17. L. B. Kier and L. H. Hall, *Eur. J. Med. Chem.*, **12**, 307 (1977).
18. S. K. Ray, S. C. Basak, C. Raychandhury, A. B. Roy and J. J. Ghosh, *Ind. J. Chem.*, **20B**, 894 (1981).
19. S. C. Basak, S. K. Roy, C. Raychandhury, A. B. Roy and J. J. Ghosh, *IRCS Med. Sci.*, **10**, 145 (1982).
20. S. C. Basak, D. P. Gieschen, D. K. Harriss and V. R. Magnuson, *J. Pharm. Sci.*, **72**, 934 (1983).
21. C. Hansch, R. M. Muir, T. Fujita, P. P. Maloney, F. Geiger and M. Streich, *J. Amer. Chem. Soc.*, **85**, 2817 (1963).
22. J. A. Montgomery, "Antineoplastic and Immunosuppressive Agents I", A. C. Sartorelli and D. G. Johns Eds., Springer-Verlag, Berlin, 1974.
23. J. H. Lister, "Purines", Wiley-Interscience, New York, N. Y., 1971.
24. W. H. Cone, "Chemotherapy of Cancer", Lea & Febiger, Philadelphia, Pa., 1970.
25. Z. Neiman and F. R. Quinn, *J. Pharm. Sci.*, **71**, 618 (1982).

Studies on the Paramagnetic Impurity Y_2BaCuO_5 in Superconducting $YBa_2Cu_3O_{7-\delta}$ Phase

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Conventional ceramic method has been used to prepare the green phase, Y_2BaCuO_5, commonly observed in 90-K superconductor $YBa_2Cu_3O_{7-\delta}$ as an impurity phase. The powder X-ray diffraction analysis indicates that Y_2BaCuO_5 has an orthorhombic symmetry with lattice parameter of a = 12.2 Å, b = 5.61 Å, and c = 7.14 Å. The average g-value 2.13 observed in ESR spectrum is attributable to Cu^{2+} stabilized in C_{4v} field. From the magnetic susceptibility (μ_{eff} = 2.29 BM) and the ESR measurements, it is confirmed that Cu(II) $3d^9$ electrons in Y_2BaCuO_5 are localized and can be characterized by Curie-Weiss behavior. Optical reflectance spectrum shows a broad absorption peak around 680 nm due to $dxy \rightarrow dx^2\text{-}y^2$ eletronic transition.

Introduction

Since the discovery of high Tc superconductor by Bednorz and Müller[1], and Wu *et al*[2], numerous studies on this system have been performed with various scientific and technological points of view.

Recently some efforts have been made to prepare the pure $YBa_2Cu_3O_{7-\delta}$ phase not by conventional ceramic processing and fabricating methods but by chemical precursor ones[3,4], because a green insulator Y_2BaCuO_5 is very often detected in the polycrystalline superconductor $YBa_2Cu_3O_{7-\delta}$ as an impurity phase.

The purpose of this work is to investigate physicochemical properties of the green phase Y_2BaCuO_5, which might suppress the superconducting behavior, and to differentiate its spectroscopic properties from the superconducting phase.

In this work, preparation, structure, magnetic susceptibility measurement, electron spin resonance, and optical reflectance spectroscopic studies have been systematically carried out on Y_2BaCuO_5.

Experimental

Y_2BaCuO_5 was prepared by two steps: at first a mixture of 1:1:1 mole ratio of Y_2O_3, $BaCO_3$, and CuO powders has been pelletized and preheated at 900 °C for 18 hours and then the sample was reground, repelletized, and finally heated at 940 °C in oxygen atmosphere for 24 hours. Color of the obtained product was green.

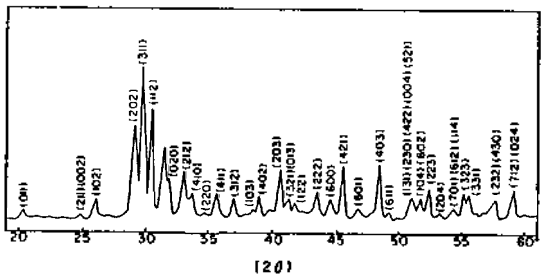

Figure 1. XRD pattern of Y_2BaCuO_5.

