# Effect of Li<sup>+</sup> co-doping on structural and luminescence properties of Mn<sup>4+</sup> activated magnesium titanate films

L. Borkovska<sup>1</sup> · L. Khomenkova<sup>1</sup> · I. Markevich<sup>1</sup> · M. Osipyonok<sup>1</sup> · T. Stara<sup>1</sup> · O. Gudymenko<sup>1</sup> · V. Kladko<sup>1</sup> · M. Baran<sup>1</sup> · S. Lavoryk<sup>1,2</sup> · X. Portier<sup>3</sup> · T. Kryshtab<sup>4</sup>

Received: 20 October 2017 / Accepted: 20 April 2018 © Springer Science+Business Media, LLC, part of Springer Nature 2018

#### Abstract

The effect of Li<sup>+</sup> co-doping on crystal phase formation and photoluminescence (PL) of Mn<sup>4+</sup> activated magnesium titanate films produced by a solid state reaction method at different temperatures (800–1200 °C) has been investigated by using X-ray diffraction (XRD), diffuse reflectance and PL spectroscopy. The chemical composition of sintered films was estimated by energy dispersive X-ray spectroscopy. The concentration of Mn impurity estimated by Electron spin resonance was about  $5 \times 10^{16}$  cm<sup>-3</sup>. The XRD study of the annealed films revealed several magnesium titanate crystal phases, such as Mg<sub>2</sub>TiO<sub>4</sub>, MgTiO<sub>3</sub> and MgTi<sub>2</sub>O<sub>5</sub>. The contribution of each phase depended strongly on the annealing temperature and the presence of Li<sup>+</sup> additive. Furthermore, Li<sup>+</sup> co-doping facilitated the formation of both MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> phases, especially at lower annealing temperatures. The PL spectra showed two bands centered at 660 and 710 nm and ascribed to the <sup>2</sup>E  $\rightarrow$  <sup>4</sup>A<sub>2</sub> spin-forbidden transition of the Mn<sup>4+</sup> ion in the Mg<sub>2</sub>TiO<sub>4</sub> and MgTiO<sub>3</sub>, respectively. In Li co-doped films, the integrated intensity of Mn<sup>4+</sup> luminescence was found several times stronger compared to Li-undoped films that was ascribed mainly to flux effect of lithium.

# 1 Introduction

Over the last decade, increasing attention has been paid to  $Mn^{4+}$ -doped inorganic luminescent materials due to their potential application as red phosphors in white phosphor-converted light-emitting diodes (pc-LEDs) with improved color-rendering index [1–4]. Generally,  $Mn^{4+}$  emitting center situated in octahedral cite of host materials exhibits two broad excitation bands in the ultraviolet (UV) and blue regions assigned to  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$  and  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  spinallowed transitions of  $Mn^{4+}$ , respectively, and a set of narrow emission bands in the red spectral region related to  ${}^{2}E \rightarrow {}^{4}A_{2}$  spin-forbidden transition. The latter is composed

L. Borkovska l\_borkovska@ukr.net

- <sup>1</sup> V. Lashkaryov Institute of Semiconductor Physics of NAS of Ukraine, 45 Pr. Nauky, 03028 Kyiv, Ukraine
- <sup>2</sup> NanoMedTech LLC, 68 Antonovycha Str., 03680 Kyiv, Ukraine
- <sup>3</sup> CIMAP, Normandie Univ, ENSICAEN, UNICAEN, CEA, CNRS, 6 Blvd. Maréchal Juin, 14050 Caen, France
- <sup>4</sup> Instituto Politécnico Nacional ESFM, Av. IPN, Ed.9, U.P.A.L.M., 07738 Mexico City, Mexico

of zero-phonon band and several vibronic modes that are extremely sharp at low temperatures and broaden at room temperature. The luminescence properties of  $Mn^{4+}$ -activated compounds meet spectral requirements for an ideal red-emitting phosphor for blue-chip excited white pc-LEDs. Furthermore, owing to simple synthetic processes and abundant starting materials, they can be considered as cheaper and more practical alternative to  $Eu^{2+}$ -doped oxynitride and nitride red phosphors dominating the current market [2]. The latter utilizes broad luminescence band due to 5d–4f transition of  $Eu^{2+}$ -ions that is strongly influenced by the crystal field strength, symmetry, anion polarizbility and covalency of the host crystal and can be tuned from the blue to near infrared region [4, 5].

