ELSEVIER

Journal of Alloys and Compounds 442 (2007) 328–330

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Growth and optical properties of transition metal oxides single crystal solid solutions

V. Skvortsova*, N. Mironova-Ulmane, A. Kuzmin, U. Ulmanis

Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063 Riga, Latvia

Received 15 May 2006; received in revised form 16 September 2006; accepted 19 September 2006

Abstract

NiO, CoO, MnO single crystals and single crystal solid solutions of $Ni_cMg_{1-c}O$, $Co_cMg_{1-c}O$ and $Mn_cMg_{1-c}O$ were grown by the method of chemical transport reaction (the “sandwich” technique). The nature of the observed absorption and luminescence bands is explained in terms of the electronic transition of bivalent nickel, cobalt and manganese. The fine structure of the observed bands in NiO and MnO are connected to the pure exciton transition and to the exciton-magnon excitation.

PACS: 81.15.Np; 78.66. −w

Keywords: Oxide materials; Crystal growth; Optical properties; Luminescence

---

1. Introduction

A single crystal solid solution containing transition metal ions (3d-ions) is an important object of investigation both for theoretical speculations and for practical applications [1–5]. By varying the 3d-ions content, it is possible to change the phase transition temperature, optical and other properties of solid solutions. Chemical transport reaction (CTR) method has been developed to obtain best quality single crystals of nickel, cobalt and manganese oxides and single crystal solid solutions of transition metal oxide–magnesium oxide. Absorption and luminescence spectra of these materials are under study.

2. Experimental details

NiO, CoO, MnO single crystals and single crystal solid solutions of NiO–MgO, CoO–MgO and MnO–MgO were grown by the method of chemical transport reaction (the “sandwich” technique [6]). The MgO single crystal cut in (1 1 1) and (1 0 0) planes with thickness of ∼1 mm are largely used as substrate for transition metal oxides and solid solution grown. The initial substances are the $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$. The substances mixed in certain molar correlation (ratio) and heated at temperatures 700–900 K during 6 h for removal NO_2, then pressed and annealed again at 1400 K during 60–100 h in air for formation of the single phase polycrystalline solid solution of $Me_cMg_{1-c}O$.

It is difficult to obtain the single MnO–MgO solid solution, because the majority of oxygen-containing manganese salts decompose without formation of monoxide MnO. Polycrystalline MnO is received in vacuum or CO_2 atmospheres with thermal decomposition of manganese oxalate or carbonate. The obtained MnO is examined by X-ray analysis and IR-spectroscopy [7]. It has been experimentally found that the best quality film can be grown in the following optimum conditions: the substrate temperature $T = 1150$–1200 K, the temperature difference between the source and the substrate $\Delta T = 50$–100 K, the hydrogen chloride pressure 40–60 mm Hg. The rate of single crystal growth in the above mentioned conditions is 0.03–0.1 μm/s. Size of the obtained crystals is 6 mm × 10 mm, thickness 50–100 μm and depends not only on the growth time but also on the concentration of metal ions in the source. It has been established that the single-crystal solid solution of $Me_cMg_{1-c}O$ has a face-centered crystal structure of NaCl type and an orientation coinciding with that of a substrate. The chemical transport reaction method was used for growth of the single-crystal solid solutions of $Ni_cMg_{1-c}O$, $Co_cMg_{1-c}O$ and $Mn_cMg_{1-c}O$, where “c” varies from 0 to 1. Lattice parameter of obtained single crystals are given in Fig. 1. The chemical composition of a solid solution was determined by instrumental neutron activation analysis [8].

