

Preparation and Properties of BaCuO_{2.5} and Its Related Oxides

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The compound BaCuO_{2.5} was obtained using BaO₂ and CuO as starting materials, and its various properties were investigated. It belongs to the orthorhombic system with $a = 8.55 \text{ \AA}$, $b = 10.56 \text{ \AA}$, and $c = 7.62 \text{ \AA}$. The p -type semiconductor BaCuO_{2.5} is paramagnetic, obeying Curie's law within the measured range from 77 to 220 K; its μ_{eff} is equal to 0.95. The effective spin-orbital coupling constant λ_e was deduced from ESR and from its electronic spectrum. Its binding energy of Cu2 $p_{3/2}$ XPS is 935.0 eV, accompanied by a weaker shake-up satellite with $I_s/I_m = 0.31$, 1.5 eV higher than that, 933.5 eV, of BaCuO_{2.0}, which is accompanied by a stronger satellite. All the above properties of BaCuO_{2.5} give evidence that there are at least two different types of coordinated Cu(III) atoms in BaCuO_{2.5}, one of which lies in an octahedral ligand field, and the cubic ligand parameter D_q is estimated to be 2000 cm^{-1} ($B = 1030 \text{ cm}^{-1}$, $C = 4.71B$). The higher valence state of copper in YBa₂Cu₃O_{7- δ} appears to be expected from a comparison of the properties of YBa₂Cu₃O_{3- δ} and BaCuO_{2.5} or other substances. © 1994 Academic Press, Inc.

INTRODUCTION

The synthesis and properties of BaCuO_{2.5} have been the subjects of increasing interest (1, 2) with the discovery of high- T_c oxide superconductors and the discussion of the oxidation state of copper. In fact, the synthesis and magnetism of BaCuO_{2.5} were reported as early as 1975 by Arjomand and Machin, who considered that BaCuO_{2.5} was antiferromagnetic with $\mu_{\text{eff}} = 3.06$ and copper(III) atom located in an octahedral coordination (3). On the basis of the ESR signal, Straub considered that there was a hexacoordinated copper(III) atom of the high spin system in BaCuO_{2.5}, consistent with the statement of Arjomand and Machin (3), but his Cu2 p XPS had no chemical shift to higher binding energy compared with that of CuO (2). The present paper will report investigations on the physical properties of BaCuO_{2.5} and its related oxides,

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and propose some new approaches to the synthesis of BaCuO_{2.5} and to its coordination chemistry.

EXPERIMENTAL CHARACTERIZATION

X-ray diffraction data were obtained using a Rigaku D/MAX-II B powder diffractometer with CuK α_1 radiation calibrated by the standard Si XRD pattern. The lattice parameters were refined by least-squares analysis of the diffraction data. The susceptibility was measured on a Model MB-2 magnetic balance. The electronic spectra were recorded on a VSU-2P spectrophotometer. Samples were put in a quartz capillary tube and mounted in a JES-FESAX ESR spectrometer. The g -factor of DPPH was used as standard. The XPS experiments were performed using a vacuum generator ESCA Lab MK II system with AlK α X-rays ($h\nu = 1486.6 \text{ eV}$) and vacuum pressure of about $2 \times 10^{-7} \text{ Pa}$; the C1s signal, which was given a binding energy at 284.6 eV, was used as a check for the sample charging. The resolution for the Ag3 $d_{5/2}$ peak was 1.8 eV full width at half-maximum (FWHM) under the experimental conditions in this work.

RESULTS AND DISCUSSION

1. Syntheses and XRD Patterns of BaCuO_x ($x = 2.5, 2.0$)

The finely ground powder mixture of BaO₂ and Cu(NO₃)₂ · 3H₂O was kept at 580°C for 24 hr and cooled naturally to room temperature under oxygen. The XRD showed that the product corresponded to the Ba(NO₃)₂ phase, which was different from the product described in Refs. (1, 2). The Ba(NO₃)₂ phase did not disappear at 650°C for 24 hr, and did not even decompose thoroughly at 700°C for 8 hr. After approximately 24 hr at 700°C, the Ba(NO₃)₂ phase disappeared almost exhaustively and the main phase was BaCuO_{2.5}. However, the results of iodometry indicated that the oxidation number of copper was as low as 2.7. All the above implied that the precursor product of BaO₂ that reacted with Cu(NO₃)₂ was Ba(NO₃)₂, whose melting point is at 592°C (4). As the

temperature rose, $\text{Ba}(\text{NO}_3)_2$ decomposed and reacted with the copper compound to yield $\text{BaCuO}_{2.5}$, which reduced to BaCuO_2 at higher temperatures (1, 3).