X-ray diffraction patterns were recorded with Ni-filtered Cu-K_α radiation (λ = 1.5418 Å) on Jeol diffractometer. Electron spin resonance spectra were obtained from 10 K to 300 K with a Bruker Et 200tt X-band spectrometer. Magnetic susceptibility measurement was carried out with a Faraday type magnetobalance from 77 to 300 K. Optical reflectance spectrum was obtained at room temperature with a Carry 16 spectrometer.

Results and Discussion

According to the X-ray powder diffraction analysis, a single phase of Y_2BaCuO_5 has been identified as an orthorhombic crystal system. Its space group is P_{nma} or P_{na2_1} with the lattice parameters a = 12.2 Å, b = 5.61 Å, and c = 7.14 Å

Table 1. Calculated d-values and Diffraction Angles for Cu-Kα Based on the Orthorhombic Structure and Comparison with the Observed Angles and Intensities[17]

h k l	d(Å)	2θ(deg.) calculated	2θ(deg.) observed	I_{obs}	h k l	d(Å)	2θ(deg.) calculated	2θ(deg.) observed	I_{obs}
1 0 1	6.162	14.36	14.32	3	4 0 3	1.876	48.47	48.52	10
1 0 2	3.426	25.98	25.95	6	1 3 1	1.789	50.99		
2 0 2	3.081	28.95	28.93	4	2 3 0	1.788	51.04		
4 0 0	3.050	29.26	29.21	8	4 2 2	1.787	51.06	51.09	8
3 1 1	2.990	29.86	29.71	100	0 0 4	1.785	51.13		
1 1 2	2.924	30.55	30.42	67	5 2 1	1.783	51.20		
			31.50	36	6 0 2	1.767	51.69	51.75	6
0 2 0	2.805	31.88	31.84	16	1 0 4	1.766	51.71		
4 0 1	2.805	31.88			2 2 3	1.739	52.57	52.34	16
2 1 2	2.701	33.14	33.03	16	7 0 1	1.693	54.12		
4 1 1	2.509	35.76	35.65	8	6 1 2	1.685	54.39	54.32	5
3 1 2	2.420	37.11	37.02	9	1 1 4	1.685	54.41		
1 0 3	2.336	38.51	38.45	5	3 2 3	1.657	55.39	55.08	14
4 0 2	2.319	38.80	38.96	10	3 3 1	1.653	55.55	55.52	12
5 0 1	2.309	38.98						55.63	10
2 0 3	2.217	40.66	40.63	20	7 0 2	1.566	58.92	58.99	11
0 1 3	2.191	41.17	41.29	10	4 2 3	1.560	59.19	59.18	6
4 1 2	2.143	42.13	42.21	4	6 0 3	1.546	59.77	59.85	4
5 1 1	2.135	42.29			7 1 2	1.509	61.41	61.43	8
2 2 2	2.074	43.60	43.60	6	0 2 4	1.506	61.52		
6 0 0	2.033	44.52	44.55	6	6 2 2	1.495	62.03	61.86	9
4 2 1	1.983	45.70	45.46	27	1 2 4	1.495	62.04	62.07	4
6 0 1	1.956	46.39	46.53	6	8 0 1	1.491	62.19		

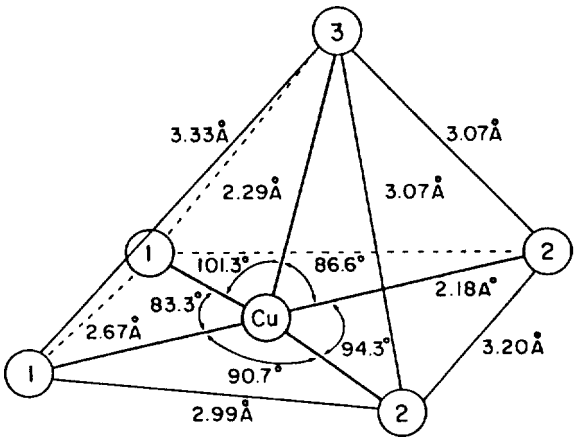

Figure 2. Local symmetry of copper in Y_2BaCuO_5. (Bond lengths (Å) and angles are also indicated).