The luminescence spectra have been measured with a SPM-2 monochromator having diffraction grating of 651 lines/mm. The crystals were exited with a high-pressure xenon lamp (DKSEL-1000) connected with the monochromator (ZMR-1) with a quartz prism. Monitoring was carried out by a synchro-detection method using a photomultiplier tube (FEU-119) in the visible region and a recording part of the spectrophotometer “VSU-2P” (Karl Zeiss Jena) in the near infrared region. The optical absorption spectra were measured using double-beam spectrophotometer “Specord M-40” (Karl Zeiss Jena) operating in region 50,000–11,000 cm^{-1} and the one-beam spectrophotometer “VSU-2P” in region-

---

* Corresponding author. Tel.: +371 7980022; fax: +371 7901212.
E-mail address: vskv@delfi.lv (V. Skvortsova).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.09.165

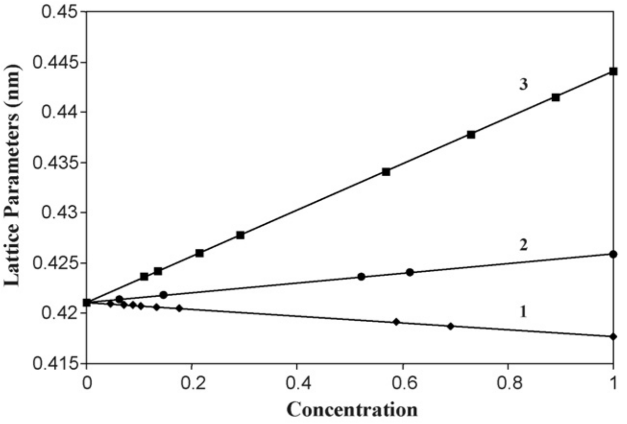

Fig. 1. Lattice parameters of 1, $Ni_cMg_{1-c}O$; 2, $Co_cMg_{1-c}O$; 3, $Mn_cMg_{1-c}O$ single-solid solution as function of metal ion concentration.

30,000–3700 cm^{-1}. The optical measurements were made in the temperature interval 300–10 K.

3. Results and discussion

The absorption spectra of $Ni_cMg_{1-c}O$ are shown in Fig. 2. In the concentration range of nickel ions smaller than $c = 0.01$, the absorption and luminescence bands are connected only with the spin-allowed transition. In the energy range 7800–8300 cm^{-1} these spectra correspond to $^3A_{2g} \rightarrow {}^3T_{2g}$ magneto-dipole transition in Ni^{2+} and consist of two zero-phonon lines (E and T) at 8005 and 8182 cm^{-1}. These two lines, previously, have been explained by the spin-orbit splitting [9]. In [10], it was suggested that these lines were due to the splitting of the $^3T_{2g}$ state by crystal field acting on Ni ions located in the off-center positions. This conclusion is supported by X-ray absorption spectroscopy (XAS) [11]: it shows that Ni ions in the $Ni_cMg_{1-c}O$ solid solution shift upon dilution to the off-center positions, so that the average Ni–Ni distance remains nearly constant. The additional sharp lines at 7822, 7888, 7921 and 7937 cm^{-1} appear at the Ni concentration $0.01 < c < 0.1$ and correspond to the zero-phonon transition, confirming the presence of the exchange coupled Ni^{2+}–Ni^{2+} pairs. The maximum number of isolated pairs appears at $c = 0.05$ [12]. An increase of the nickel ions concentration ($0.1 < c < 0.3$) results in an appearance of new bands and in a shift of the bands maxima. These new bands are caused by spin forbidden electric-dipole transition: $^3A_{2g}(F) \rightarrow {}^1E(D)$, $^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$; $^1T_{2g}(D)$, $^3A_{2g}(F) \rightarrow {}^1T_{1g}(G)$, $^3A_{2g}(F) \rightarrow {}^1E_g(G)$; $^1T_{2g}(G)$. The investigation of the band intensity dependence from temperature and nickel concentration shows that the restriction due to the spin selection rule is removed by the exchange interaction. In the transition metal concentration range $0.3 < c < 0.85$, a transition to the magnetically ordered state is observed. The dependence of optical absorption bands intensity on temperature has an anomaly at the point of phase transition. We have shown [13] that the energy difference between two peaks, located at the low energy side of the band due to the magnetic-dipole $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition in NiO is related to the zone-center ($k = 0$) one-magnon energy, so that the low-energy peak was attributed to the pure exciton transition, whereas the high-energy peak to the exciton-magnon excitation.

