



# Luminescent and structural properties of $Zn_xMg_{1-x}WO_4$ mixed crystals



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## HIGHLIGHTS

- The structural and luminescent properties of  $Zn_xMg_{1-x}WO_4$  were studied.
- The energy of Raman modes, the bandgap width, TSL peak position linearly depend on  $x$ .
- Each  $Zn_xMg_{1-x}WO_4$  possesses its original crystalline structure.

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## ABSTRACT

The structural and luminescent properties of perspective scintillating  $Zn_xMg_{1-x}WO_4$  mixed crystals were studied. The following characteristics were found to depend linearly on  $x$  value: the energy of several vibrational modes detected by Raman spectroscopy, the bandgap width deduced from the shift of the excitation spectrum onset of a self-trapped exciton (STE) emission, the position of thermally stimulated luminescence peaks. It is also shown that the thermal stability of the STE luminescence decreases gradually when  $x$  decreases. These data indicate that each  $Zn_xMg_{1-x}WO_4$  mixed crystal is not a mixture of two constituents, but possesses its original crystalline structure, as well as optical and luminescent properties.

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## 1. Introduction

High light output for scintillating materials is one of the main requirements for their successful application. Recently it has been demonstrated that the scintillation light yield increases in the mixed crystals relatively to the yield in their constituents. The effect is observed for the compounds with activator as well as intrinsic luminescence (Gektin et al., 2014; Spassky et al., 2014) and is presumably due to the decrease of the mean free path of charge carriers at the stage of thermalization and subsequent migration of thermalized electrons and holes.

Recently it has been demonstrated that the light output of undoped  $Zn_xMg_{1-x}WO_4$  mixed crystals has a maximum value at  $x = 0.5$  at  $T = 300$  K. The luminescence of these crystals is connected with the emission from excitons, which are self-trapped at

$WO_6$  complexes. Using the data of luminescence spectroscopy and by means of the numerical simulation it has been shown that the enhancement is connected with the increase of the probability of exciton formation from separated geminate  $e-h$  pairs as far as the distance between thermalized electrons and holes is minimal at the value of  $x = 0.5$  (Spassky et al., 2014). The constituents of the  $MgWO_4$  and  $ZnWO_4$  mixed crystals belong to the same wolframite structural type (space group  $P2_1/c$ ) that allows to expect the  $Zn_xMg_{1-x}WO_4$  crystals to have the same structure through the whole set of  $x$  values. The above mentioned properties allow considering the  $Zn_xMg_{1-x}WO_4$  crystals as a new and promising scintillating material for various applications, including cryogenic scintillating detectors.

In this work we present new experimental data on  $Zn_xMg_{1-x}WO_4$  mixed crystals, including the results of Raman spectroscopy and thermostimulated luminescence (TSL) studies. Linear dependences of a set of structural and luminescent parameters on  $x$  value will be demonstrated.

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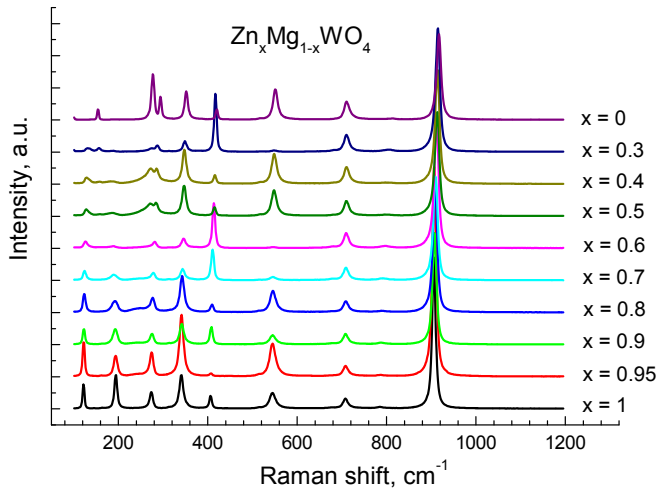


Fig. 1. The Raman spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$  crystals at  $T = 300$  K.

## 2. Experimental details

The set of  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$  ( $x = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 1$ ) single crystals were grown by the Czochralski method from platinum crucibles using high-frequency heating. Growth conditions were the following: gradient  $\Delta Tz \leq 10\text{--}20$  °/cm, pulling speed  $v = 1.2\text{--}1.4$  mm/h, weight gain  $dm/dt = 2.0\text{--}2.5$  g/h. The  $\text{MgWO}_4$  single crystal was grown from melted flux solution by pulling on a rotating seed from a platinum crucible.

The Raman measurements were made using a micro Raman spectroscope Renishaw inVia at wavelength 514 nm. A deuterium 400 W discharge lamp DDS-400 and a double-quartz prism monochromator DMR-4 were used for measuring the luminescence excitation spectra near the fundamental absorption edge (3.4–4.4 eV) at room temperature.