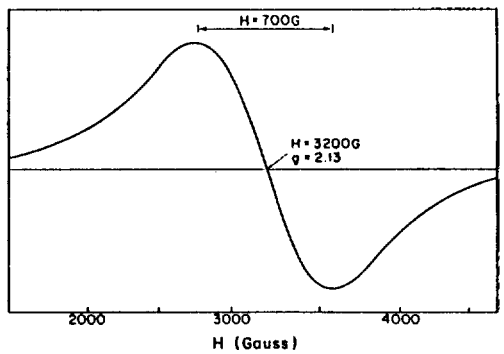

Figure 3. ESR spectrum for Y_2BaCuO_5 at room temperature.

which are in good agreement with the previous work[5]. Figure 1 shows the X-ray powder diffraction patterns for Y_2BaCuO_5, and expected d-values for various indices are calculated and presented in Table 1. Michel and Raveau first reported the Y_2BaCuO_5 in 1982 as one of a series of rare earth barium copper oxides[5]. They showed that yttrium is coordinated by 7 oxygen atoms with the local symmetry of distorted trigonal prism and barium is coordinated by 11 oxygen atoms, and the coordination polyhedron of copper is a distorted tetragonal pyramid, CuO_5, as presented in Figure 2. The local symmetry of copper in Y_2BaCuO_5 is very similar with that of C_{4v} copper in superconducting $YBa_2Cu_3O_{7-\delta}$ phase. Therefore, the experimental results of magnetic susceptibility and electronic spectroscopy on the superconducting 123 phase could be influenced by the existence of impurity phase, Y_2BaCuO_5.

X-band ESR experiments have been carried out on Y_2BaCuO_5 from 10 K to room temperature. Figure 3 shows the ESR spectrum with $< g > = 2.13$ at room temperature, and the signal can be attributed to localized Cu^{2+} states. This result is consistent with that of Kojima *et al.*[6], that is, the following relation can be deduced from the van Vleck equation on paramagnetism, $< g^2 > = (g_{\parallel}^2 + 2g_{\perp}^2)/3$, and the calculated $< g >$ value using the g-values obtained by Kojim *et al.* is 2.12 where $g_{\parallel}$ and $g_{\perp}$ correspond to 2.24 and 2.06 respectively. What is noticeable on the ESR spectrum is the possibility that similar signal can be observed from $YBa_2Cu_3O_{7-\delta}$

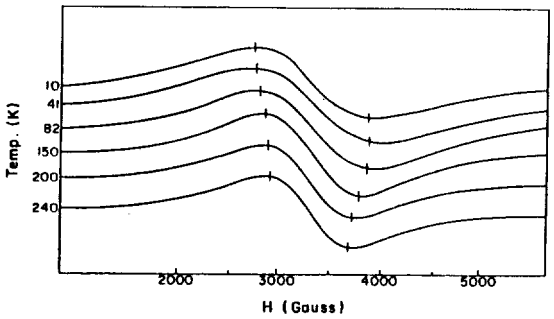

Figure 4. Temperature dependent ESR spectra for Y_2BaCuO_5.

