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Synthesis and characterization of nonstoichiometric $NiGa_2O_4$ transparent thin films

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ABSTRACT

Transparent nickel gallate spinel films were synthesized by means of an inter-diffusion reaction between NiO ceramics and (0 0 1) β-Ga_2O_3 single crystalline substrates at 1300 °C and annealed at various temperatures after removal of NiO pellets. The as-prepared films were characterized by X-ray diffraction, electron microscopy, energy dispersive X-ray spectroscopy, and optical absorption spectroscopy. It is revealed that the transparent reaction layers are single phase crystalline spinel with preferred orientations. Results from the EDX analysis show a homogeneous composition after equilibration, with a Ga/Ni atomic ratio of about 2.4 and 2.7 for samples quenched from 1300 °C and 1400 °C, respectively. Optical absorption spectra of spinel films are dominated by ligand field transitions of Ni^{2+} ions in octahedral sites with overlapping absorption bands of Ni^{2+} ions on tetrahedral sites.

1. Introduction

Spinel (AB_2O_4) materials are of great interest for a number of technical applications due to their physical and chemical properties originating from the fact that various cations of different sizes and charges can be accommodated in the crystal structure [1]. Among them, gallate spinels have been attracted special attention [2–6]. Some of the transition metal-containing $MgGa_2O_4$ spinels exhibit absorption and luminescence properties usable for opto-electronic devices [3–6]. Nickel gallates were also found to be a potential catalyst for the NO reduction as well as for the photocatalytic dissociation of water [7,8].

In the crystal structure of spinel (space group $Fd\bar{3}m$), the oxygen ions form a face centred cubic lattice providing tetrahedral and octahedral sites for cations. Considering the cation distribution, the structural formula of a AB_2O_4 spinel can be expressed in detail as $^{T}(A_{1-x}B_x)^{O}(B_{2-x}A_x)O_4$, where the superscripts T and O denote the tetrahedral site and octahedral site, respectively. x is the so called inversion parameter. In a normal spinel, $x=0$ while $x=1$ for an inverse spinel. A value of $x=2/3$ corresponds to a random distribution of cations between the tetrahedral and octahedral sites. In most of the spinels, x is between 0 and 2/3 (largely normal) or between 2/3 and 1 (largely inverse). With the input of energy to a spinel system, e.g., by increasing the temperature or by mechanochemical milling, x approaches the random distribution [9,10].

The present paper reports on the preparation of transparent nickel gallate spinel films for high temperature optical absorption experiments. Although there are several approaches to synthesizing spinels, such as solid state reactions [1], mechanochemistry [9], wet chemical routes including sol–gel method [11], and hydrothermal synthesis [8,12], these methods result in either spinel powders or ceramics which cannot be used for our purpose. We have synthesized transparent $NiGa_2O_4$ spinels by means of an inter-diffusion method modified according to Laqua and Reuter [13]. Another advantage of this method in comparison to single crystal growth is its ability to control and adjust the composition of the spinel, i.e. its Ga/Ni ratio. The as-prepared materials were characterized with respect to their phase structure, chemical composition, and cation distribution.

2. Materials and methods

NiO powder (99.99%, Sigma–Aldrich) was pressed into pellets and sintered at 1300 °C for 8 h. Single crystal substrates of β-Ga_2O_3 cut perpendicular to the [0 0 1]

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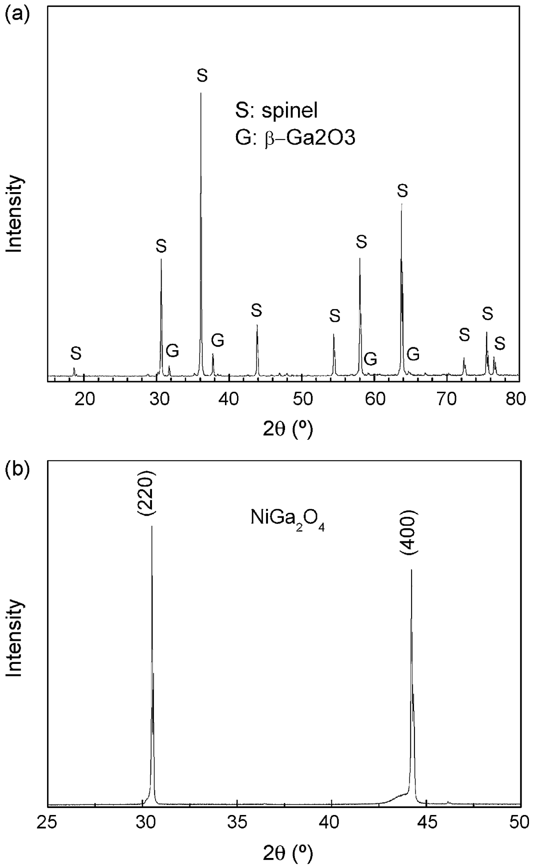