The measurements of radioluminescence spectra were carried out under irradiation by an X-ray source with a tungsten anode operating at  $U = 30$  keV. The spectra were registered using Shamrock 500i spectrograph equipped with Newton EMCCD DU970P. TSL glow curves and spectra were recorded in the temperature region 80–470 K after X-ray irradiation of samples for 600 s at  $T = 80$  K.

## 3. Results and discussion

### 3.1. Raman spectroscopy data

The phase composition of  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$  was controlled by X-ray phase analysis. All grown crystals are crystallized in the wolframite structural type. According to a group theory, the wolframite structure presents 18 Raman active modes – 8  $A_g$  + 10  $B_g$ . In these compounds, due to the differences in valence and mass between  $\text{W}^{6+}$  and  $\text{A}^{2+}$  cations, the lattice dynamics can be understood assuming two kinds of modes (Ruiz-Fuertes et al., 2011). Six of them are related to the vibrations inside the covalently bounded  $\text{WO}_6$  octahedra (so-called internal modes) and other modes originate as motions of the A cations against the  $\text{WO}_6$  units (external modes). The internal modes have higher frequencies than the external ones and usually there is a phonon gap between them.

The Raman spectra of  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$  mixed crystals are presented in Fig. 1. It should be noted, that some of the modes were not observed due to the uncertain orientation of the samples or low intensity of these Raman modes. The frequencies of detected Raman bands in  $\text{ZnWO}_4$  ( $x = 1$ ),  $\text{MgWO}_4$  ( $x = 0$ ) and  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{WO}_4$  as well as their attribution to the corresponding modes are listed in Table 1. It can be seen from Table 1 that the observed Raman-active modes for  $\text{ZnWO}_4$  and  $\text{MgWO}_4$  are in good agreement with literature data (Liu et al., 1988; Fomichev and Kondratov, 1994; Ruiz-Fuertes et al., 2011). The frequencies 909 ( $A_g$ ), 788 ( $B_g$ ), 708.5 ( $A_g$ ), 677 ( $B_g$ ), 409 ( $A_g$ ) and 341.4 ( $A_g$ )  $\text{cm}^{-1}$  in  $\text{ZnWO}_4$  correspond to the stretching vibrations of W–O atoms in the  $\text{WO}_6$  group (Liu et al., 1988; Perakis et al., 2000). The bands with the frequencies 197 ( $A_g$ ), 165 ( $B_g$ ), 150 ( $B_g$ ) and 125 ( $A_g$ )  $\text{cm}^{-1}$  are attributed to vibrations involving zinc cations (Fomichev and Kondratov, 1994). In the case of  $\text{MgWO}_4$  the internal modes are the  $A_g$  modes at 420, 552, 713 and 917  $\text{cm}^{-1}$  and the  $B_g$  modes at 684 and 809  $\text{cm}^{-1}$  (Ruiz-Fuertes et al., 2011).

A strong Raman mode at  $\sim 910$   $\text{cm}^{-1}$  is typical for wolframites and corresponds to a symmetric  $A_g$  internal vibration of the  $\text{WO}_6$  octahedron. Fig. 2 represents the wavenumber variation of the maximum position of this mode from 906 to 917  $\text{cm}^{-1}$  depending on  $x$  value in  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ . The dependence of the mode maximum on  $x$  is linear (see Fig. 2, inset). The same tendency is observed for the Raman mode at  $\sim 120$   $\text{cm}^{-1}$  connected with external vibrations involving cations. The observed linear shift is caused by the linear increase of cell parameters with the increase of  $x$  value. The intensity of Raman modes under discussion decreases with the increase of  $x$  value in both cases. The width of the internal

Table 1  
Vibrational frequencies of some  $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$  compositions with the wolframite structure.

$\text{ZnWO}_4$			$\text{MgWO}_4$			$\text{Zn}_{0.5}\text{Mg}_{0.5}\text{WO}_4$		
$\Omega$ ( $\text{cm}^{-1}$ )		Mode	$\omega$ ( $\text{cm}^{-1}$ )		Mode	$\omega$ ( $\text{cm}^{-1}$ )		
Present	Liu et al., 1988		Present	Ruiz-Fuertes et al., 2011		Present		
122	124	$A_g$	154	155.9	$A_g$	128		
				185.1	$B_g$	158		
194	196	$A_g$				186		
274	276	$A_g$	277	277.1	$A_g$	272		
			294	294.1	$A_g$	294		
340	343	$B_g$				347		
	356	$B_g$	353	351.9	$A_g$			
406	409	$A_g$		405.2	$B_g$			
			420	420.4	$A_g$	416		
545	546	$A_g$	551	551.6	$A_g$	547		
708	711	$A_g$	710	713.2	$A_g$	709		
786	788	$B_g$						
906	909	$A_g$	917	916.8	$A_g$	913		

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