Among different  $Mn^{4+}$ -activated materials, magnesium titanates are known to be relatively inexpensive, environmental friendly, easy-to-obtain and demonstrate excellent stability [1, 2]. Thought, the efficient red phosphors of  $Mg_2TiO_4:Mn^{4+}$  produced by the solid-state reaction method and wet chemical route have been demonstrated [3, 6–9], quantum efficiency of  $Mn^{4+}$  activated titanates remains lower than that of  $Mn^{4+}$ -doped fluoride compounds [1]. One of the reasons of insufficient quantum efficiency of Mn-doped materials is the disposition of Mn ions in order



to change the charge state from  $Mn^{4+}$  to  $Mn^{2+}$  and  $Mn^{3+}$ . Another one is their tendency to form complexes in which energy migration along Mn<sup>4+</sup> ions is possible. To overcome these drawbacks, a strategy of impurity co-doping has been proposed [9-18]. In those cases, the impurity ions provided charge compensation as well as a minimization of energy transfer mechanisms. The role of impurity doping as a flux was also discussed [16, 17]. Recently, the co-doping of Mg<sub>2</sub>TiO<sub>4</sub>:Mn<sup>4+</sup> with Bi<sup>3+</sup> and Li<sup>+</sup> ions has shown to be efficient for the increasing of Mn<sup>4+</sup> emission [9]. The largest effect was found for 0.5 mol % of Bi<sup>3+</sup> and 0.5 mol % of Li<sup>+</sup> [9]. The role of Li<sup>+</sup> ions was ascribed mainly to compensate the Bi<sup>3+</sup> charge. However, the effect of Li<sup>+</sup> ions per se on the luminescence intensity of Mg<sub>2</sub>TiO<sub>4</sub>:  $Mn^{4+}$  phosphor has not been elucidated yet. At the same time, even a small quantity (< 1 wt%) of lithium oxide can be an efficient sintering additive affecting crystal phase formation [19]. When lithium oxide is used in larger quantity, it can form the solid solutions with crystallized magnesium titanate phases as well as single-phase compounds, in particular, Li<sub>2</sub>TiO<sub>3</sub>, Li<sub>2</sub>MgTiO<sub>4</sub>, Li<sub>2</sub>MgTi<sub>3</sub>O<sub>8</sub>, etc. [20, 21].

In this paper, we present the results of the investigation of the effect of  $Li^+$  co-doping on the photoluminescence (PL) of  $Mn^{4+}$ -doped magnesium titanate films produced by a solid state reaction method. By controlling the crystal phase formation and  $Mn^{4+}$  luminescence spectra, the role of  $Li^+$  as a flux in the PL enhancement is distinguished.

#### 2 Experimental details

The raw  $\text{TiO}_2$  and Mn-doped MgO powders were mixed according to a stoichiometric ratio of Mg<sub>2</sub>TiO<sub>4</sub>. At first, a 1.5 g of TiO<sub>2</sub> powder (with mixture of anatase and rutile phases) and a 1.5 g of MgO powder were milled in agate ball milling device for 2 h. Then, a 0.5 ml of distilled water and a 0.5 ml of propylen glycol were added to powder mixture to obtain a cream-like homogeneous paste. In the case of Li co-doped samples a 15 mg of LiNO<sub>3</sub> dissolved in 0.5 ml of distilled water was added instead of a water to get a 0.5 wt% of LiNO<sub>3</sub> in the dried product. The films were formed on polished Si substrates by doctor-blade approach. After drying at normal conditions during a day, the films were sintered in air for 1 h at 800–1200 °C and cooled down to the room temperature in the furnace chamber. The thickness of the annealed films was about 20 µm.

X-ray diffraction (XRD) study was realized using X-ray diffractometer Philips X'Pert-MRD with the Cu  $K\alpha_1$  radiation. Chemical maps using energy dispersive X-ray spectroscopy (EDX) were recorded with a double corrected cold FEG ARM200 JEOL scanning electron microscope equipped with a Centurio EDX JEOL setup. Electron paramagnetic resonance (EPR) measurements were carried out

using X-band EPR spectrometer Varian E12 (~9.5 GHz) with a sensitivity limit of about  $10^{12}$  EPR centers, and the signal of a MgO:Mn sample containing  $3 \times 10^{15}$  spins was used as a reference. The PL spectra were excited by a 409-nm continuous-wave diode laser, by a 325 nm He–Cd laser and by the light of a Xe lamp (150 W) passed through a grating monochromator and recorded using an IKS spectrometer equipped with a photomultiplier tube. Diffuse reflectance spectra were recorded by using a two-beam spectrophotometer Shimadzu UV-3600. The diffuse reflectance spectra were converted with the Kubelka–Munk function employing the equation [22]:

$$F(R) = (1 - R)^2 / (2R) = \alpha / S$$
(1)

where R is the reflectance,  $\alpha$  and S represent molar absorption and scattering coefficient, respectively. Assuming that the scattering coefficient in the spectral range studied is constant, a spectral dependence of Kubelka–Munk function can be considered as a spectral dependence of absorption coefficient  $\alpha(h\nu)$ . All measurements were carried out at room temperature.

