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Raman and infrared spectromicroscopy of manganese oxides

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ABSTRACT

Confocal micro-Raman and micro-FT-IR spectroscopies have been used to probe the phase composition of nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples, grown by the method of chemical transport reactions on MgO(1 0 0) substrate. The presence of spinel Mn_3O_4 phase has been clearly detected in both samples by Raman and FT-IR spectroscopies. The size of the spinel Mn_3O_4 phase regions has been estimated to be below 20 μm.

1. Introduction

Manganese oxide (MnO) having a rock-salt structure is a classical antiferromagnet [1] ordered below about 118 K. While being studied for a long time, it still attracts much experimental and theoretical interest [2,3], which has been recently extended to nanostructured MnO [4–7]. It is known that magnetic properties of MnO are strongly affected by the presence of the spinel-type Mn_3O_4 impurity phase [4,7,8], which is ferrimagnetic below about 43 K. Therefore, it is important to control the phase purity of MnO.

Hausmannite Mn_3O_4 exists in two forms: low-temperature tetragonal and high-temperature cubic with a transition occurring at about 1170 °C [9]. Besides, it was found that the cubic Mn_3O_4 phase stabilizes at room temperature in films grown by MOCVD on single-crystal MgO(1 0 0) substrate [10].

Among different experimental techniques the micro-Raman spectroscopy is a useful tool to study non-homogeneous samples. It combines the ability to scan a sample with micro-level lateral resolution and the possibility to distinguish different Raman-active phases, thus providing the information on phases distribution across the sample. A micro-FT-IR spectroscopy can also be used as a complementary method.

In this work we have performed confocal micro-Raman and micro-FT-IR spectroscopies of nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples, which were epitaxially grown by the method of chemical transport reactions from polycrystalline MnO source on MgO(1 0 0) substrate.

2. Experimental

Polycrystalline MnO and Mn_3O_4 were prepared by thermal decomposition of oxalate or manganese carbonate in vacuum and in air, respectively, in the temperature interval 340–570 K [11,12]. Single-crystal MnO (manganosite) and Mn_3O_4 (hausmannite) were epitaxially grown by the method of chemical transport reactions from polycrystalline sources on single-crystal MgO(1 0 0) substrate using the "sandwich" technique [11]. The MgO(1 0 0) substrate was placed at about 1 mm above the polycrystalline source. The substrate temperature was maintained at 1150–1200 K, and the temperature difference between the substrate and the source was 50–100 K. The hydrogen chloride (HCl) gas at the pressure 40–60 mm Hg was used as a transport medium. The growth rate was about 0.03–0.1 μm/s.

The samples were characterized by X-ray diffraction. The experiments were performed at room temperature using the diffractometer DRON UM-2. The X-ray tube with an iron anode (Fe Kα) was used as an X-ray source. The tube operated at 50 kV and 20 mA. To discriminate phase content in oriented samples, the 2θ scan was performed in the interval from 100° to 140°, which includes contributions from MgO(4 0 0), MnO(4 0 0) and Mn_3O_4(2 0 0) reflections. More details can be found in Ref. [11].

Raman spectra were collected at RT using a confocal microscope with spectrometer "Nanofinder-S" (SOLAR TII, Ltd.). The "Nanofinder-S" system consists of an

