$, is apparently characterized by a broad isotropic signal with peak-to-peak width of 470 G centered at $g = 1.9543$ and another signal observed at low magnetic field intensity ($g = 4.3449$). The spectrum is characteristic of V^{4+} in dipolar interaction with other V^{4+} ions. Similar spectra have been obtained in other samples containing vanadium(IV).[12,13]

When copper partially replaces vanadium in the solid, the intensity of the first spectrum decreases drastically whereas a new signal, axial and without hyperfine structure, appears. Without ambiguity, this new signal can be attributed to Cu^{2+} ions in spite of the fact that the $g_\perp$ value is larger than $g_\parallel$ (Table 1). Indeed, the inversion in *g* anisotropy values has already been observed in the copper(II) EPR.[14-17] According to the Jahn–Teller theorem, copper(II) complexes can never be rigorously octahedral. The idealized geometry must be tetragonally distorted, and this distortion can result either in the elongation or in the compression of the octahedron. In principle EPR spectroscopy can distinguish between these: $g_\parallel > g_\perp$ for elongation, and $g_\parallel < g_\perp$ for compression. However, these patterns are only trends if the complexes are magnetically dilute, since exchange interactions tend to average EPR spectra, and therefore crystal **g** tensors are not necessarily the same as molecular **g** tensors. Certain authors[18-20] have taken $g_\parallel > g_\perp$ to be typical when the ground state of the unpaired spin is $d_{x^2-y^2}$. This situation appears when the coordination geometry of the Cu^{2+} ions is tetragonally elongated octahedral, square pyramidal or square planar. The inverted signals ($g_\perp > g_\parallel$) are generally obtained when the ground state is d_{z^2} and appear when the coordination geometry is a tetragonally compressed or rhombohedrally distorted octahedron, tetragonally elongated tetrahedron, cis-distorted octahedron, or trigonal bipyramidal configuration. Since the structural data previously obtained by X-ray diffraction[3] are the following: the (V,Cu)O octahedron, drawn from idealized atomic positions in the perovskite-like slabs of BiCUVOX.10, is strongly compressed (1.54 Å with O in apical position and 1.95 Å with O in the basal plane parallel to the Bi_2O_2 layers (Figure 2)), these values have to be compared with those found in γ Bi_2MoO_6 (1.66 and 1.97 Å) and in Bi_2WO_6 (1.69 and 1.82 Å) in the F_{mmm} parent structure. Consequently, the inversion of $g_\parallel$ and $g_\perp$ of the copper(II) signal appears more probably due to a com-

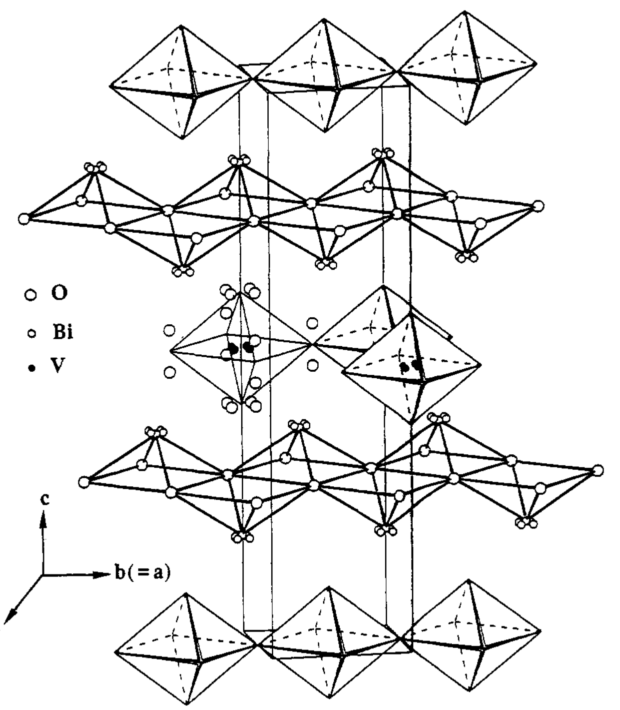

Figure 2. Schematic representation of the BICUVOX.10 structure.