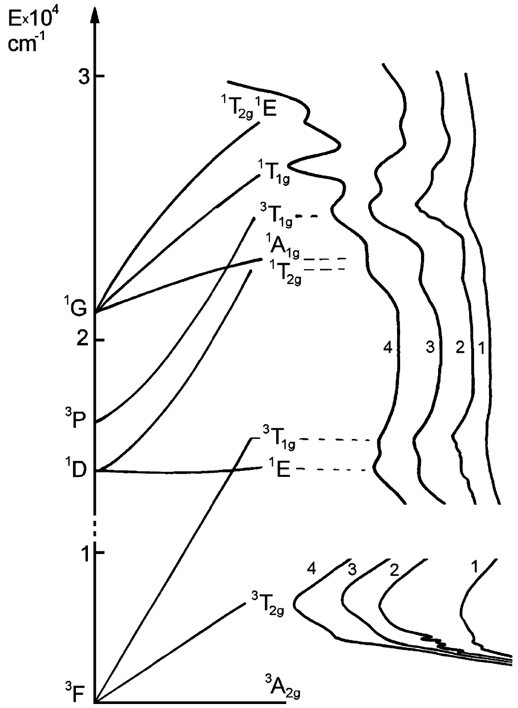

Fig. 2. Optical absorption spectra of Ni^{2+} ions in single-crystal $Ni_cMg_{1-c}O$ ($1 - c = 0.01$; $2 - c = 0.1$; $3 - c = 0.5$; $4 - c = 0.85$).

The optical absorption spectra of single-crystal solid solutions $Co_cMg_{1-c}O$ can be interpreted using the energy level diagram of a free ion Co^{2+} in a cubic crystal field. The observed absorption bands are related to d–d transitions from the ground state $^4T_{1g}(F)$ to the excited states $^4T_{2g}(^4F)$, $^4T_{1g}(^4P)$, which are spin-allowed ($\Delta S = 0$) and to excited states $^2A_{1g}(^2G)$, $^2T_{2g}(^2D)$, $^2T_{1g}(^2P)$, $^2T_{1g}(^1G)$, $^2E(^2D)$, which are spin-forbidden.

The optical absorption spectra of single-crystal solid solutions $Mn_cMg_{1-c}O$ at different manganese concentration are shown in Fig. 3. The Mn^{2+} ions have a $3d^5$ electron configuration. All electron transitions for this configuration are forbidden. Previous absorption measurement of $MgO:Mn^{2+}$ has been made by Koidl and Blazey [14]. The manganese ions concentration increase in $Mn_cMg_{1-c}O$ leads to the appearance of the bands related with d–d transition in Mn^{2+} ions in the optical absorption spectra. Comparing the obtained results with the Tanabe–Sugano diagram [15], the experimental results from [16] and the calculated values from [17], we conclude that the absorption bands in $Mn_cMg_{1-c}O$ correspond to the transitions from the ground state $^6A_{1g}$ (S) to the excited state: the band 37,500 cm^{-1}, $^4T_{1g}(P)$; 28,000 cm^{-1}, $^4E_g(D)$; 26,000 cm^{-1}, $^4T_{2g}(D)$; 23,500 cm^{-1}, ^4E_g, $^4A_{1g}(G)$; 20,500 cm^{-1}, $^4T_{2g}(G)$; and band 16,000 cm^{-1}, $^4T_{1g}(G)$. The restrictions caused by the selection rule are removed owing to the exchange interaction. Our last investigation of the high-resolution optical absorption spectra in the region of the $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ transition in single crystal MnO shows two peaks at 15,680 cm^{-1}, which are attributed to pure exciton transition (E) and exciton – one-magnon excitation ($E + M$).