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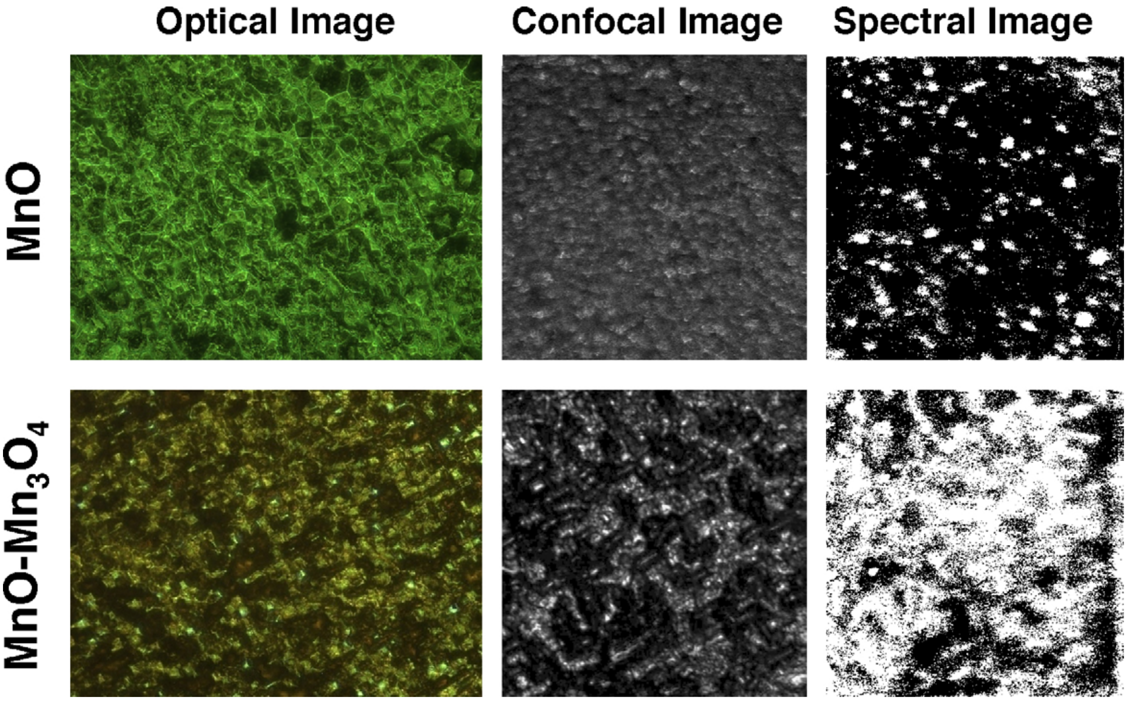

Fig. 1. Optical and confocal spectromicroscopy of nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples. Optical images (size 222 μm × 165 μm) were obtained using bright field illumination. Confocal and spectral images have a size 275 μm × 330 μm. Spectral images show a variation of the 660 cm^{-1} Raman band intensity. (For the interpretation of the references to colour in Fig. 2 legend, the reader is referred to the web version of the article.).

inverted Nikon ECLIPSE TE2000-S optical microscope connected simultaneously to a laser confocal microscope unit with Hamamatsu R928 photomultiplier tube (PMT) and to a monochromator-spectrograph (SOLAR TII, Ltd., Model MS5004i, 520 mm focal length) with attached Hamamatsu R928 PMT detector and Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024 × 58 pixels). The colour video CCD camera (Kappa DX20H) is used for optical image detection. All measurements were performed through Nikon Plan Fluor 40× (NA = 0.75) optical objective. The Raman spectra were excited by a He–Cd laser (441.6 nm, 50 mW cw power) and dispersed by 600 or 1800 grooves/mm diffraction grating. The elastic component of the laser light was eliminated by the edge filter (Omega, 441.6AELP-GP). More details can be found in Refs. [13,14].

The FT-IR measurements were performed at room temperature using a Bruker Vertex 70 spectrometer equipped with the Hyperion 2000 IR microscope. The reflectivity FT-IR spectra were registered in the range from 400 to 4000 cm^{-1} by liquid nitrogen cooled MCT detector. The measurements were performed using attenuated total reflection (ATR) and IR (15×) objectives for point and mapping acquisition modes, respectively.

3. Results and discussion

X-ray diffraction measurements of two samples did not reveal the presence of Mn_3O_4 in nominally pure single-crystal MnO, but indicated unambiguously the co-existence of two (MnO and Mn_3O_4) phases in the mixed sample.

In Fig. 1 one can see the optical and confocal images of nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples. 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 Mn_3O_4 phase. On the opposite, the reddish-brown colour dominates in mixed MnO–Mn_3O_4 samples.