#### **3** Experimental results

Chemical maps of as-deposited films obtained by using EDX showed the homogeneous distribution of all chemical elements involved in the sintering process. The EPR profile of raw MgO powder shows six components between 300 and 400 mT characteristic for manganese ions in cubic phase (Fig. 1a). To study the EPR spectrum of sintered films, they were removed from the substrate to prevent contribution of substrate's EPR signals. The EPR spectrum of the MgO–TiO<sub>2</sub> powder sintered at 1100 °C (Fig. 1b) shows a wide signal caused by native defects of magnesium titanate and the signals of Mn ions similar to those of the raw Mndoped MgO powder. The concentration of Mn dopant was estimated to be about  $5 \times 10^{16}$  cm<sup>-3</sup> both in the raw Mndoped MgO and sintered MgO-TiO<sub>2</sub> powders. The EDX study did not reveal the presence of Mn impurity in the raw MgO powder apparently due to low Mn content and limit sensitivity of EDX method.

The XRD patterns of the as-deposited films and sintered at different temperatures without and with Li additive are shown in Fig. 2a, b, respectively. Crystallographic database cards were used for the identification of the formed phases. The XRD patterns reveal the peaks of several magnesium titanate crystal phases, such as  $Mg_2TiO_4$  (JCDD PDF 000-25-1157),  $MgTiO_3$  (JCDD PDF 010-75-3957) and  $MgTi_2O_5$ (JCDD PDF 010-79-0832). In the diffraction patterns of as deposited films and the films annealed at low temperatures, the peaks of raw materials, i.e. MgO (JCDD PDF 010-77-2364), rutile TiO<sub>2</sub> (JCDD PDF 010-76-0317) and anatase



Fig. 1 EPR spectra of raw MgO powder (a) and MgO– $TiO_2$  powder sintered at 1100 °C for 1 h (b). The spectra were normalized with respect to the intensity of the signal of MgO:Mn reference as well as on the mass of each powder studied

**Fig. 2** X-ray diffraction  $\Theta$ -2 $\Theta$  scans of as-deposited MgO-TiO<sub>2</sub> films and the films sintered for 1 h in the range of 800–1200 °C without (**a**) and with Li addition (**b**) and concentrations of different crystal phases in the annealed film without (**c**) and with Li addition (**d**) versus annealing temperature



TiO<sub>2</sub> (JCDD PDF 010-78-2486), are also observed. Relative contribution of different crystal phases in the XRD patterns was found to depend strongly on the annealing temperature and the presence of Li additive. To quantify the contribution of each crystal phase the reference intensity ratio (RIR) method was used. The method is based on the scaling of obtained diffraction data to the diffraction of a standard reference material (usually corundum is used as the international reference). The scale factor is defined by the ratio of intensity of analyte (I) to the intensity of corundum  $(I_c)$ ,  $I/I_c$ , for each phase. Despite some shortcomings, the RIR method is straight forward, easy to implement and is widely used in powder XRD for quantitative analysis. The concentrations of individual crystal phases (the weight fraction of individual phase expressed in percent) obtained by RIR method for Li-undoped and Li-co-doped films are shown in Fig. 2c, d.

The XRD patterns of Li-undoped films sintered at 800 and 900 °C show the peaks from MgTiO<sub>3</sub>, MgO, rutile  $TiO_2$  and anatase  $TiO_2$ . The presence of  $TiO_2$  in these films implies an incomplete sintering of the raw materials. As the annealing temperature increases, the concentration of TiO<sub>2</sub> phases decreases, and the intensity of the diffraction peaks from anatase TiO<sub>2</sub> decreases stronger as compared to those of rutile TiO<sub>2</sub>. The films sintered at 1000 °C contained both MgTiO<sub>3</sub> and MgO with small addition of MgTi<sub>2</sub>O<sub>5</sub>. The latter is often formed as an intermediate phase of MgTiO<sub>3</sub>. The XRD peaks of Mg<sub>2</sub>TiO<sub>4</sub> appeared upon the annealing at 1100 °C and increased in intensity after the annealing at 1200 °C. The formation of MgTiO<sub>3</sub> second phase is caused by the partial thermal decomposition of Mg<sub>2</sub>TiO<sub>4</sub> in the temperature range used [19, 23]. According to the results of [23], this process proceeds in the following way:  $Mg_2TiO_4 \rightarrow Mg_{2+2\delta}Ti_{1-\delta}O_4 + MgTiO_3$ . In fact, a singlephase Mg<sub>2</sub>TiO<sub>4</sub> product is usually reported for the temperatures higher than 1300 °C [3, 19, 23].