We failed to obtain $\text{BaCuO}_{2.5}$ powder using $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as starting material as reported in Ref. (1) because $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ melted and spilled out from the crucible.

A brown-black powder of $\text{BaCuO}_{2.5}$ was successfully prepared by calcining a mixture of BaO_2 and CuO at 550°C for 60 hr under oxygen. The powder XRD pattern is illustrated in Table 1. $\text{BaCuO}_{2.5}$ is in the orthorhombic system with $a = 8.55 \text{ \AA}$, $b = 10.56 \text{ \AA}$, and $c = 7.62 \text{ \AA}$. After calcination at 850°C for 48 hr in ambient atmosphere, $\text{BaCuO}_{2.05}$ (for short $\text{BaCuO}_{2.0}$) was prepared. Its XRD pattern is similar to that found by Migeon *et al.* (5). In this article, both of the $\text{BaCuO}_{2.5}$ and $\text{BaCuO}_{2.0}$ samples described below were prepared from BaO_2 and CuO .

2. Electrical and Magnetic Properties

Arrhenius plots of the relation $\sigma = \sigma_0 \exp[-E_a/RT]$ under conductivity (σ) and temperature (T) for $\text{BaCuO}_{2.5}$ and $\text{BaCuO}_{2.0}$ are presented in Fig. 1. There is a slope change at 97°C for $\text{BaCuO}_{2.5}$ with $E_a = 0.22 \text{ eV}$ and $E_a = 0.30 \text{ eV}$ in the lower and higher temperature ranges, while there is a knee at 127°C for $\text{BaCuO}_{2.0}$ with $E_a = 0.28 \text{ eV}$ and $E_a = 0.33 \text{ eV}$ in the lower and higher temperature ranges, respectively. The conductivity of $\text{BaCuO}_{2.5}$ is higher than that of $\text{BaCuO}_{2.0}$, which may be attributed to the increase in the number of hole carriers with increased oxygen content.

The superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, prepared by common ceramic processing from $\text{BaCuO}_{2.5}$ or $\text{BaCuO}_{2.0}$,

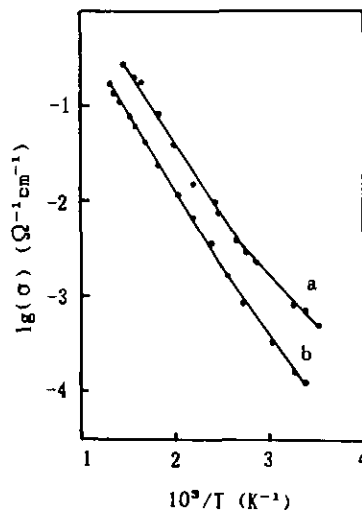


FIG. 1. The electrical properties of (a) $\text{BaCuO}_{2.5}$ and (b) $\text{BaCuO}_{2.0}$.

is analogous to that of the substance from which it is prepared.

$\text{BaCuO}_{2.5}$ is paramagnetic, following Curie's law in the measured range from 80 to 220 K with effective magnetic moment μ_{eff} of $0.95\mu_B$, whereas the μ_{eff} of $\text{BaCuO}_{2.0}$ is $1.87\mu_B$ (5). A family of BaCuO_x with different values of x has been obtained. The molar magnetic susceptibility decreases with an increase in the formal oxidation state of copper, which confirms that the $\text{Cu}3d$ electronic configuration in $\text{BaCuO}_{2.5}$ is mainly low spin (LS) with a ratio of about 12% high spin (HS). The conclusion is contrary to that of Arjomand and Machin (3).

3. Electronic Spectra and ESR

Only a wide band is observed in the diffuse reflectance spectrum of $\text{BaCuO}_{2.0}$; it is assigned to the superposition of various transitions (curve a in Fig. 2) for several types of coordinations of copper atoms in a unit cell (6). There are two broad absorption bands at 525 and 830 nm for the diffuse reflectance spectrum of $\text{BaCuO}_{2.5}$ (curve b in Fig. 2); the former corresponds to the spin-allowed $d-d$ transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ in the O_h symmetry, and its cubic ligand field parameter D_q can be estimated at 2000 cm^{-1} ($B = 1030 \text{ cm}^{-1}$, $C = 4.71B$) in comparison to the optical absorption spectrum of Cu^{3+} in corundum described by Blumberg *et al.* (7). The electronic spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with 90 K superconductivity is given in curve d of Fig. 2, which shows a band at 815 nm that is likely to have some relation to the higher oxygen content (8, 9). $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has another absorption band at 450 nm, which might be a hint of the presence of $\text{Cu}(\text{III})$ (9). The absorption is also found at 450 nm for CuO (curve c of Fig. 2). CuO and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have some similar physical features; for instance, neither of them produces ESR sig-