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pressed octahedral symmetry of such ions with a d_{z^2} ground state. Moreover, it has been suggested that the degree of anisotropy of the g factors in the complexes depends on the number of donor oxygen atoms and on atoms surrounding the concerned ions. Table 1 indicates that the g value remains constant for copper concentration up to 5%. In this domain the solid exists in form of α-type. For copper content where $7\% < x < 12.5\%$, a decrease of $g_\perp$ value is obtained. In this range, the solid corresponds to γ-type tetragonal solid solution. Therefore, the decrease of the $g_\perp$ value when the copper(II) concentration increases can be correlated with increasing oxygen vacancies in BICUVOX.x. This is in agreement with the diffusivity coefficient values as the ionic conductivity at room temperature is higher when copper is present in $Bi_4V_2O_{11}$.[4] This observation is also in agreement with the evolution of the unit cell characterizing the BICUVOX.x solid solution: the higher the x content, the higher the c parameter and therefore the spacing between the $Bi_2O_2^{2+}$ sheets.[4] The results obtained in UV–visible spectroscopy, carried out on the powdered samples and presented hereafter, will confirm our hypothesis.

When x becomes larger than 12.5, another signal ($g_\perp$ = 2.279; $g_\parallel$ = 2.078) appears. It is characteristic of Cu^{2+} ions localized in sites with also an octahedral symmetry strongly distorted. Since at such copper concentrations, another $Bi_4Cu_3V_2O_{14}$ compound is formed with the initial solid (BICUVOX.x),[21] it is then obvious to attribute the latter signal to Cu^{2+} ions present in this solid.

Moreover, Figure 1 shows the presence of a weak signal just at half the normal magnetic field intensity. This signal which is produced by forbidden transition (Δm_s = 2) is characteristic of the existence of copper(II) ion pairs in the solid.[22–24] When the spectrum is recorded at 4.2 K instead of 77 K or room temperature, the signal observed at the normal magnetic field (Δm_s = 1) changes in shape and becomes more characteristic of a dimer signal (Figure 3), whereas the weak signal (Δm_s = 2) does not change. The signal at normal magnetic field consists of two peaks separated by 370 G, which corresponds to the value of the anisotropic exchange constant D or to the splitting between the triplet levels when the magnetic field is equal to zero.

The intensities ratio I_{rel} of the signals respectively observed at $\Delta m_s = 2$ and $\Delta m_s = 1$ is theoretically correlated with the distance r between both copper(II) ions in the dimer,[25] by the equation

$$I_{relative} = \frac{I(\Delta m_s{=}2)}{I(\Delta m_s{=}1)} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2$$

where A is a constant [$A = (21 + 2) \times 10^{-6}$], with r in nanometers and ν in gigahertz. In our case $I_{rel} = 7.5 \times 10^{-4}$ and r = 0.549 nm. This latter value is very close to the parameter of BICUVOX.10 crystallographic unit cell when taking into account the superlattice incommensurate reflections: $a = b$ = 5.543 Å.[4]

Comparing the spectrum intensity obtained without copper with that obtained from BICUVOX.10, we have calculated the V^{4+}/V^{5+} ratio in $Bi_4V_2O_{11}$. The weak value (3.2×10^{-3}) found shows that V^{5+} ions are predominant in this compound in agreement with the oxygen content. Moreover, this value explains why the intensity of the spectrum attributed to copper increases rapidly when the vanadium (4+) and (5+) are replaced by this species.

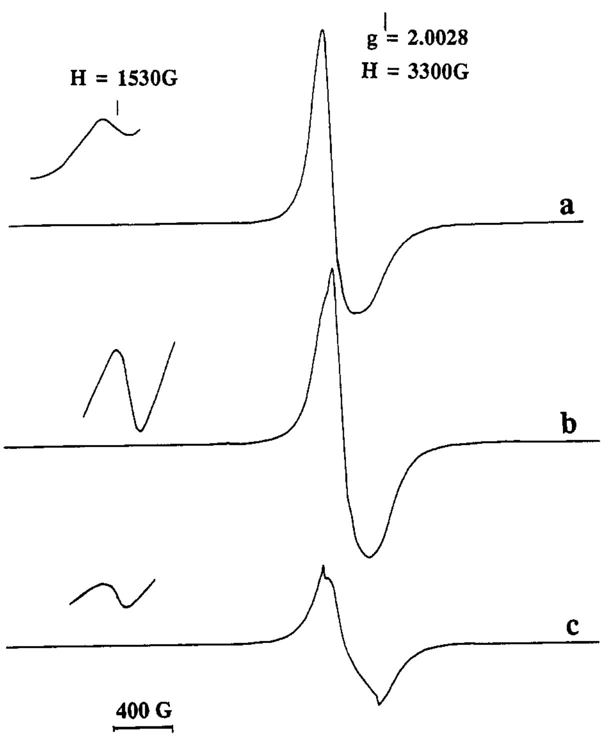

Figure 3. EPR spectra of BICUVOX.10 calcined under dried air at 1093 K and recorded at (a) room temperature, (b) 77 K, and (c) 4.2 K.