The XRD patterns of Li co-doped films prove that Li additive strongly promotes the increase of MgTiO<sub>3</sub> crystal phase concentration, especially at low annealing temperatures. In fact, there is no indication that TiO<sub>2</sub> phase remains in the films annealed at 800–900 °C. At the same time, the effect of Li co-doping on concentration of Mg<sub>2</sub>TiO<sub>4</sub> phase is not so obvious. In particular, the concentration of Mg<sub>2</sub>TiO<sub>4</sub> phase is twice larger in the films sintered with Li at 1100 °C as compared with Li-undoped MgO–TiO<sub>2</sub> films, while an addition of Li in the films annealed at 1200 °C has no positive effect on Mg<sub>2</sub>TiO<sub>4</sub> phase formation.

The UV–vis absorption spectra of the films recalculated from their diffuse reflectance spectra using Kubelka–Munk theory are shown in Fig. 3. The changes in the absorption spectra reflect mainly crystal phase transformation caused by thermal annealing. Since MgO, TiO<sub>2</sub>, MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> are characterized by different band gap energies as well as the concentration of each crystal phase varies

with the annealing temperature, the absorption edge of the film is determined by the phase with the smallest band gap energy. In fact, in the spectra of Li-undoped MgO-TiO<sub>2</sub> films annealed at 800 and 900 °C the intense absorption band in the range of 300-400 nm is observed. This band can be ascribed to optical absorption in both rutile and anatase  $TiO_2$  whose band gap energies are known to be about 3.0 and 3.2-3.4 eV, respectively [24]. In fact, the intensity of this band correlates with concentration of TiO<sub>2</sub> phases estimated by RIR method. This band decreases in intensity as the annealing temperature rises and is hardly observed in the spectra of all Li co-doped films, where TiO<sub>2</sub> phases were not detected by XRD. Moreover, in the film annealed at 800 °C, the concentration of anatase phase prevails over that of rutile, meanwhile in the film annealed at 900 °C an opposite trend is found (Fig. 2c). This agrees with the shifting of the onset of the absorption band to longer wavelengths in accordance with decreasing band gap energy when passing from anatase to rutile  $TiO_2$  (Fig. 3a). The absorption band caused by both MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> is found at shorter wavelengths. In accordance with the results of the XRD study, the MgTiO<sub>3</sub> is formed at low annealing temperatures, while the concentration of Mg<sub>2</sub>TiO<sub>4</sub> prevails over MgTiO<sub>3</sub> at higher annealing temperatures. Therefore, the band gap energies of MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> were displayed for Li codoped films annealed at 800 and 1100 °C, respectively. The optical band gaps were determined by the method proposed by Wood and Tauc using the relation [25]:

$$(h\nu \cdot \alpha(h\nu))^{1/n} = A(h\nu - E_g)$$
<sup>(2)</sup>

where h is the Planck's constant,  $\nu$  is the frequency,  $\alpha(h\nu)$  is the absorption coefficient (Kubelka–Munk function),  $E_g$  is the band gap energy, A is a proportional constant, and n is a constant associated with different types of electronic transitions (for direct allowed transitions n =  $\frac{1}{2}$ ; for indirect allowed ones n = 2). Taking into account that MgTiO<sub>3</sub> is characterized by indirect allowed electronic transitions, the extrapolation of the linear part of the  $[h\nu \cdot \alpha(h\nu)]^2$  plot versus h $\nu$  toward energy axis at  $\alpha(h\nu) = 0$  gives the value of  $E_g(MgTiO_3) = 4.2$  eV. In turn, Mg<sub>2</sub>TiO<sub>4</sub> is characterized by direct allowed transitions, and therefore, extrapolation of the linear part of the [h $\nu \cdot \alpha(h\nu)$ ]<sup>1/2</sup> plot versus h $\nu$  towards zero provides  $E_g(Mg_2TiO_4) = 4.33$  eV. The estimated values are comparable with the band gaps reported for these compounds in the literature [26, 27].