TABLE 1
X-Ray Powder Diffraction Pattern of $\text{BaCuO}_{2.5}$

h	k	l	d_{obs}	d_{calc}	I_{obs}	h	k	l	d_{obs}	d_{calc}	I_{obs}
1	0	1	5.75	5.69	4	1	4	2	2.107	2.103	9
0	0	2	3.74	3.81	50	1	5	0	2.047	2.051	11
2	0	1	3.68	3.73	32	4	1	1	2.021	2.019	13
2	1	1	3.50	3.51	26	2	2	3	2.017	2.017	12
1	0	2	3.44	3.48	20	1	3	3	2.000	2.002	10
1	3	0	3.24	3.26	8	1	5	1	1.962	1.980	10
0	3	1	3.17	3.19	7	3	4	0	1.947	1.937	13
0	2	2	3.10	3.09	100	2	4	2	1.936	1.935	13
3	0	0	2.85	2.85	32	1	0	4	1.859	1.859	5
2	3	0	2.70	2.72	14	0	5	2	1.843	1.848	8
0	4	0	2.63	2.64	13	4	1	2	1.836	1.835	12
3	1	1	2.60	2.59	14	5	1	0	1.685	1.687	16
3	1	2	2.24	2.23	14	5	3	2	1.427	1.426	6
2	3	2	2.21	2.21	11	4	0	4	1.422	1.422	6
2	4	1	2.15	2.15	16	5	2	3	1.368	1.369	6
3	3	1	2.12	2.13	13	3	4	4	1.363	1.358	6

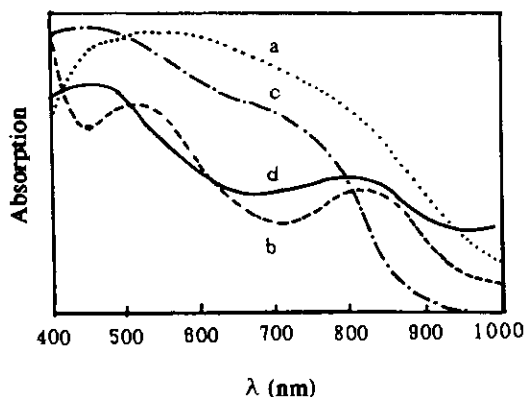


FIG. 2. Diffuse reflectance spectra of (a) BaCuO_{2.0}, (b) BaCuO_{2.5}, (c) CuO, and (d) YBa₂Cu₃O_{7-δ}.

nals. Thus it is likely that the 450-nm absorption bands are results of particular electronic configurations. The broad band of CuO at 730 nm with four different coordinated copper atoms in it may be the overlap of various *d-d* transitions.

The ESR spectrum of BaCuO_{2.5} is illustrated in curve a of Fig. 3. The symmetrical ESR signal has mainly a Gaussian shape, with a ΔH_{pp} of 240 G and a *g*-factor of 2.097 which is the same as that reported in Ref. (2) and approximately equal to that of Cu³⁺ in Al₂O₃, whose *g*-

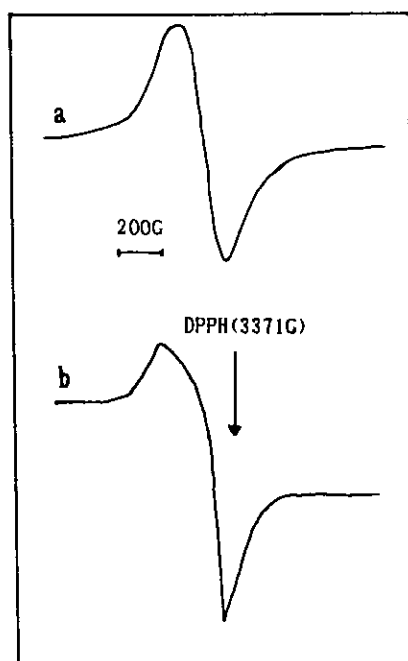


FIG. 3. ESR spectra of (a) BaCuO_{2.5} and (b) BaCuO_{2.0}.

factor is 2.078 (7). Assuming the Cu(III) atom to be sited in an ideal hexacoordination and $g_{\perp} = g_{\parallel}$, from the equation

$$g = g_e - 8\lambda_e / \Delta[E(^3T_{2g}) - E(^3A_{2g})]$$

the value λ_e of -226 cm^{-1} is obtained, which is approximately equal to that of Cu³⁺ in Al₂O₃, -214 cm^{-1} . All the above mean that such a Cu(III) atom exists in an octahedral ligand field.

