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BRIEF COMMUNICATION

Comments on the Paper "Synthesis and Properties of a Barium Copper Oxide Chloride, $Ba_2Cu_3Cl_2O_4$," by Zhigang Zou and Laina Ma

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The paper dealing with the synthesis and structure of $Ba_2Cu_3Cl_2O_4$ is commented upon. The space group proposed is in conflict with the powder diagram given. The crystal structure determined by the authors of the paper is shown to be already known. © 1997 Academic Press

The study of properly chosen model compounds containing Cu(II) and Cu(III) coordinated to oxygen is important for improved understanding of the electronic properties of the superconducting cuprates (1). Zou and Ma (2) prepared deep red single crystals of tetragonal symmetry. Systematic absences found are $h + k + l = 2n + 1$, $a = b = 5.519(1)$, $c = 13.8342(2)$ Å. From these diffraction data the authors arrived at the space group $I4/mmm$, $Z = 2$ from density considerations. The crystal structure of the "new" compound, $Ba_2Cu_3Cl_2O_4$, is to be published elsewhere. Electric measurements indicating metallic behavior within the temperature range 213–273 K are reported. A figure depicting the powder diffraction diagram is given as well.

Conflicting evidence contained in the paper caused us to consult the crystal structure information system Cristin (Hundt and Sievers, University of Bonn, Germany). The particulars of the compound $Ba_2Cu_3Cl_2O_4$, with cell constants $a = b = 5.517$, $c = 13.808$ Å, space group $I4/mmm$, $Z = 2$ are given there. The structure of this compound was determined by Kipka and Müller-Buschbaum in 1976 (3). The structures of several related barium copper oxygen chlorides have been determined by these authors as well.

Zou and Ma indexed their X-ray powder pattern using the lattice constants and space group obtained from the single crystals. However, even a cursory inspection of the indexing given shows this to be impossible: The strongest reflection in the powder pattern is indexed as (111). Also, for a tetragonal lattice it is impossible for the (301) reflection to occur at 2Θ lower than (220).

From their TG experiments the authors conclude that $Ba_2Cu_3Cl_2O_4$ heated in flowing oxygen decomposes into $Ba_2Cu_3O_5$, referring to a paper by Kubel and Janner (4). However, this reference reports on the compound $Fe_3B_7IO_{13}$. Thompson *et al.* (5) reported on the compound $Ba_2Cu_3O_{5+\delta}$. Their δ values range between 0.5 and 0.9, depending on the oxygen pressure and the temperature during preparation. In any case, the conclusion of Zou and Ma, that the compound obtained on heating $Ba_2Cu_3Cl_2O_4$ in oxygen is $Ba_2Cu_3O_5$, is questionable. Only a proper structure determination can resolve this point.

Thus, Zou and Ma succeeded in preparing single crystals of a compound in the Ba–Cu–Cl–O system with interesting electrical properties, the structure of which has been known for approximately 20 years. Furthermore, a powder diffractogram obtained from the bulk material obtained by these authors cannot be indexed using the unit cell of $Ba_2Cu_3Cl_2O_4$, contrary to what the authors stated.

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