The PL spectra of the as-deposited films do not show any PL under UV or blue excitation. In contrast, all annealed films show red PL (Fig. 4a, b). In the PL spectra, two PL bands centered at about 660 and 710 nm are found. The band at 710 nm is present in all spectra. The band at 660 nm appears in the films sintered at 1100  $^{\circ}$ C and increases in intensity in the films annealed at 1200  $^{\circ}$ C (Fig. 4a). The



Fig. 3 UV-vis absorbance spectra of MgO-TiO<sub>2</sub> (a) and Li co-doped MgO-TiO<sub>2</sub> films (b) annealed in the range of 800–1200 °C and Tauc's plots for Li co-doped films annealed at 800 °C (c) and 1200 °C (d)

changes in the intensity of 710 nm PL band correlate with MgTiO<sub>3</sub> phase concentration, while those of 660 nm band are in good agreement with the changes of  $Mg_2TiO_4$  phase concentration. Thus, it can be concluded that 660 and 710 nm bands originate from  $Mg_2TiO_4$  and  $MgTiO_3$  crystal phases, respectively. As the PL spectra were measured at room temperature with a low wavelength resolution, the vibronic modes with zero phohon line are not resolved and the individual titanate phase shows a single broadened PL band.

The PL spectrum recorded with higher wavelength resolution proves that each of two bands composes of a series of sharper peaks (Fig. 4c). The same peaks are also found in Li co-doped films. The shape of the PL spectra is typical for  $Mn^{4+}$  emission observed by other authors in Mn-doped magnesium titanates produced by different methods [6–9, 28–30]. The excitation spectra of the PL bands are shown in Fig. 4c. The detection wavelengths for both spectra are marked by arrows. Each excitation spectrum contains two broad intense bands, one in the UV and another in the bluegreen spectral ranges, as well as one band with a low intensity between these two. The maxima of the excitation bands of the 710 nm PL band are shifted to longer wavelengths as compared to those of 660 nm band, being at 335, 440 and 542 nm, and 328, 410 and 490 nm, respectively. The PL bands can be ascribed to  ${}^{2}E \rightarrow {}^{4}A_{2}$  spin-forbidden transition of the Mn<sup>4+</sup> ion, and the PL excitation bands to  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ ,  ${}^{4}A_{2} \rightarrow {}^{2}T_{1}$  and  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  transitions of Mn<sup>4+</sup> ion in corresponding matrices.

When introduced in crystal lattice  $Mn^{4+}$  ion experiences strong crystal field (CF) due to its high effective positive charge. The strength of the CF depends on arrangement of the impurity ion's site, in particular, on the  $Mn^{4+}-O_2$ bond distance, the strength increases with bond distance decreasing [31]. In the ideal octahedral site, the dependence of  $Mn^{4+}$  energy levels on CF strength can be well illustrated by Tanabe–Sugano energy diagram. In accordance with this diagram the energy of both  ${}^{4}A_2 \rightarrow {}^{4}T_1$  and



Fig. 4 Room temperature PL spectra of MgO–TiO<sub>2</sub> (a) and Li co-doped MgO–TiO<sub>2</sub> films (b) annealed in the range of 800–1200 °C; PL and PL excitation spectra of Li co-doped film annealed at 1200 °C (c) and integrated intensity of Mn<sup>4+</sup> PL versus annealing temperature (d)

 ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  transitions is strongly influenced by CF strength [1]. At the same time, the energy of  ${}^{2}E \rightarrow {}^{4}A_{2}$  luminescent transition is almost independent on the CF strength, but it is significantly affected by different host lattices [1, 2]. It has been proposed that the energy of Mn<sup>4+</sup> emission is influenced mainly by the covalence of the "Mn<sup>4+</sup>ligand" bonding: the more covalent is the chemical bonding, the larger is nephelauxetic effect, i.e. the greater is the overlap of the wave functions of the impurity ion and the ligand, and the smaller is the energy of  ${}^{2}E$  level of  $Mn^{4+}$  [31]. The nephelauxetic effect depends not only on the nature of surrounding ligands, but also on the chemical bond lengths and the angles between those chemical bonds [31]. It affects the energy of the <sup>2</sup>E level by reducing the Racah parameters. In general, the Mn<sup>4+</sup>–O<sub>2</sub>-bond length in Mg<sub>2</sub>TiO<sub>4</sub> is shorter than that in MgTiO<sub>3</sub>, being about 1.99 A [6] and 2.059 A [28], respectively. It results in larger CF strength and larger energies of  ${}^4\!A_2 \to {}^4\!T_1$ 

and  ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$  transitions in Mg<sub>2</sub>TiO<sub>4</sub> [7] in comparison with MgTiO<sub>3</sub> [28]. In turn, the Racah parameter C is smaller in MgTiO<sub>3</sub> resulting in smaller energy of the  ${}^{2}E$  level as compared to Mg<sub>2</sub>TiO<sub>4</sub> [7, 28]. Therefore, in MgTiO<sub>3</sub> the energies of Mn<sup>4+</sup> emission and absorption transitions should be shifted to the red as compared to the corresponding transitions in Mg<sub>2</sub>TiO<sub>4</sub>. This trend is in fact observed in the PL and PL excitation spectra of the films studied (Fig. 4c), and the corresponding peak positions are in agreement with those reported by other authors [7, 28–30].