The ESR shape of the BaCuO_{2.0} signal is more asymmetrical than that of BaCuO_{2.5}. The g_{\perp} and g_{\parallel} factors are estimated to be about 2.06 and 2.23, respectively (curve b of Fig. 3).

4. Cu2p XPS

The binding energy of Cu2p_{3/2} for BaCuO_{2.5} is 935.0 eV (curve a of Fig. 4), 1.5 eV higher than that of BaCuO_{2.0}, 933.5 eV (curve b of Fig. 4), and 1.4 eV higher than that of CuO, 933.6 eV (curve c of Fig. 4), whereas the chemical shift between BaCuO_{2.5} and CuO was not observed by Straub and his co-workers due to some contaminants on the surface of their BaCuO_{2.5} sample (2). The intensity ratio of the shake-up satellite to the main peak (I_s/I_m) of Cu2p_{3/2} for BaCuO_{2.5} is only equal to 0.31, much weaker than that for BaCuO_{2.0} or CuO, 0.50. The silence of the shake-up satellite of Ni2p XPS corresponds to the LS configuration and diamagnetism (12). The weaker satellite and magnetic moment of BaCuO_{2.5} confirm that there is not only a type of octahedrally coordinated Cu(III) atom

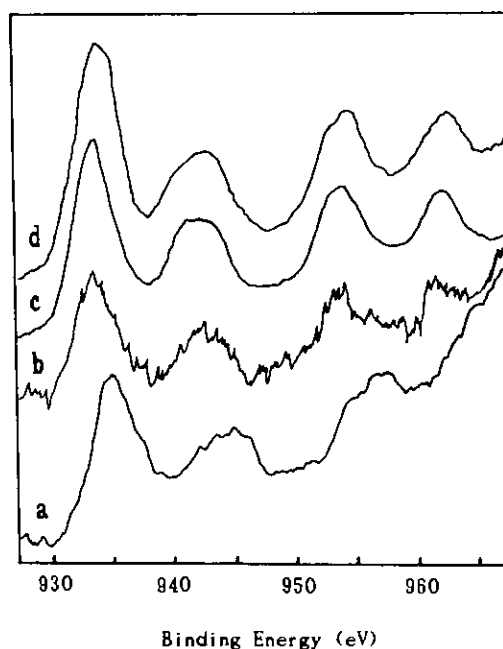


FIG. 4. Cu2p XPS of (a) BaCuO_{2.5}, (b) BaCuO_{2.0}, (c) CuO, and (d) YBa₂Cu₃O_{7-δ}.

with HS configuration but another type of nonoctahedrally coordinated Cu(III) atom with a LS configuration in $\text{BaCuO}_{2.5}$ as well. The FWHM values of $\text{Cu}2p_{3/2}$ for $\text{BaCuO}_{2.5}$, $\text{BaCuO}_{2.0}$, CuO , and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are 3.9, 3.8, 3.6, and 3.9 eV, respectively. Generally speaking, the FWHM of a paramagnetic Ni(II) compound is wider than that of its related diamagnetic Ni(II) compound (12), which mainly results from the intercoupling between the $\text{Ni}2p$ core hole and the $\text{Ni}3d$ electrons, $2s + 1 = 2$ and 4 at the final state for the paramagnetic Ni(II) compound and $2s + 1 = 2$ at the final state for the diamagnetic Ni(II) compound (not the $d-d$ transitions described in Ref. (12)). However, the main peak of $\text{BaCuO}_{2.5}$ does not appear to be sharper than that of $\text{BaCuO}_{2.0}$, although its $\text{Cu}3d$ configuration is mainly LS. It can be expected that the higher the valence state of copper, the shorter the core hole's life, and the broader the shape of $\text{Cu}2p$ XPS (uncertainty principle).

The I_s/I_m of $\text{Cu}2p_{3/2}$ of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is 0.49 eV with FWHM 3.9 eV for the main line at 933.9 eV accompanied by a shoulder at 934.7 eV (curve d of Fig. 4) assigned to the higher valence state of copper. Summarizing all of the characterizations of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ described above, we conclude that there is a higher valence state of copper in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

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