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 and 1050 cm^{-1}, of which only the first one has been attributed previously in Refs. [15,16] to 2TO mode. One should note that MnO is similar to another antiferromagnetic material NiO, which has a high Neèl temperature around 523 K and those Raman signal is rather well understood [17]. The two oxides have

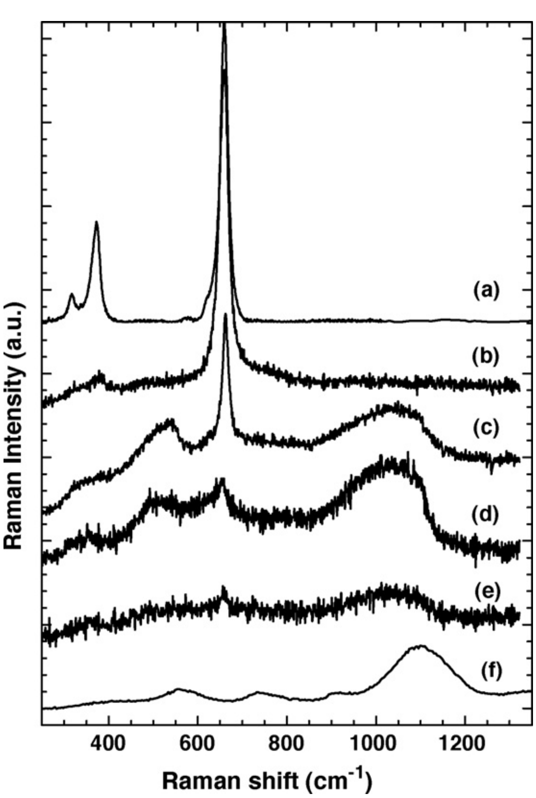

Fig. 2. Representative room temperature Raman spectra of (a) tetragonal hausmannite Mn_3O_4, (b, c) mixed MnO–Mn_3O_4, (d, e) nominally pure single-crystal MnO, and (f) single-crystal NiO. Spectra (b) and (d) were taken in reddish-brown coloured points of optical images in Fig. 1, whereas spectra (c) and (e) correspond to greenish coloured points.

also close values of the lattice parameters (a(MnO) = 4.446 Å and a(NiO) = 4.176 Å [3]), therefore one can expect some similarity in their Raman signals. In NiO (Fig. 2(f)) there are five vibrational bands: one-phonon (1P) TO (at 440 cm^{-1}) and LO (at 560 cm^{-1}) modes, two-phonon (2P) 2TO modes (at 740 cm^{-1}), TO + LO (at 925 cm^{-1}) and 2LO (at 1100 cm^{-1}) modes [17]. Comparing Raman signals in NiO and MnO one can attribute the lowest band at 530 cm^{-1} to the LO mode, predicted theoretically at about 484 cm^{-1} in Ref. [18] or 500 cm^{-1} in Ref. [19]. The highest frequency band at 1050 cm^{-1} has complex origin: it envelops two bands related to the TO + LO (a band wing at 950 cm^{-1}) and 2LO modes. The intermediate band due to the 2TO modes has weak intensity and is masked by a narrow band contribution at 660 cm^{-1} being due to the Mn_3O_4 phase.

The Raman signal in tetragonal hausmannite Mn_3O_4 (Fig. 2(a)) consists of a very sharp peak at about 660 cm^{-1} and two smaller peaks at about 318 and 370 cm^{-1} [20,21]. Similar to bulk Mn_3O_4 spectra were observed for nanostructured Mn_3O_4 films [22], powders [23], nanocrystals [24,25] and nanorods [26].

The confocal spectromicroscopy results for nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples are shown in Fig. 1. In these experiments two images (confocal and spectral) have been acquired simultaneously by two PMT detectors. The confocal image gives a variation of the reflected laser light intensity, whereas the spectral image shows the variation of the 660 cm^{-1} Raman band intensity. The presence of the Mn_3O_4 phase is well evidenced in both samples. This result has been confirmed by the reflectivity FT-IR measurements using the mapping at the characteristic Mn_3O_4 IR band, located at about 566 cm^{-1}.

4. Conclusions

Confocal micro-Raman and micro-FT-IR techniques were used to probe the phase composition of nominally pure single-crystal MnO and mixed MnO–Mn_3O_4 samples, grown by the method of chemical transport reactions on MgO(1 0 0) substrate. We found that nominally pure single-crystal MnO contains an admixture of spinel Mn_3O_4 phase. The sizes of the spinel Mn_3O_4 phase regions are below 20 μm. This result indicates that micro-Raman technique is a useful tool to control the phase purity of manganese oxide MnO.

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