In Li co-doped films, the integrated intensities of Mn<sup>4+</sup> luminescence are found to be in several times larger than those in Li-undoped films sintered at the same temperatures (Fig. 4d). The effect is more pronounced at lower annealing temperatures. Moreover, for Li co-doped films the band at 660 nm arises for the film annealed already at 1000 °C, and exceeds the intensity of 710 nm band for the film sintered at 1100 °C. The latter agrees with the XRD data revealing the increased concentration of  $Mg_2TiO_4$  phase in Li co-doped films annealed at 1100 °C.

#### **4** Discussion

The impurity atoms introduced to modify luminescence, electrical, magnetic and other properties of solid state can also affect the crystallization process, i.e. modify crystal morphology [32], increase or decrease the crystallite sizes [33, 34] as well as influence the crystal phase formation [19]. The results of our structural and optical investigations definitely indicate that the Li works as a flux, i.e. promotes the crystallization of magnesium titanate phases and decreases their sintering temperature. In fact, both XRD data and UV-vis absorption spectra prove that concentration of raw TiO<sub>2</sub> powders decreases significantly in the Li co-doped films sintered at 800 and 900 °C, and the concentration of MgTiO<sub>3</sub> phase increases. Besides, an increased  $Mn^{4+}$  luminescence from the Mg<sub>2</sub>TiO<sub>4</sub> phase found in Li codoped films annealed at 1000 and 1100 °C compared to Liundoped films testifies to the increased presence of  $Mg_2TiO_4$ phase too. The fact that XRD data do not reveal  $Mg_2TiO_4$ phase in the film annealed at 1000 °C can be caused by much lower sensitivity of this method in comparison with PL investigation.

At elevated temperatures (475–650 °C) LiNO<sub>3</sub> converts to Li oxide in accordance with chemical reaction:

$$4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 3\text{NO}_2 + \text{O}_2 \tag{3}$$

In turn, lithium oxide is widely known as a flux used for processing silica and ceramics, reducing the melting point and viscosity of the materials and leading to glazes with improved physical properties. Lithium salts, such as LiCl, LiF, Li<sub>2</sub>CO<sub>3</sub>, LiNO<sub>3</sub>, are also used for the synthesis of a variety of ceramic powders and phosphors [19, 34-40]. In this process, the salts melt at elevated temperatures and generate liquid phase at the grain boundaries, which promotes the diffusion of ions and enhance elementary sintering mechanisms [19, 35]. Specifically, it has been shown that adding 0.2-0.5 wt% of Li<sub>2</sub>O or Li<sub>2</sub>CO<sub>3</sub> decreases on 200-400 °C the sintering temperature of (Ba,Sr)TiO<sub>3</sub> and Zn<sub>2</sub>SiO<sub>4</sub> powders [19]. Lithium salts not only facilitate crystal growth, but also affect crystal morphology and improve the luminescence of phosphors [35-40]. We have observed earlier that adding 0.03 wt % of LiNO<sub>3</sub> to ZnO powders promotes the increase of both grain sizes and exciton PL intensity in polycrystalline ZnO films sintered at 800 and 900 °C [34]. The effect was not found at higher annealing temperatures as well as for larger concentrations of Li. In the MgO-TiO<sub>2</sub> samples studied, Li<sup>+</sup> accelerates crystallization process of MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> in the temperature range of 800–1100 °C, but

it is not efficient as a flux at higher annealing temperatures as well as does not prevent the thermal decomposition of Mg<sub>2</sub>TiO<sub>4</sub> on MgTiO<sub>3</sub>.

