

Structural and Vibrational Spectroscopy of Manganese Oxides

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In this study we have performed investigation of stoichiometric and non-stoichiometric manganese oxides (polycrystalline and single-crystal) using x-ray diffraction (XRD), micro-Raman and FT-IR spectroscopy.

Polycrystalline MnO and Mn₃O₄ were prepared by thermal decomposition of oxalate or manganese carbonate in vacuum and in air, respectively. Single-crystals MnO and Mn₃O₄ (hausmannite) were grown by the method of chemical transport reactions from polycrystalline sources on MgO(100) substrate. All samples were characterized by x-ray diffraction. It is known that MnO phase with a NaCl-type structure is a weak Raman scatterer. Its Raman signal consists of two broad asymmetric bands at about 530 cm⁻¹ and 1050 cm⁻¹, of which only the first one has been attributed to 2TO mode.

The Raman spectrum of polycrystalline tetragonal hausmannite Mn₃O₄ consists of a narrow strong band at 660 cm⁻¹ and two small bands at about 318 and 370 cm⁻¹. The contribution from hausmannite phase is well visible in mixed single-crystal MnO-Mn₃O₄ sample and is also present in a small amount in nominally pure single-crystal MnO. However, the three bands become broadened in the Raman spectrum of single-crystal Mn₃O₄/MgO(100), which corresponds to the cubic hausmannite Mn₃O₄ phase.

Infrared spectra were measured using the KBr pellet method in the energy range from 200 to 700 cm⁻¹ employing vacuum Fourier transform infrared spectrometer Bruker Vertex 80v equipped with the closed circle optical helium cryostat. The low temperature (7 K) infrared spectrum of polycrystalline MnO contains one band at 285 cm⁻¹, whereas three bands at 420, 480 and 513 cm⁻¹ were observed for Mn₃O₄.

The phase composition of nominally pure single-crystal MnO and mixed MnO-Mn₃O₄ samples was probed by micro-Raman and micro-FT-IR mapping techniques. The optical image of nominally pure MnO is dominated by green colour; however, reddish-brown colour can be observed in some points mostly homogeneously distributed across the sample: it is attributed to the presence of the Mn₃O₄ phase.

To conclude we have shown that the vibrational spectroscopies can be successfully used to control the presence of the hausmannite Mn₃O₄ phase in polycrystalline and single-crystal manganese oxides. However, micro-Raman spectroscopy should be used with care, since local heating of MnO phase by laser can easily induce an oxidation of manganese ions leading to a formation of Mn₃O₄ phase.