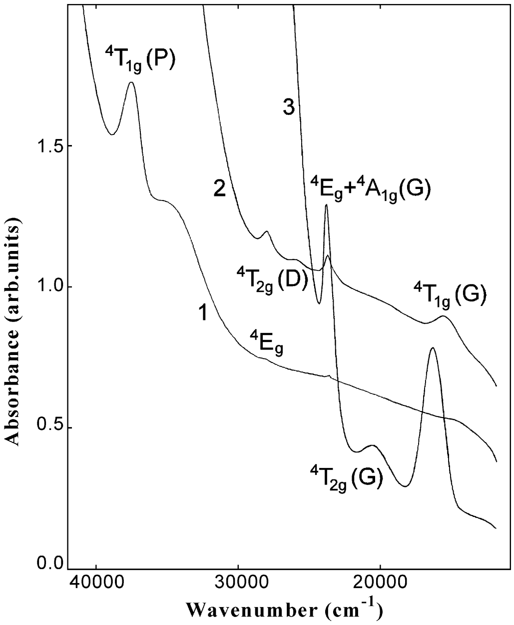

Fig. 3. Optical absorption spectra of single-crystal $Mn_cMg_{1-c}O$ ($1-c=0.1$; $2-c=0.3$; $3-c=0.85$).

4. Conclusions

Very good quality single crystals of nickel, cobalt and manganese oxides and single-crystal solid solution of transition metal oxide–magnesium oxide were obtained by the chemical transport reaction (CTR) method. The optical absorption and luminescence spectra have been measured in the near infrared and visible regions in the temperature range from 10 to 300 K. The nature of the observed absorption and luminescence bands is explained in terms of the d–d electronic transitions within bivalent nickel, cobalt and manganese. The fine structure of the observed bands in NiO and MnO is connected to the pure exciton transition and to the exciton-magnon excitation.

Acknowledgements

This work was partially supported by the grants of Latvian Government (No, 05.1718).

References

[1] A. Menshikov, Yu. Dorofeev, A. Klimenko, N. Mironova, Phys. Status Solidi B 164 (1991) 275–283.
[2] Z. Feng, M.S. Seehra, Phys. Rev. B 45 (1992) 2184–2189.
[3] M.T. Hutchings, E.J. Samuelsen, Phys. Rev. B 6 (1972) 3447–3461.
[4] W.L. Roth, Phys. Rev. 110 (1958) 1333–1341.
[5] M.S. Seehra, T.M. Giebultowicz, Phys. Rev. B 38 (1988) 11898–11900.
[6] H. Schafer, Chemical Transport Reaction, Academic Press, NewYork, 1964.
[7] V. Skvortsova, N. Mironova-Ulmane, Adv. Sci. Tech., Techna, Faenza 29 (2000) 815–822.
[8] V. Skvortsova, D. Riekstina, Adv. Sci. Tech., Techna, Faenza 19 (1999) 245–252.
[9] K.Y. Wong, D. Sengupta, E.R. Krausz, Chem. Phys. Lett. 21 (1973) 137–139.
[10] N. Mironova, A. Kuzmin, J. Purans, V. Skvortsova, J. Lumin. 72–74 (1997), 231-231.
[11] A. Kuzmin, N. Mironova, J. Purans, A. Rodionov, J. Phys.: Condens. Matter 7 (1995) 9357–9367.
[12] G.A. Grinvald, N.A. Mironova, Phys. Status Solidi B 99 (1980) K101–K103.
[13] N. Mironova, V. Skvortsova, A. Kuzmin, I. Sildos, N. Zazubovich, in: G. Borstel, et al. (Eds.), Defects and Surface-Induced Effects in Advanced Perovskites, Kluwer, Dordrecht, 2000, pp. 155–160.
[14] P. Koidl, K.W. Blazey, J. Phys. C: Solid State Phys. 9 (1976) L167–L170.
[15] Y. Tanabe, S. Sugano, J. Phys. Soc. Jpn. 9 (1954) 753–766.
[16] M. Okada, T. Kawakubo, T. Seiyama, M. Nakagava, Phys. Status Solidi (b) 144 (1987) 903–907.
[17] Du Mao-Lu, Zhaomin Guang, J. Phys. C: Solid State Phys. 18 (1985) 3241–3247.