Synthesis and Characterization of $Sr_2Cu(W_{1-x}Mo_x)O_6$: a Quasi-Two-Dimensional Magnetic System with a Possibility of Magnetic Frustration

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The *B*-site ordered double-perovskite system $A_2B'MoO_6$, where *A* = Ca, Sr, Ba and *B*' = alkaline earth or transition metal, has in the last two decades demonstrated several interesting electrical and magnetic properties, with a range of possible applications, such as spintronics (Sr_2FeMoO_6 [1]) and anode materials for solid oxide fuel cells (Sr_2MgMoO_6 [2]). We have investigated compounds with *A* = Sr and *B*' = Mg, Mn, Fe, Co, Ni or Zn, with an emphasis on the materials applicability as SOFC anodes [3-5]. In this series of materials there has been one notable omission: the *B*' = Cu members, A_2CuMoO_6. The tungsten analogues Sr_2CuWO_6 and Ba_2CuWO_6 have both been synthesized and characterized previously and they have shown intriguing quasi-two-dimensional magnetic properties due to orbital ordering in the Jahn-Teller active Cu^{II} ion [6-9]. The $S = ½$ Cu^{II} ions form a square lattice in the (001) planes, with a possibility of frustration between the nearest-neighbor and next-nearest-neighbor interactions.

In this work [10] we use both the common solid-state synthesis method and a high-pressure high-temperature synthesis method to prepare the whole series of $Sr_2Cu(W_{1-x}Mo_x)O_6$, $x = 0…1$. The $0 \leq x \leq 0.6$ phases are synthesized under ambient pressure and the $0.7 \leq x \leq 1.0$ phases under a pressure of 4 GPa. While the synthesis is successful, the high pressure phases show an anomalous deviation in unit cell parameters compared to the normal pressure phases. Moreover, a first-order tetragonal-cubic cooperative Jahn-Teller transition at ~920 °C in Sr_2CuWO_6 is lowered to ~500 °C in Sr_2CuMoO_6. At $x = 0.5$, the transition occurs over an extended interval 650 °C < *T* < 850 °C, which implies the presence of W-rich and Mo-rich regions.

Electronic structure calculations and color changes in the samples with *x* both indicate that the $Sr_2Cu(W_{1-x}Mo_x)O_6$ compounds are insulators with an optical band gap between a Cu^{II}-O valence band and the bottom of a $W_{1-x}Mo_x$-O d^0 conduction band that is below the Cu^{II}/Cu^{I} redox energy, separated from the conduction band by a relatively large Hubbard *U*. Magnetic-susceptibility data confirm frustrated 2D magnetic interactions on the square-centered Cu^{II} lattice of the (001) planes and the absence of long-range magnetic order down to at least 5 K; an up-turn in the magnetic susceptibility below 20 K appears to be caused by ferrimagnetic defects in the double-perovskite matrix that are introduced by segregation of a $Sr(W_{1-x}Mo_x)O_4$ second phase. In addition, the data indicate that the magnetic frustration in the square lattice increases with the Mo concentration *x*.

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