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Crystallography, microstructure and morphology of $Mg_4Nb_2O_9$/MgO and $Mg_4Ta_2O_9$/MgO interfaces formed by topotaxial solid state reactions

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Abstract

$Mg_4Nb_2O_9$/MgO and $Mg_4Ta_2O_9$/MgO interfaces of definite crystallography were formed by topotaxial thin film solid state reactions in the systems MgO–Nb_2O_5 and MgO–Ta_2O_5. MgO (0 0 1) single crystal substrates, heated to different temperatures, were subjected to Nb–O and Ta–O vapors generated by e-beam evaporation in high vacuum. Thin films mainly containing the phases $Mg_4Nb_2O_9$ and $MgNb_2O_6$, respectively $Mg_4Ta_2O_9$ and $MgTa_2O_6$, were formed by gas–solid reactions. The crystallographic relationships between the product phases and the MgO substrate were systematically studied by X-ray diffractometry and transmission electron microscopy (TEM). Surprisingly pole figure analysis revealed more than one orientation relationship for some of the phases: $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ grew with (1 1 .4), (1 1 .6) and (1 1 .9) orientations, depending on temperature. Selected area diffraction patterns and high resolution TEM images show that these three orientations have a common $Mg_4(Nb/Ta)_2O_9$ $[1\,\bar{1}\,.0]$/MgO $[1\,\bar{1}\,0]$ axis and differ by the angle between the $Mg_4(Nb/Ta)_2O_9$ (0 0 .1) and MgO (1 1 1) planes. Crystallographic illustrations of this phenomenon are given, and possible origins and consequences for the solid state reaction are discussed. Indications for two different interfacial reaction mechanisms are found.

Keywords: Interfaces; Defects; Electron microscopy; Niobates; Tantalates

1. Introduction

Solid state reactions in oxide ceramics are being widely studied due to their importance for both fundamental condensed matter research and practical use.[1–3] AB_2O_4 spinel-forming reactions, in which a binary oxide AO of rock-salt structure reacts with another binary oxide B_2O_3 of, e.g., corundum structure to form a spinel, are among the most interesting model systems for solid state reactions that lead to ternary or quaterny oxides as product phases.[1,4–6] Topotaxial reactions involving a certain orientation relationship between the initial and product phases are particularly useful, if reaction mechanisms are to be studied. In many cases the latter can be deduced from the atomic-scale structure of the reaction front.[4,15]

Previously, some of us studied a series of topotaxial reactions with MgO (0 0 1) single crystals,[5,6] forming $MgAl_2O_4$ (−4.1% lattice misfit with MgO), $MgCr_2O_4$ (−1.1%), $MgFe_2O_4$ (−0.4%), Mg_2TiO_4 (+0.17%), Mg_2SnO_4 (+2.5%), and $MgIn_2O_4$ (+4.5%) spinels with different values of spinel/MgO lattice misfit (given in parentheses). In such cases of cube-on-cube orientation, the structure of the reaction fronts and the mechanism of the interfacial reaction were determined by the sign and amount of the lattice misfit.[4,15] At positive misfit, the Burgers vector of the misfit dislocations present at the reaction front points out of the interface, enabling the dislocation to glide, when coping with the movement of the advancing reaction front. At negative misfit, the Burgers vector lies in the interface plane, so that a climb process is required for the movement of the dislocations. (At very low misfit, e.g., 0.17%, no interfacial dislocations form and the misfit is accommodated by point defects.) In the present work, these studies are extended to two systems of higher complexity, viz. Nb_2O_5–MgO[7,8] and Ta_2O_5–MgO,[9,10] which involve more than one product phase, none of which has a cubic lattice.

Some of the formed phases have a technical significance. $Mg_4Nb_2O_9$ is known to exhibit luminescence in the blue–green region and it is studied as a potential candidate material for high-definition television (HDTV) and projection TV applications.[11]

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In the scope of candidates for nonlinear-optical and laser materials, Bruck et al.[12] reported the growth and optical properties of compounds in the MgO–Nb_2O_5 binary system. Generally, interfaces in ceramic composite materials play an important role in many technologically relevant composite materials.[13] The mechanical properties of such materials are, to a large extent, controlled by the microstructure of the interfaces.[14] Detailed knowledge of the microstructure of these interfaces is helpful for tailoring the properties of composite materials for advanced applications. High resolution transmission electron microscopy (HRTEM) is particularly suited to obtain information about the atomic structure of interfaces.

In this work, TEM and HRTEM are employed in addition to XRD, to study the microstructure of reaction fronts forming during topotaxial reactions in non-cubic systems.

2. Experimental

In the reaction experiments, polished (0 0 1) surfaces of MgO single crystals 10 mm × 10 mm × 1 mm in size (from CrysTec GmbH, Berlin, Germany) were subjected to either Nb–O or Ta–O vapor, respectively. The vapors were produced by electron-beam evaporation of either an Nb_2O_5 or Ta_2O_5 target in a high-vacuum system. The targets were made of Nb_2O_5 or Ta_2O_5 powder of 99.9985% purity (from Johnson Matthey GmbH) by cold pressing under 35 kN and sintering at 1200 °C for 1 h. Prior to the reaction experiments the MgO substrates were heated in air at 1200 °C for 1 h.