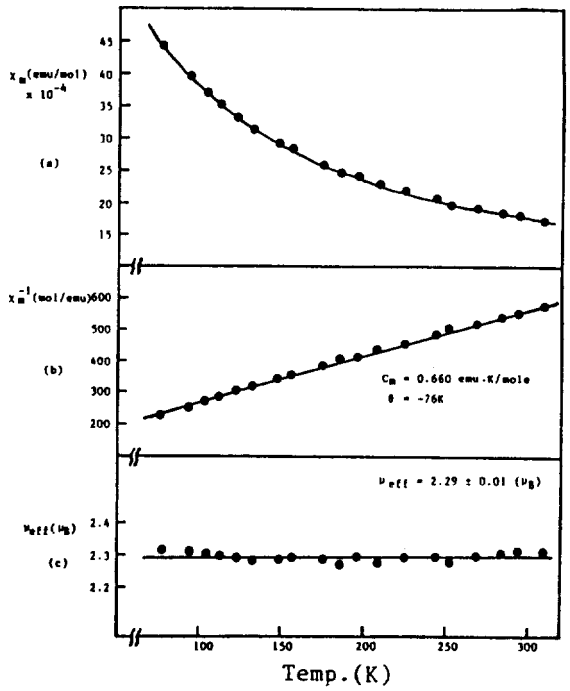

Figure 5. Temperature dependence of molar magnetic susceptibility χ_m (a), inverse χ_m (b), and effective magnetic moment μ_{eff} (c) of Y_2BaCuO_5.

the 90-K superconductor, because of the similarity of the local symmetry of paramagnetic copper ion. As shown in Figure 4, the signal becomes broad and the line width increases as the temperature decreases. Namely line width of 700 Gauss at room temperature increases gradually to 800 Gauss at 150 K, and up to 1000 Gauss at 10 K. Such a temperature dependent broadening effect could be explained by the enhancement of the spin-spin interaction between neighboring paramagnetic Cu^{2+} ions due to the considerable lattice contraction at the extremely low temperature, which causes the shorter Cu^{2+}—Cu^{2+} distance actually.

Magnetic susceptibility of Y_2BaCuO_5 has been measured from 77 to 300 K, and correction for diamagnetic contributions was performed. Temperature dependence of molar magnetic susceptibility (Figure 5) shows that Y_2BaCuO_5 obeys the Curie-Weiss law down to 77 K with the effective magnetic moment of 2.29 BM resulting from the localized $3d^9$ electrons in Cu^{II} ions, which is not consistent with the magnetic moment of 1.3 BM due to the formation of mixed valency of $Y_2BaCu^{2+}_{1-x}Cu^{+}_{x}O_{5-x/2}$, reported by Kojima *et al.*[6], but with that of 2.1 BM by Michel and Raveau.[5] The Curie

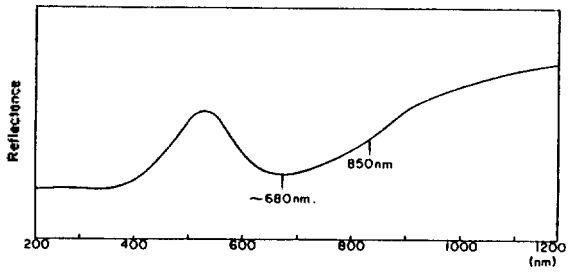

Figure 6. Optical reflectance spectrum for Y_2BaCuO_5.

constant C_m and Weiss constant θ obtained from the least square fit of $\chi^{-1} = (T-\theta)/Cm$ have been estimated as 0.660 emu·K/mole and −76 K, respectively. In general the observed effective magnetic moment of Cu^{2+} is in the range of 1.7-2.2 BM due to a considerable orbital contribution.

