Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 795–796. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 864–865.

LETTERS TO THE EDITOR

Local Structural Excitations and Critical Temperature of Supported Superconducting Oxides

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Received February 3, 2003

This study concerns the mechanism of origination of physicochemical and electrophysical properties of superconducting oxide ceramics, their stabilization, and role of the oxygen sublattice in the process. Since the superconducting transition temperature strongly depends on the state of the oxygen sublattice, elucidation of how the energy gap 2Δ and its thermal behavior correlate with the vibrational activity and oxygen deficiency of the lattice is an urgent problem. As investigation objects we chose oxides of three classes according to the classification of [1]: (1) layered cuprates with the hole conductivity, based on La_2CuO_4 and $YBa_2Cu_3O_{7-x}$; (2) three-dimensional compounds based on $BaBiO_3$; and (3) compounds with the electronic conductivity based on Nd_2CuO_4, and also five-component compounds HgCaBaCuO (cation ratio 1223). The samples were prepared by layer-by-layer (five layers) deposition from solutions containing a mixture of the nitrates onto the surface of porous magnesium aluminum oxide ceramics (cordierite, S_{sp} 42 $m^2\,g^{-1}$), followed by drying, thermolysis, and annealing in oxygen. The average content of the new phase was 20 wt %. We performed X-ray phase, elemental emission, and photocolorimetric analyses (mean measurement error ~2%) to determine the polycrystallinity and stoichiometry of the samples. The IR spectra were recorded in the temperature range 298–1198 K in air or in an inert atmosphere using an IKS-25M high-resolution spectrometer. Samples with the required oxygen stoichiometry were prepared by quenching preceded by annealing in oxygen at 600–1200 K [2]. The content of labile oxygen and its species were quantitatively determined by sorption calorimetry [3]. Methods of quantum-chemical computer simulation [4] were used to correct the band assignments and analyze transformations of the electronically and vibrationally excited states of the oxygen and cationic sublattices.

Analysis of the vibrational spectra of the cuprate samples $YBa_2Cu_3O_{7-x}$ shows that the lines corresponding to fully symmetrical vibrations of the oxygen sublattice (ν_1 495, ν_2 435, ν_3 337 cm^{-1}), which are strong and well-resolved in polarized Raman spectra [5], are also reliably detected in the IR spectra. The ν_1 and ν_2 frequencies originating from stretching vibrations of the bridging oxygen atoms and synphase shifts of oxygen atoms within a CuO_2 layer are the most sensitive to the lattice distortions in the tetragonal-to-orthorhombic phase transition.

The frequencies of the ν_1 and ν_2 lines appreciably depend on the oxygen content. As x in $YBa_2Cu_3O_{7-x}$ is increased from 0 to 1, ν_1 decreases from 520 to 470 cm^{-1}, and ν_2 increases from 430 to 460 cm^{-1}. The highest critical temperature corresponds to complete filling of the labile oxygen sublattice (x 0.1–0.2).

The compounds with the electronic and hole conductivity from the Ln_2CuO_4 ($Ln_{0.85}Sr_{0.15}CuO_4$) and Nd_2CuO_4 ($Nd_{1.85}Ce_{0.15}CuO_4$) families, having the layered perovskite-type structure of the K_2NiF_4 type, and three-dimensional compounds based on $BaBiO_3$ ($Ba_{0.6}K_{0.4}BiO_3$), having relatively low critical temperatures and classical perovskite ($CaTiO_3$) structure, show virtually no vibrational activity in the range 500–520 cm^{-1}. Their specific feature is characteristic absorption at 667 cm^{-1}, corresponding to peroxide fragments of the oxygen sublattice. The possibility of the presence of these fragments in the structure of superconducting ceramics was noted previously [6]. The intensity of this band correlates with the desorption activity with respect to singlet oxygen. Well-resolved strong absorption bands at 250–280 cm^{-1} correspond to stretching vibrations of the metal–metal bonds in the system of extended clusters of the cationic sublattice, which in the case of $Ba_{0.6}K_{0.4}BiO_3$ suggests the presence of bismuth ions in low intermediate oxidation states ($Bi^4+ \rightarrow Bi^{2+}$).

The five-component compounds characterized by the highest critical temperatures show relatively low desorption activity with respect to oxygen, with the electronically excited states prevailing. The spectra exhibit series of strong absorption and emission bands assignable to stretching vibrations in molecular and oligomeric electronically excited oxygen species. A characteristic feature of these samples is the set of emission bands which are observed throughout the spectrum and can be assigned to manifestation of the superconducting gap with $2\Delta/kT > 10$ at temperatures above T_c.

The detection of a well-resolved intense spectrum of the vibrational activity of the ground and electronically excited states of the O–O bond involving neutral and charged atoms (1900–1700, 1556–1240, 800–250 cm^{-1}) in the structure of the oxide systems under consideration gives insight into the origin of abnormally high frequencies and intensities in the Raman spectra [7] of high-T_c oxide superconductors.

We found that the optical densities D of strong bands at 1557, 1456, 1400–1340, and 1240 cm^{-1}, assignable to the fundamental vibrational transitions in triplet and singlet oxygen molecules, linearly correlate with the critical temperature. Our results furnish structural-chemical support for the Cardona's concept [8] of the presence of localized states in crystals, the hypothesis of "local structural excitations" [9], and the hypothesis that donor–acceptor interactions play a basic role in origination of high-temperature superconductivity [10].

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