At the same time, the integrated PL intensity of Li codoped film sintered at 1200 °C is found somewhat larger as compared to Li-undoped film. The role of co-dopant in the enhancement of the luminescence can be explained by different mechanisms: (i) it can promote Mn<sup>3+</sup> to Mn<sup>4+</sup> conversion acting as charge compensator [10], (ii) it can reduce the concentration quenching of Mn<sup>4+</sup> PL by lowering the concentration of close Mn<sup>4+</sup>–Mn<sup>4+</sup> pairs [14, 35], and (iii) it can affect concentration of intrinsic defects as well as create new ones [36, 38, 40]. The first mechanism seems to be unlikely in our case since no pronounced increase of the Mn<sup>4+</sup> absorption is found in the UV-vis absorption spectra of the Li co-doped films sintered at 1200 °C. The second mechanism is also hardly probable because of the low concentration of Mn ions in the samples studied. Therefore, it can be supposed that Li<sup>+</sup> affects the concentration of defects. In fact, it has been shown that the role of excess Li<sub>2</sub>CO<sub>3</sub> in the pronounced improvement of the PL efficiency of  $Ba_2SiO_4$ :Eu<sup>2+</sup> phosphor is the extraction of undesirable impurities from the low-purity precursors in the melt, leading to the decreasing impurity concentrations in the phosphor product [38]. Though the concentration of lithium salt applied in the current research for MgO-TiO<sub>2</sub> film fabrication is much lower than those used in  $Ba_2SiO_4$ :Eu<sup>2+</sup> phosphor synthesis [38], it can be supposed that Li promotes the lowering of concentration of the defects acting as the centers of non-radiative recombination in the Mg<sub>2</sub>TiO<sub>4</sub> crystal phase.

### 5 Conclusions

The effect of Li<sup>+</sup> co-doping on crystal phase formation and PL intensity of lightly Mn<sup>4+</sup>-doped MgO-TiO<sub>2</sub> films produced by solid state reaction is investigated. The films are sintered in air for 1 h at temperatures in the range of 800–1200 °C. Formation of both MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> crystal phases is proven by the XRD, diffuse reflectance spectroscopy and PL study. The MgTiO<sub>3</sub> crystal phase is found in all annealed films, meanwhile Mg<sub>2</sub>TiO<sub>4</sub> appears at 1000-1100 °C. It is shown that Li facilitates the crystallization process for both MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> in the temperature range of 800-1100 °C, but it is not efficient as a flux at higher annealing temperatures, as well as it does not prevent thermal decomposition of Mg<sub>2</sub>TiO<sub>4</sub> on MgTiO<sub>3</sub>. The PL bands caused by  ${}^{2}E \rightarrow {}^{4}A_{2}$  transitions of Mn<sup>4+</sup> ions in two titanate phases are revealed. In Li<sup>+</sup> co-doped films, the PL intensity related to Mn<sup>4+</sup> ions is found several times larger as compared to Li-undoped films that is attributed mainly to a flux effect. It is assumed that Li also helps to reduce the concentration of the centers of non-radiative recombination in the Mg<sub>2</sub>TiO<sub>4</sub> crystal phase.

Acknowledgements This work was partly supported via Bilateral DNIPRO program (project M/7-2017 in Ukraine and #37884WC in France) funded by the Ministry of Education and Research of Ukraine, by the Ministries of Foreign Affairs and International Development (MAEDI) and the Ministry of Education, Higher Education and of Research (MENESR) in France, as well as by National Academy of Sciences of Ukraine (project III-10-15).

# References

- 1. D. Chen, Y. Zhou, J. Zhong, RSC Adv. 6, 86285 (2016)
- Z. Zhou, N. Zhou, M. Xia, Y. Meiso, H.T.B. Hintzen, J. Mater. Chem. C 4, 9143 (2016)
- T.-M. Chen, J.T. Luo, United States Patent, US 7(846), 350 B2 (2010)
- 4. X. Huang, Nat. Photonics 8, 748 (2014)
- 5. G. Li, Y. Tian, Y. Zhao, J. Lin, Chem. Soc. Rev. 44, 8688 (2015)
- T. Ye, S. Li, X. Wu, M. Xu, X. Wei, K. Wang, H. Bao, J. Wang, J. Chen, J. Mater. Chem. C 1, 4327 (2013)
- M.M. Medic, M.G. Brik, G. Drazic, Z.M. Antic, V.M. Lojpur, M.D. Dramicanin, J. Phys. Chem. C 119, 724 (2015)
- S. Kawakita, H. Kominami, K. Hara, Phys. Status Solidi C 12, 805 (2015)
- Z. Qiu, T. Luo, J. Zhang, W. Zhou, L. Yu, S. Lian, J. Lumin. 158, 130 (2015)
- J. Lu, Y. Pan, J. Wang, X. Chen, S. Huang, G. Liu, RSC Adv. 3, 4510 (2013)
- R. Cao, J. Huang, X. Ceng, Z. Luo, W. Ruan, Q. Hu, Ceram. Int. 42, 13296 (2016)
- M. Peng, X. Yin, P.A. Tanner, M.G. Brik, P. Li, Chem. Mater. 27, 2938 (2015)
- J. Long, Y. Wang, R. Ma, C. Ma, X. Yuan, Z. Wen, M. Du, Y. Cao, Inorg. Chem. 56, 3269 (2017)
- 14. Y.X. Pan, G.K. Liu, J. Lumin. 131, 465 (2011)
- D. Chen, Y. Zhou, W. Xu, J. Zhong, Z. Ji, W. Xiang, J. Mater. Chem. C 4, 1704 (2016)
- T. Murata, T. Tanoue, M. Iwasaki, K. Morinaga, T. Hase, J. Lumin. 114, 207 (2005)
- 17. K. Seki, S. Kamei, K. Uematsu, T. Ishigaki, K. Toda, M. Sato, J. Ceram. Process. Res. 14, s67 (2013)