Fig. 1. XRD patterns of nickel gallate spinel prepared at 1300 °C, (a) powdered sample and (b) a nickel gallate spinel film on the (0 0 1) β-Ga_2O_3 single crystal substrate.

direction were tightly contacted with the NiO ceramic pellet under pressure and reacted at 1300 °C for 90 h to form a green reaction layer on the β-Ga_2O_3 surface. After removal of the NiO pellet and of NiO residuals from the surface, the β-Ga_2O_3 substrate together with the reaction layer was annealed at various temperatures for about 2 days in order to get spinels of different stoichiometries.

The phase identification of as-prepared samples was carried out by X-ray diffractometry (XRD). The data were collected on a Philips PW1820 diffractometer operating with CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). Chemical compositions of the reaction layer were analyzed using energy dispersive X-ray spectroscopy (EDX) attached to a Scanning Electron Microscope (JEOL JSM 6400). The structure of the spinel phase is further studied by means of Transmission Electron Microscope (TEM) and electron diffraction on a Philips CM300 UT/FEG equipped with a field-emission electron source. The micrographs were taken with a 2k × 2k CCD camera. The optical absorption spectra were measured using an UV-Vis-NIR optical spectrometer (Perkin-Elmer Lambda 900) at room and elevated temperatures.

3. Results and discussion

The XRD patterns of the reacted layer and powdered samples are shown in Fig. 1. The pattern of the powdered sample (Fig. 1a) scraped from the β-Ga_2O_3 substrate is composed of diffraction peaks from a spinel phase with two small peaks at $2\theta = 31.6^\circ$ and 58.5° from β-Ga_2O_3 which is attached to the reaction layer. In Fig. 1b only two strong reflection peaks from the (2 2 0) and (4 0 0) planes of spinel phase on the (0 0 1) β-Ga_2O_3 substrate were observed indicating that the nickel gallate spinel film is grown with preferential orientations on the β-Ga_2O_3 substrate. The formation of nickel gallate spinel phase is also confirmed by the TEM investigation of the samples prepared in cross-section. The reaction layer is found to be polycrystalline and dense without porosity. The spinel structure is proven by electron diffraction as shown in the diffraction pattern of a crystal in [1 0 0] orientation in Fig. 2a. The high-resolution TEM lattice image of a nickel gallate spinel crystal shown in Fig. 2b exhibits interplanar spacings of 2.86 Å which correspond to the distance of crystallographic (2 2 0) planes of the nickel gallate spinel. Preferential orientations of spinel films on substrates were also observed in the case of $NiAl_2O_4$ on sapphire and $SrTiO_3$ substrates [14,15]. The detailed orientation relationships between the $NiGa_2O_4$ spinel films and β-Ga_2O_3 substrate are under investigation.