Optical reflectance spectrum of Y_2BaCuO_5 (Figure 6) shows a broad band at 680 nm with a low energy shoulder at 850 nm. From the crystal field energy levels for d-orbitals in square pyramidal (C_{4v}) symmetry of Cu(II)[7], the band maximum at 680 nm can be assigned as the $dxy \rightarrow dx^2\text{-}y^2$ electronic transition and the shoulder at 850 nm as the $dz^2 \rightarrow dx^2\text{-}y^2$. Most of the five coordinate copper (II) complexes have been studied and it was revealed that such ligands as halides and oxygen can introduce the complication of a possible π-bonding function for the donor atom[8] and lead to difficulties in correlating the stereochemistry and electronic properties[9-11] of the five coordinate copper (II) ion. But generally regular trigonal bipyramidal copper (II) complexes have peaks extending from 950 to 660 nm and greater absorption intensity to lower energy, and the square pyramidal copper (II) complexes have a similar band envelope with peaks extending from 1000 to 580 nm but with the greater intensity absorption to higher energy[12]. Optical reflectance spectrum of Y_2BaCuO_5 shows a high energy maximum and confirms that local symmetry of copper (II) in Y_2BaCuO_5 is a distorted square pyramid. As the energy difference between the $dx^2\text{-}y^2$ and dxy in square pyramidal symmetry of Cu (II) is 10 Dq, we can approximate 10 Dq of Cu (II) in distorted square pyramid to 680 nm, namely 14,700 cm^{-1}.

One more notice for Y_2BaCuO_5 compared with $YBa_2Cu_3O_{7-\delta}$ is the water stability of Y_2BaCuO_5. The superconducting $YBa_2Cu_3O_{7-\delta}$ phase, which is unstable in water and water vapor[13-15], decomposes to $Y_2(CO_3)_3{\cdot}3H_2O$, $BaCO_3$, and CuO[16]. But the powder sample of Y_2BaCuO_5 treated with water more than 7 days did not degraded. Therefore we can confirm that Y_2BaCuO_5 found in degradation condition of $YBa_2Cu_3O_{7-\delta}$ is not the decomposition product of $YBa_2Cu_3O_{7-\delta}$ but the impurity phase remained in $YBa_2Cu_3O_{7-\delta}$.

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References

1. J. G. Bednorz and K. A. Müller, *Z. Phys.*, **B64**, 189 (1986).
2. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.*, **58**, 908 (1987).
3. B. Dunn, C. T. Chu, L-W Zhou, J. R. Cooper, and G. Gruner, *Adv. Ceramic Mater.*, **2**, No. 3B, 343 (1987).

4. B. W. Kim and J. H. Choy, *Bull. Kor. Chem. Soc.*, in press (1988).
5. C. Michel and B. Raveau, *J. Solid State Chem.*,**43**, 73 (1982).
6. K. Kojima, K. Ohbayashi, M. Udagawa, and T. Hihara, *Jpn. J. Appl. Phys.*, **26**, L766 (1987).
7. J. H. Choy, S. H. Byeon, S. T. Hong, D. Y. Jung, S. Y. Choy, B. W. Kim, J. T. Kim, D. Y. Noh, H. I. Yoo, D. N. Lee, D. Y. Seung, T. S. Park, *J. Kor. Cer. Soc.*,**25**, 154 (1988).
8. A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).
9. D. E. Billing, R. J. Dudley, B. J. Hathaway, and A. A. G. Tomlinson, *J. Chem. Soc. (A)*, 691 (1971).
10. R. J. Dudley, B. J. Hathaway, P. G. Hodgson, P. C. Power, and D. J. Loose, *J. C. S. Dalton*, 1005 (1974).
11. B. J. Hathaway, *J.C.S. Dalton*, 1196 (1972).
12. A. B. P. Lever, *"Inorganic Electronic Spectroscopy"* Elsevier, p.568 (1984).
13. M. F. Yan, R. L. Barns, H. M. O'Bryan, Jr., P. K. Gallagher, R. C. Sherwood, and S. Jin, *Appl. Phys. Lett.*,**51**, 532 (1987).
14. B. G. Hyde, J. G. Thompson, R. L. Withers, J. G. Fitz-Gerald, A. M. Stewart, D. J. Bevan, J. S. Anderson, J. Bitmead, and M. S. Paterson, *Nature*, **327**, 402 (1987).
15. A. Barkatt, H. Hojaji, and K. A. Michael, *Adv. Ceramic Mater.*, **2**, No. 3B, 701 (1987).
16. J. H. Choy, S. H. Chun, B. W. Kim, D. Y. Jung, S. T. Hong, and S. H. Byeon, *Bull. Kor. Chem. Soc.*, **9**, 240 (1988).
17. Y. Kitano, K. Kifune, I. Mukouda, H. Kamimura, J. Sakurai, Y. Komura, K. Hoshino, M. Suzuki, A. Minami, Y. Maeno, M. Kato, and T. Fujita, *Jpn. J. Appl. Phys.*, **26**, L394 (1987).

