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SYNTHESIS OF Sr2MnSbO6, Sr2MnNbO6, Ca2MnSbO6, Ca2MnNbO6 AND Ca2MnRuO6: INVESTIGATION OF THE CHEMISTRY AND CRYSTALLOGRAPHY USING THE SOFTWARE PROGRAM SPuDS

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The interplay between cooperative Jahn-Teller distortions (orbital ordering), cation ordering and octahedral tilting has been investigated via structural studies of the perovskites Sr_2MnSbO_6, Sr_2MnNbO_6, Ca_2MnSbO_6, Ca_2MnNbO_6 and Ca_2MnRuO_6. X-ray and neutron powder diffraction (ANSTO) data were collected, and the crystal structures were solved using the Rietveld refinement method. The refinements clearly show that long range ordering of the octahedral site cations does not occur. However, other techniques suggest the possibility of short range ordering of the octahedral cations. Octahedral cation distributions in A_2MMO_6 perovskites, where M is a Jahn-Teller ion, varies from long range order (e.g., Ba_2CuWO_6), to short range order (e.g., Sr_2MnRuO_6 and Sr_2MnSbO_6), to disorder (e.g., Sr_2MnNbO_6), to temperature induced charge order (e.g., $Nd_{1/2}Sr_{1/2}MnO_3$). In each case changes in the cation ordering influence the orientation and magnitude of the cooperative Jahn-Teller distortion. The software program SPuDS has been developed to predict the crystal structures of perovskites. SPuDS calculates complete crystal structures for 10 different Glazer tilt systems with a single B-site cation, Jahn-Teller distorted B-site cation, or a 1:1 disordered arrangement of B-site cations. SPuDS calculates structures for 6 tilt systems with two B-site cations in a 1:1 rock salt ordered arrangement. A comparison of experimental and SPuDS predicted positions is presented for the synthesized perovskites. SPuDS calculations are also utilized in an attempt to deconvolute the effects of octahedral tilting, cation ordering, and Jahn-Teller distortions on the final crystal structure.

Keywords: PEROVSKITE SPUDS MODELING

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STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF OXYSULFIDE $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ SPINEL MATERIALS

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Spinel $LiMn_2O_4$ have generated great interest as the most promising cathode materials (positive electrodes) for lithium secondary batteries, due to its high energy density, low cost, abundance, and non-toxicity. However, a severe capacity fading is induced in the 3V region because of the phase transition from cubic to tetragonal. So several groups have attempted to overcome the problem by doping of Mn site although its property did not show good results. In this paper we report the new materials obtained by doping of oxygen site. $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ and $LiAl_{0.24}Mn_{1.76}O_{4.00}$ powders were synthesized by the sol-gel method. Both structures were refined by Rietveld method, its structure refined as a cubic spinel, space group *Fd*-3*m*, a = 8.17937(3) Å and 8.18331 (2) Å respectively. The capacity fading in the 3V/4V region was investigated through the charge/discharge experiment above 20 times and also the refined composition of the compound was confirmed with the ICP analysis.

Keywords: RIETVELD METHOD SPINEL STRUCTURE X-RAY

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ZIGZAG CHARGE ORDERING STRUCTURE OF THE QUARTER-FILLED LADDER COMPOUND NaV_2O_5

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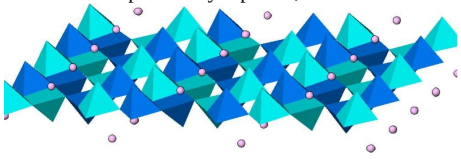
The low-temperature (LT) superstructure of NaV_2O_5 was determined by synchrotron radiation X-ray diffraction. Below the phase transition temperature associated with atomic displacement and charge ordering at 34 K, we observed splitting Bragg peaks, which provide evidence that the LT structure is monoclinic. It was determined that the LT structure is (a-b) X 2b X 4c with the space group *A*112, where a, b and c represent the high-temperature orthorhombic unit cell. The valence estimation of V ions according to the bond valence sum method shows that the V sites are clearly separated into two groups of V^{4+} and V^{5+} with a zigzag charge-ordering pattern. This LT structure is consistent with resonant X-ray and NMR measurements, and is in striking contrast to the LT structure previously reported, which includes $V^{4.5+}$ sites.



Keywords: LOW TEMPERATURE CRYSTAL STRUCTURE, CHARGE ORDER, SPIN SINGLET STATE

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EVIDENCE OF INTERMEDIATE SPIN STATE OF Co^{3+} AND Co^{4+} IONS IN $LaBaCo_2O_6$

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Since the discovery of colossal magnetoresistance in manganese oxide, other related perovskite systems have attracted a lot of studies. Amongst these compounds, the perovskite-based cobaltites $LnBaCo_2O_{5+\delta}$ ($0<\delta<1$) (Ln=Ho,Tb,Dy...) are of particular interest (1). Their transport behaviours depend strongly on the oxygen stoichiometry which also induces several complex crystallographic structures. Furthermore, the possibility of having various Co spin states in these compounds is the key for explaining their rich and complex magnetic properties. Here, we present the study of $LaBaCo_2O_6$ where the complexity of the system is increased by the existence of Co^{4+} ($3d^5$) which coexist with Co^{3+} with a 50:50 ratio, and are both suceptible to adopt several spin-state configurations. This compound is an ideal cubic perovskite and using both high resolution neutron and synchrotron powder diffraction technics, we have evidenced the onset of a Jahn-Teller (JT) induced long range tetragonal phase at 180K, accompanied by a para-ferromagnetic transition. This JT effect is the signature of the intermediate configuration of both Co^{3+} and Co^{4+} cations in the structure. This compound is metallic, but a metal to insulator like transition occurs at 120K, due to the gradual ordering of d^3_{z2-r2} orbitals.

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