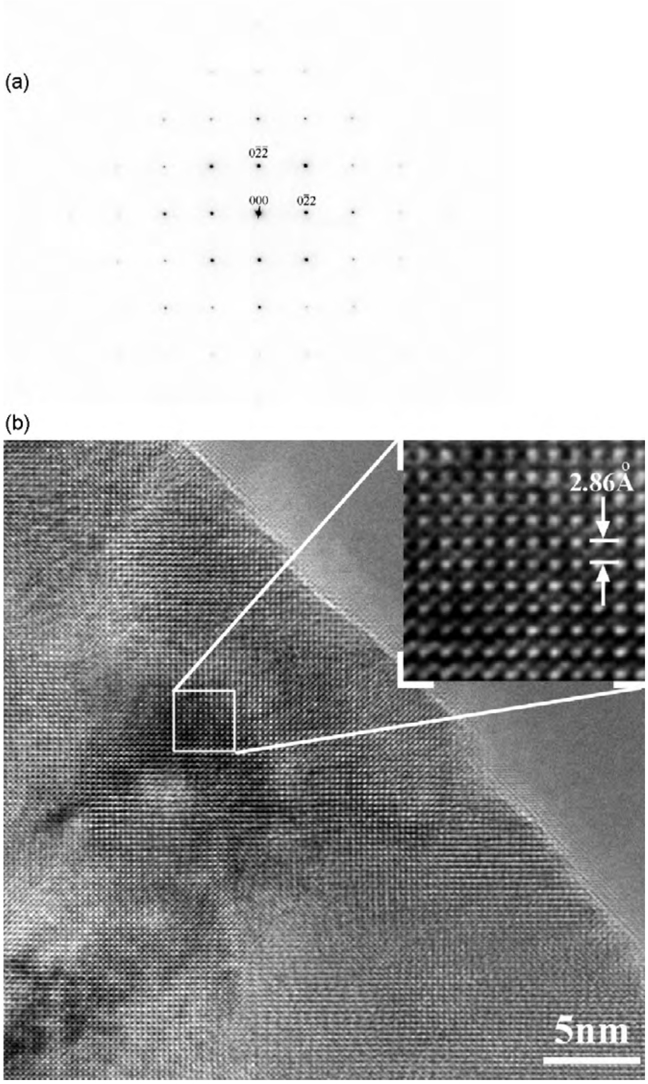

Fig. 2. Electron diffraction pattern with Miller indices (a) and HRTEM image (b) of nickel gallate spinels equilibrated at 1400 °C.

The chemical compositions of the spinel films after anealing at different temperatures were determined using EDX. Fig. 3a shows the optical pictures of the samples quenched after annealing at 1300 °C (NGO13) and 1400 °C (NGO14), respectively. The different green colors are due to the different nonstoichiometries (Ga/Ni ratio) of the spinel phase as revealed from the chemical composition analysis as well as optical aborption measurements. As an example, in Fig. 3b are shown the elemental line scans of Ga, Ni and O along the white line in the micrograph of the cross-section of the sample NGO13. As seen in Fig. 3b, the reaction front is located in the gallium oxide substrate, confirming the fact that the formation of spinel from oxides is due to the counter flux of divalent and trivalent cations with the larger diffusivity of divalent cations [13]. It is also evident that there is no compositional gradient in the spinel film of thickness of about 50 μm as shown in Fig. 3c. The average of the atomic Ga/Ni ratio of 20 measurements in the spinel region

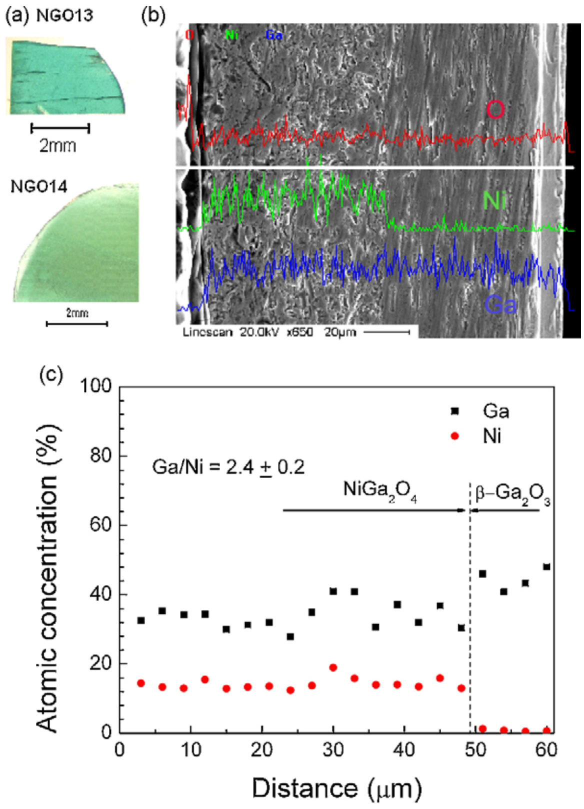

Fig. 3. (a) Optical micrographs of nonstoichiometric nickel gallate spinels annealed at and quenched from 1300 °C (NGO13) and 1400 °C (NGO14). (b) Elemental line scans of O, Ni, Ga in the cross-section of the sample NGO13 showing a homogeneous composition of the spinel film on the β-Ga_2O_3 substrate. (c) The atomic concentrations of Ni and Ga in the NGO13 spinel film with a thickness of about 50 μm and in the unreacted Ga_2O_3 substrate.

yields 2.4 ± 0.2 and 2.7 ± 0.3 for NGO13 and NGO14, respectively, indicating an excess of Ga_2O_3 in the spinel phase (Fig. 3b). The nonstoichiometry of the Ni–Ga spinels was also substantially evidenced in temperature-jump-induced cation redistribution experiments with the result that the kinetics of cation redistribution in NGO14 are much faster than that in NGO13 due to the higher concentration of vacancies in NGO14 which result from the higher Ga/Ni ratio in the NGO14 spinel layer. The kinetics of cation redistribution in nickel gallate spinels is out of the scope of this paper and will be reported eleswhere.