Preparation, Structural and Magnetic Properties of Ordered Perovskite (BaLa)(MgMo)O_6

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The polycrystalline powder of (BaLa)(MgMo)O_6 has been prepared at 1350 °C in a nitrogen flowing atmosphere. The powder X-ray diffraction pattern indicates that (BaLa)(MgMo)O_6 has a cubic perovskite structure (a_o = 8.019(3) Å) with 1:1 ordering or Mg^{2+} and Mo^{5+} in the oxide lattice. The infrared spectrum shows two strong absorption bands with their maxima at 600(ν_3) and 365 (ν_4) cm^{-1}, which are attributed to $2T_{1U}$ modes of molybdenum octahedra MoO_6 in the crystal lattice. According to the magnetic susceptibility measurement, the compound shows a paramagnetic behavior which follows the Curie-Weiss law below room temperature with the effective magnetic moment 1.60(1) μ_B, which is consistent with that of spin only value (1.73 μ_B) for Mo^{5+} ($4d^1$ electronic configuration). From the thermogravimetric and X-ray diffraction analyses, it has been found that (BaLa)(MgMo)O_6 decomposes gradually into $BaMoO_4$, MoO_3 and unidentified phases above 900 °C in an ambient atmosphere, absorbing about 0.25 mole O_2 per mole of Mo ion, which also supports that oxidation state of Mo^{5+} in the (BaLa)(MgMo)O_6.

Introduction

In perovskite type compounds as $A_2(BB')O_6$ and (AA')(BB')O_6, the A and A' cations are coordinated with twelve oxygen ions and B and B' cations with six. It is well known that an ordered distribution of B and B' ions along (111) planes is most probable when a large difference exists in either their charges or ionic radii.[1] Figure 1 shows the arrangement of ions in the (100) plane of the cubic perovskite lattice for (AA')(BB')O_6 type compounds, where B and B' cations are alternatively arranged between oxygen ions. Holes denoted by * in Figure 1 are randomyl occupied by A and A' cations. In the ordered structure oxygen atoms are slightly shifted toward the more highly charged cation, but the octahedral symmetry of the B and B' cations is retained. Many compounds are known to have such an ordered structure on the octahedral sublattice (B-site), while few compounds[2] have been found to have a crystallographic ordered structure on the twelve-coordinated cation sublattice (A-site).

Sleight and Weiher[3] reported the valency pairs (M,Re) (M = Mn,Fe,Co and Ni) in the ordered perovskites $Ba_2(MRe)O_6$, where they confirmed the valency state from the structural point of view rather than from physical characterizations.

When A cation is divalent and A' trivalent in (AA')(BB')O_6, the valency pair (B,B') should be one of three possible pairs (1+,6+), (2+,5+) and (3+,4+) by the charge neutrality condition.

The ordered perovskite structure were reported for all the compounds with the formula of (CaLa)(B(II)B(V))O_6, where (B(II), B'(V)) = (Mg^{2+}, Mo^{5+})[4], (Mg^{2+}, Ru^{5+}), (Mg^{2+}, Ir^{5+}), (Ca^{2+}, Ta^{5+}), (Mn^{2+}, Mo^{5+}) and (Mn^{2+}, Ta^{5+}), while random distribution was observed for the valency pair (B(III), B'(IV)) = (Mn^{3+}, Ti^{4+}).[5-7]

In the present study an attention was paid to the formation of ordered valency pair of (Mg^{2+}, Mo^{5+}) in the complex