

Simple cationic order versus La-O covalency: origin of all physical properties in LaA(Ca,Sr,Ba)VMoO₆ double perovskites

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Abstract

We have investigated the structural and physical properties of double perovskite (DP) LaAVMoO₆ (A= Ca²⁺, Sr²⁺, Ba²⁺; abbreviated as LCVMO, LSVMO, and LBVMO from now onwards) compounds as possible half metallic antiferromagnet (HM-AFM) candidates. The more prominent member of this series is LaSrVMoO₆ (LSVMO) which was actually claimed to be a HM-AFM in presence of substantial V/Mo ordering^{1,2}. However, we have earlier shown that other than the complex issue of A-(La/Sr) and B-(V/Mo) site ordering within the given DP structure, strong La-O covalency brings forth another important parameter which dominates the site-disorder issues and introduces an unusual microscopic phase separation in LSVMO^{3,4}. It is evident that substitution of Sr²⁺ by Ca²⁺ and Ba²⁺ at the A-site would offer a tool to modify the A-site ordering and thereby manipulating the above mentioned phase separation, which is entirely driven by La-O covalency. Our experimental results reveal⁵ that LCVMO sits at the extreme end of phase separation among the LaAVMoO₆ family forming large volumes of La, V and Ca, Mo-rich phases, which finally accounts for all unusual electronic and magnetic properties of LCVMO. On the other hand, LBVMO does not endorse such phase separation and maintains chemical homogeneity by and large. LBVMO is more correctly described as a layered A-site ordered and nearly complete B-site disordered double perovskite. The general trend of our experimental findings is in agreement with the ab-initio electronic structural calculations, carried out on realistic structures based on local coordination obtained from extended x-ray absorption fine structure (EXAFS) study. It further confirms that the energy stability, gained by typical La-O covalency, leads to the preferential La, V and Ca, Mo ionic proximity in LCVMO, while ordering of A-site cations plays the crucial role in achieving ground state-energy minimization over La-O covalency in LBVMO.

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