In order to get the information on the cation distribution in the prepared nonstoichiometric nickel gallate spinels, optical absorption spectra of the samples equilibrated at 1300 °C were measured at room temperature, 900 °C and 1200 °C as depicted in Fig. 4. The room-temperature spectrum is dominated by ligand field transitions of Ni^{2+} in octahedral sites. The three main bands, O-I, O-II and O-III which are centred at about 9400 cm^{-1}, 15 800 cm^{-1} and 26 300 cm^{-1}, respectively, are assigned to transitions of Ni^{2+} in an octahedral field from the ground state $^3A_{2g}(F)$ to the electronic energy levels $^3T_{2g}(F)$, $^3T_{1g}$ (F) and $^3T_{1g}(P)$, respectively. The absorption features at around 22 400 cm^{-1} and 13 000 cm^{-1} can be assigned to spin-forbidden d–d transitions from the $^3A_{2g}(F)$ ground state to $^1T_{2g}(D)$ and $^1E_g(D)$ of the octahedrally coordinated Ni^{2+}, respectively [3]. At 900 °C, the bands O-I and O-II exhibit a shift to lower energies as well as a broadening which is a typical effect of temperature on electronic absorption bands. However, asymmetric shapes of the O-II band at room temperature and elevated temperatures indicate an overlap with transitions of Ni^{2+} located on tetrahedral sites. Indeed, in the isostructural $NiAl_2O_4$ spinel, two sharp absorption bands from Ni^{2+} in tetrahedral sites have been observed in this region [10]. From the temperature dependence of optical spectra, it can be concluded qualitatively that most of the Ni^{2+} ions occupy the octahedral sites at low temperatures and that the increasingly asymmetric shape of the band O-I and O-II provides evidence for an increasing concentration of Ni^{2+} ions in tetrahedral sites with rising temperatures. This result is compatible with the cation distribution in $NiGa_2O_4$ spinel as obtained from the Rietveld refinement of XRD data on a sample quenched from 1000 °C [16] yielding a degree of inversion, $x = 0.92$. The optical absorption spectra of NGO14 exhibit similar characteristics in respect of band shape and temperature dependence.

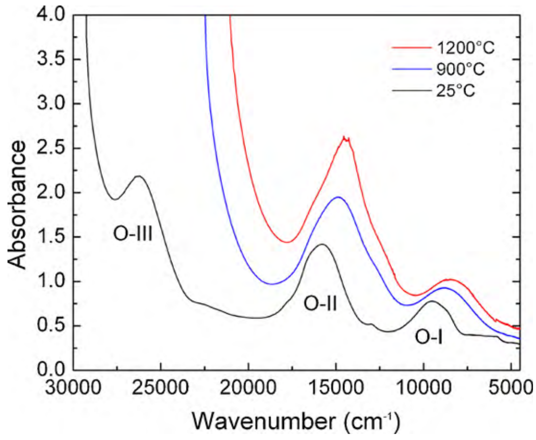

Fig. 4. Optical absorption spectra of nonstoichiometric Ni–Ga spinel at room temperature, 900 °C, and 1200 °C.

4. Conclusions

Transparent films of nonstoichiometric nickel gallate spinel were prepared by means of the inter-diffusion reaction of Ga_2O_3 and NiO and by subsequent equilibration at high temperatures. Structural characterization techniques showed that the spinel film is a single phase spinel grown on β-Ga_2O_3 single crystal substrates with preferred orientations. The homogeneity of composition of the spinel films with an excess of Ga_2O_3 in the spinel phase was revealed by EDX analysis. The distribution of Ni^{2+} on both tetrahedral and octahedral sites is demonstrated by optical absorption spectroscopy at room temperature and elevated temperatures.

Acknowledgement

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