Study of the electronic transport mechanism in Mn-Zn-Ni spinel oxides

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Manganese based spinel oxides are a class of ceramic materials with a broad range of industrial interest, in the area of sensors, electrochemical energy storage-conversion and (photo)catalysis.[1][2] Among them, nickel manganese oxides $NiMn_2O_4$, represent a class of materials with negative temperature coefficient (NTC) of resistance, superb resistivity response, robustness and stability.[3]

In the current work, the ternary spinel system of nickel manganese oxide alloyed with zinc is studied. Transport in $Zn_{0.5}Ni_xMn_{2.5-x}O_4$ pellets, as a function of Ni content ($0 \leq x \leq 1.25$) with two different cooling procedures was studied, along with structural characterization and theoretical calculations of their electronic and structural properties. The electronic transport mechanism in transition metal spinel oxides is usually associated with small polaron hopping.[4] In these alloys a super-Arrhenius temperature dependence of conductivity was observed, which cannot be accounted for by current small polaron hopping models. In respect of the structural properties, the coexistence of cubic Spinel and tetragonal Hausmannite was observed with relative phase ratio strongly dependent on composition. Ab-initio calculations pointed to the presence of metastable structures with similar formation energies but different electronic structure. In such inhomogeneous energy system Nearest-neighbour polaron hopping can account for the unconventional thermally activated conductivity behaviour. In conclusions, combing this peculiarity in conductivity along with the theoretical predicted electronic conformations, a model for the resistance functional dependence on temperature that consistently describes the experimental data deduced.

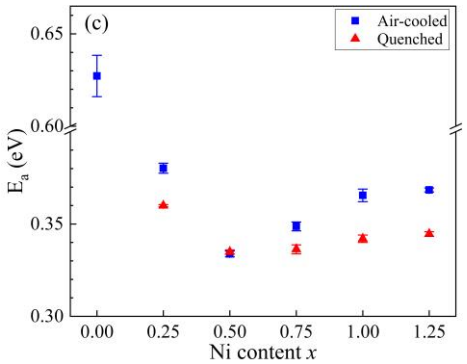

Figure 1: Calculated activation energies for all Ni content for both air-cooled and quenched pellets.

References

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