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ELECTROCERAMICS - I

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SOLID SOLUTIONS IN THE $Y-Ba-W-Cu-O$ SYSTEM, **George D.NIPAN**, T.N.KOL'TSOVA, K. S. GAVRICHEV (Kurnakov Institute of General and Inorganic Chemistry Russian Academy of Sciences, Leninsky prosp. 31, Moscow, 117907, Russia), and P. MANCA (Department of Physical Sciences, University of Cagliari, via Ospedale 72, 09124, Cagliari, Italy).

The new multinary ceramics were obtained in the $Y-Ba-W-Cu-O$ system after synthesis in air at 900°C by solid-state reaction and the row of solid solutions was detected by X-ray powder diffraction. The magnetic susceptibility data indicated new superconducting phase (T_c^{init} near 90K) with the structure different from 123 ($YBa_2Cu_3O_{7-\delta}$). This phase which was conventionally designated as $Y_2Ba_yWCu_6O_x$ dissolved considerable amount of barium oxide (y from 3 to 4). After annealing in oxygen $Y_2Ba_4WCu_6O_x$ was decomposed on nonsuperconducting $YBa_2WCu_2O_9$ and superconducting 123 solid solutions whereas $Y_2Ba_3WCu_6O_x$ was transformed in orthorhombic nonsuperconducting phase.

The phase relations in the quasi-quaternary approximation were studied and concentration diagram of $Y_2O_3 - BaO - WO_3 - CuO$ system was constructed.

E-TUE-19

ELECTRONIC STRUCTURE OF $Pr_{1-x}Y_xBa_2Cu_3O_y$ ($x=0, 0.5$ and 1.0), **KATSUYOSHI KAKINUMA**, HIROSHI YAMAMURA (Dept. Appl. Chem., Fac. of Eng., Kanagawa Univ. Yokohama, Japan 221-8686), and **KAZUO FUEKI** (Dept. Ind. Chem, Fac. of Sci. and Tech. Science University of Tokyo, Yamazaki, Noda-shi, Chiba, Japan 278-8510)

In order to elucidate the electronic structure of $Pr_{1-x}Y_xBa_2Cu_3O_y$ ($x=0, 0.5$ and 1.0), we examined the Pr valence and measured the oxygen nonstoichiometry, optical spectra at room temperature and conductivity (σ) at temperatures up to 1200 K for three oxides. The valence of Pr was found to be +3. Any difference was not found in oxygen nonstoichiometry among three kinds of oxides. From the slope of the Arrhenius plot for σ_{min} , the CT gap was determined to be 1.21, 1.32 and 1.37 eV for $Pr_{1-x}Y_xBa_2Cu_3O_y$ ($x=0, 0.5$ and 1.0) respectively. The energy gap between acceptor level and top of valence band agrees well with the absorption edge of optical spectra. The behavior of conductivity and optical spectra supports the conclusion that electronic structure of these oxides was explained by P-type semiconducting model in which the excess oxygen acts as acceptor.