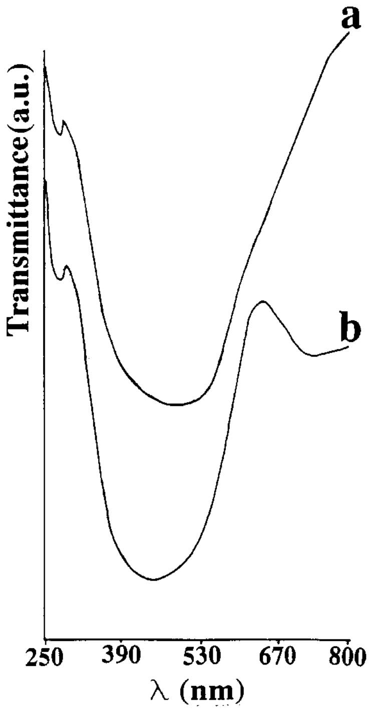

Figure 4. UV–visible spectra recorded at room temperature of BICUVOX.x calcined at 1093 K under dried air: (a) x = 0 and (b) x = 10.

UV–Visible Spectroscopy. Figure 4 shows the UV–visible transmittance bands recorded at room temperature for BICUVOX.10. In absence of copper, the solid exhibits one broad band in the range 350–550 nm and another

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weak one at 285 nm. In copper-substituted compounds, another band appears at 730 nm and becomes larger when the concentration increases. It is then evident to assign this band to the presence of such Cu^{2+} species.

The bands observed at 350–550 and 285 nm can be attributed either to the presence of V^{5+} in the solid or to the presence of Bi^{3+} ions. Indeed, Praliaud et al.[26] have demonstrated in the case of V_2O_5 supported on MgO, Al_2O_3, and SiO_2 that the absorption bands obtained between 250 and 330 nm are due to charge transfer from one orbital of the O^{2-} ligand to the vacant d orbital of the V^{5+} ions. Moreover, the same authors attributed the bands observed in the range 340–490 nm to V^{5+} with an octahedral symmetry and those in the 700–750-nm area to the V^{4+} obtained after reduction. Similarly, the Bi^{3+} ions give rise to absorption bands in the same domain as the V^{5+} species (335 and 415 nm). It is then normal, to attribute the bands observed in pure $Bi_4V_2O_{11}$ (absence of copper), to V^{5+} ions and/or to Bi^{3+} ions. Since the concentration of V^{4+} ions in the solid is negligible compared to that of V^{5+}, no band has been observed in the domain 700–750 nm.

In the case of UV–visible spectroscopy of copper(II), it has been shown that the wavelength of the transmittance or absorption band decreases from the range 1000–1500 to 500–700 nm when the symmetry of Cu^{2+} ions changes from tetrahedral to octahedral. Indeed, Sengupta et al.[27] have observed on Cu–Zn oxides an absorption band in the region of 570 nm which has been ascribed to the presence of Cu–O–Cu clusters and to the pure copper oxide (CuO). This band is due to charge transfer from the nonbonding p_z orbital of the bridging ligands to the vacant d orbital of the Cu^{2+} ions. Choisnet et al.[28] have attributed the band obtained at 649 nm to copper(II) ions in octahedral sites with a tetragonal distortion. Srinivasa Rao et al.[29] have detected in alkaline cadmium borosulfate glasses a broad absorption band of Cu^{2+} ions between 800 and 845 nm which has been attributed to an octahedral symmetry with a strong tetragonal distortion. It is then evident to attribute the transmittance band observed at 730 nm in the BICUVOX.10 solid to copper(II) ion pairs with an octahedral symmetry strongly distorted.

Conclusion

In this work it has been demonstrated that the copper replacing vanadium in $Bi_4V_2O_{11}$ gives an idea about the environment symmetry of that atom. The inversion in g-anisotropy values of the copper(II) ions EPR signal obtained ($g_\perp > g_\parallel$) has been interpreted by an octahedral symmetry strongly distorted with a compression of oxygen atoms along the apical direction. Work is in progress to determine the accurate crystal structures of this family of compounds using combined X-ray diffraction and neutron diffraction data collected from the single crystals and ceramic samples.

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