The base pressure of the vacuum system was 1×10^{-3} Pa. During deposition, 99.999% pure oxygen was introduced to establish a pressure of 1.0×10^{-2} Pa. The deposition rate and the overall amount of Nb_2O_5 or Ta_2O_5 deposited were monitored in situ by a quartz microbalance. An amount of Nb_2O_5 and Ta_2O_5 equivalent to a nominal thickness of 100 nm was deposited for all samples. The nominal deposition rate was typically 0.03 nm/s. A complete deposition/reaction experiment required about 55 min. The substrate temperature was varied from 500 to 1100 °C, determined by a Pt/PtRh10 thermocouple. After deposition the samples were kept in the chamber and cooling down to room temperature while the oxygen partial pressure was held to avoid an additional oxygen deficiency.

The phases present in the samples after the reaction, and their orientation relationships, were investigated by X-ray diffraction (XRD) (Philips X'pert MRD) with Cu Kα radiation. The 2θ angle was scanned at a speed of 0.18°/min, and pole figures were taken with 2° steps of the ψ value.

Specimen preparation for (high-resolution) transmission electron microscopy, (HR)TEM, was straightforward using the standard grinding and ion milling tools. The final ion milling step was performed in a Gatan DuoMill at 3 kV, and at an incidence angle of 13–14°. The TEM observations were carried out in a Philips CM20 operated at 200 kV and a JEOL 4010 operated at 400 kV. For the JEOL 4010, a spherical aberration of 1 nm, a defocus spread of 8.0 nm, and a beam semi-convergence angle of 0.7 mrad were characteristic. HRTEM images were recorded by either negatives or a digital CCD camera. HRTEM negatives were then digitized by scanning (2048 × 2048 pixels) and the gray scale was adapted to achieve reasonable contrast.

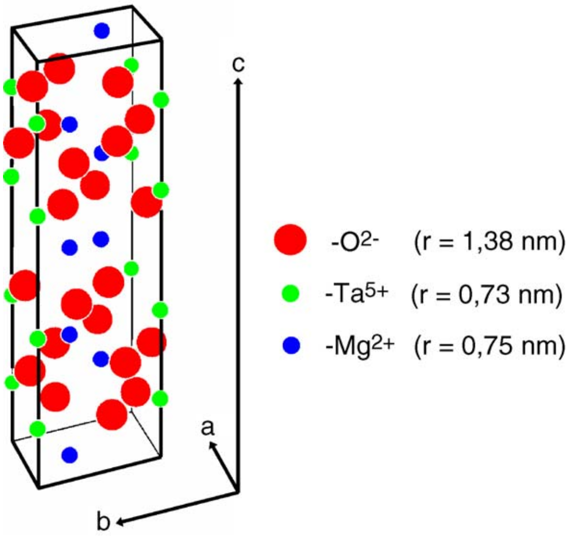

Fig. 1. Crystal structure of $Mg_4Ta_2O_9$.[9]

3. Results and discussion

3.1. X-ray diffraction

Mainly two product phases were found in each of the two systems MgO–Nb_2O_5 and MgO–Ta_2O_5, viz. $Mg_4Nb_2O_9$ and $MgNb_2O_6$, and $Mg_4Ta_2O_9$ and $MgTa_2O_6$ phases, respectively. In this paper, we concentrate on $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$. Details on phase formation and on the $MgNb_2O_6$ and $MgTa_2O_6$ phases have been published elsewhere.[27,28] $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ are both hexagonal (space group $P\bar{3}c1$, No. 165) with the lattice parameters $a = b = 0.51624$ nm and $c = 1.4024$ nm for $Mg_4Nb_2O_9$ [JCPDS 38-1459], and $a = b = 0.51611$ nm and $c = 1.40435$ nm for $Mg_4Ta_2O_9$ [JCPDS 38–1458].

Fig. 1 shows the crystal structure of $Mg_4Ta_2O_9$.[9] It has a distorted hexagonal close packed stacking of oxygen ions along the c axis. It is isotypic with the corundum-type (α-Al_2O_3) structure, with cations occupying two thirds of the octahedral interstices of the oxygen frame. The structure of $Mg_4Nb_2O_9$[16,17] is quite similar to that of $Mg_4Ta_2O_9$, with a very small difference in the lattice parameters. Due to this fact the results obtained on $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ were most similar to each other. Thus the obtained results are presented in this paper on the example of either the one or the other of the two materials.

The formation of $Mg_4Nb_2O_9$ and $Mg_4Ta_2O_9$ phases was systematically investigated by XRD as a function of temperature. Table 1 shows the orientation relationships at different temperatures and the misfit values observed for these two phases. Fig. 2 shows typical pole figures taken at $2\theta = 19.8°$ corresponding to $Mg_4Ta_2O_9$ (1 0 .0)[1] for samples prepared at 800,

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[1] In this paper, the hexagonal three-index system is used, the dot indicating the omitted fourth index.[29,30]