- 18. M.G. Brik, Y.X. Pan, G.K. Liu, J. Alloys Compd. **509**, 1452 (2011)
- M. Valant, D. Suvorov, R.C. Pullar, K. Sarma, N. Mc, N. Alford, J. Eur. Ceram. Soc. 26, 2777 (2006)
- Yi-D. Zhang, Di Zhou, N. Alford, J. Am. Ceram. Soc. 99, 3645 (2016)
- J. Bernard, D. Houivet, M. Hervieu, J.M. Haussonne, Solid State Sci. 8, 598 (2006)
- 22. G. Kortüm, W. Braun, G. Herzog, Angew. Chem. Int. Edit. 2, 333 (1963)
- M.A. Petrova, G.A. Mikirticheva, A.S. Novikova, V.F. Popova, J. Mater. Res. 12, 2584 (1997)
- 24. M. Landmann, E. Rauls, W.G. Schmidt, J. Phys. 24, 195503 (2012)
- 25. J. Tauc, A. Menth, J. Non-Cryst. Solids 8-10, 569 (1972)
- T.S. Kumar, R.K. Bhuyan, D. Pamu, Appl. Surf. Sci. 264, 184 (2013)
- 27. R.K. Bhuyan, T.S. Kumar, A. Perumal, S. Ravi, D. Pamu, Surf. Coat. Technol. **221**, 196 (2013)
- V. Đorđević, M.G. Brik, A.M. Srivastava, M. Medić, P. Vulić, E. Glais, B. Viana, M.D. Dramićanin, Opt. Mater. 74, 46 (2017)
- J. Long, C. Ma, Y. Wang, X. Yuan, M. Du, R. Ma, Z. Wen, J. Zhang, Y. Cao, Mat. Res. Bull. 85, 234 (2017)
- 30. R. Louat, A. Louat, E. Duval, Phys. Status Solidi B 46, 559 (1971)
- M.G. Brik, S.J. Camardello, A.M. Srivastava, ECS J. Solid State Sci. Technol. 4, R39 (2015)
- J.R. Ramya, K.T. Arul, K. Elayaraja, S.N. Kalkura, Ceram. Int. 40, 16707 (2014)
- K.T. Arul, E. Kolanthai, E. Manikandan, G.M. Bhalerao, V.S. Chandra, J.R. Ramya, U.K. Mudali, K.G.M. Nair, S.N. Kalkura, Mat. Res. Bull. 67, 55 (2015)
- L. Khomenkova, V.I. Kushnirenko, M.M. Osipyonok, O.F. Syngaivsky, T.V. Zashivailo, G.S. Pekar, Y.O. Polishchuk, V.P. Kladko, L.V. Borkovska, Phys. Status Solidi C 12, 1144 (2015)
- 35. J. Chen, C. Li, Z. Hui, Y. Liu, Inorg. Chem. 56, 1144 (2017)
- J. Zhou, Y. Wang, B. Liu, J. Liu, J. Phys. Chem. Solids. 72, 995 (2011)
- A. Lacanilao, G. Wallez, L. Mazerolles, V. Buissette, T. Le Mercier, F. Aurissergues, M.-F. Trichet, N. Dupre', B. Pavageau, L. Servant, B. Viana, Mat. Res. Bull. 48, 2960 (2013)
- D. Kim, K.-W. Jeon, J.S. Jin, S.-G. Kang, D.-K. Seo, J.-C. Park, RSC Adv. 5, 105339 (2015)
- 39. S.M. Rafiaei, Mater. Sci. 34, 780 (2016)
- S. Khan, H. Choi, S.Y. Lee, K.-R. Lee, O.M. Ntwaeaborwa, S. Kim, S.-H. Cho, Inorg. Chem. 56, 12139 (2017)