

STRUCTURE OF INORGANIC COMPOUNDS

Structural Features of $Zn_xMg_{1-x}WO_4$ Mixed Crystals

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Abstract—The structural features of a series of $Zn_xMg_{1-x}WO_4$ mixed crystals ($x = 0, 0.26, 0.41, 0.68$ or 1) have been investigated using X-ray diffraction analysis and Raman spectroscopy; the luminescence properties of the grown crystals have also been studied. The dependence of the unit-cell volume on the substitution-cation concentration x is determined. It is shown that the geometric parameters of WO_6 octahedra are independent of the ratio of Zn and Mg atomic concentrations in crystals. Consistency between the luminescence and structural properties of $Zn_xMg_{1-x}WO_4$ crystals is established.

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INTRODUCTION

Most of new scintillation materials developed in the recent years belong to the class of mixed crystals (or substitutional solid solutions) [1, 2]. In comparison with stoichiometric crystals, mixed crystals with the component concentrations in the range of 20–80% often have enhanced scintillation characteristics (such as the scintillation response and energy resolution) and are characterized by a smaller contribution from the slow components of afterglow decay [3].

An increase of the light yield of $Zn_xMg_{1-x}WO_4$ mixed crystals by a factor of about 2 (in comparison with that of the components) makes them promising scintillation materials [4]. The increase in the light yield is assumed to be related to disordering of the substitution cation sublattice, which limits the carrier thermalization length. Disorder of the $Zn_xMg_{1-x}WO_4$ structure also manifests itself in an increase in the number of nonequivalent hole traps in mixed crystals [5]. $Zn_xMg_{1-x}WO_4$ nanocrystals also exhibited an increase of the intrinsic luminescence intensity in comparison with single crystals, which may be related to the decrease in both the thermalization length of electron–hole pairs and the concentration of electron traps arising during the formation of oxygen vacancies as a result of cation substitution [6].

Thus, structural features of mixed crystals affect significantly the relaxation of charge carriers and determine the optical, luminescence and scintillation properties of these crystals. The purpose of this work was to investigate the structural features of $Zn_xMg_{1-x}WO_4$

single crystals using X-ray diffraction analysis, Raman spectroscopy, and luminescence spectroscopy.

EXPERIMENTAL

A series of $Zn_xMg_{1-x}WO_4$ mixed crystals ($x = 0, 0.3, 0.5, 0.7$ or 1 in a charge) was grown by Czochralski technique using high-frequency heating. The raw materials were initial ZnO (99.995%), MgO (99.95%), and WO_3 (99.995%) oxides. $MgWO_4$ crystal was grown from melt–solution by pulling on a rotating seed from a platinum crucible.

X-ray diffraction analysis was carried out for one single crystal of each composition (with the best diffraction peak profiles and convergence of intensities of symmetry-equivalent diffraction reflections). The total diffraction experiment for five $Zn_xMg_{1-x}WO_4$ single crystals with different compositions was performed at room temperature on an Xcalibur S diffractometer (Oxford Diffraction) equipped with a 2D CCD detector. Integration of peaks, LP correction and sample shape absorption correction were performed using a program entering the mathematical package of CrysAlis CCD diffractometers [7]. All other crystallographic calculations (introduction of anomalous scattering corrections, and averaging of symmetry-equivalent reflections) were performed using the Jana2006 software [8]. The model of the atomic crystal structure was obtained by the Charge flipping method using the SUPERFLIP program from the Jana2006 software package. The structural

Table 1. Crystallographic characteristics, experimental data, and structure refinement parameters for $Zn_xMg_{1-x}WO_4$ compounds

Chemical formula	$ZnWO_4$ (I)	$Mg_{0.32}Zn_{0.68}WO_4$ (II)	$Mg_{0.59}Zn_{0.41}WO_4$ (III)	$Mg_{0.74}Zn_{0.26}WO_4$ (IV)	$MgWO_4$ (V)
Sp. gr., Z			$P2/c, 2$		
$a, b, c, \text{\AA}$	4.6891(1), 5.7164(2), 4.9248(1)	4.6870(1), 5.7052(1), 4.9240(1)	4.6874(3), 5.6908(3), 4.9282(3)	4.6879(2), 5.6878(1), 4.9249(1)	4.6881(1), 5.6749(1), 4.9274(1)
β, deg	90.653(2)	90.597(2)	90.579(6)	90.610(2)	90.700(2)
$V, \text{\AA}^3$	132.000(6)	131.662(5)	131.453(14)	131.309(7)	131.081(4)
M_r	313.2	299.9	289.1	282.9	272.2
$D_x, \text{g/cm}^3$	7.881	7.565	7.303	7.155	6.895
Radiation; $\lambda, \text{\AA}$			Mo $K\alpha$; 0.71069		
μ, mm^{-1}	52.41	49.88	48.36 293	46.54	44.14
T, K					
Diffractometer			Xcalibur S		
Scan mode			ω		
Sample size, mm	0.31 × 0.20 × 0.15	0.31 × 0.21 × 0.20	0.20 × 0.16 × 0.15	0.28 × 0.23 × 0.10	0.28 × 0.24 × 0.20
T_{\min}, T_{\max}	0.004, 0.086	0.005, 0.074	0.009, 0.092	0.008, 0.118	0.009, 0.096
$\theta_{\max}, \text{deg}$			45.0		
Ranges of indices h, k, l	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -12 ≤ l ≤ 13	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -12 ≤ l ≤ 13	-11 ≤ h ≤ 12, -15 ≤ k ≤ 15, -13 ≤ l ≤ 13	-12 ≤ h ≤ 11, -15 ≤ k ≤ 15, -13 ≤ l ≤ 13	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -13 ≤ l ≤ 13
Numbers of reflections: measured/unique, R_{av} /with $I > 3\sigma(I)$	13524/1871, 0.064/1833	13800/1679, 0.076/1665	13630/1797, 0.060/1676	13732/1671, 0.055/1619	13826/1366, 0.073/1352
R/wR	0.0176/0.0170	0.0174/0.0173	0.0160/0.0158	0.0136/0.0137	0.0121/0.0123
S	2.87	2.95	2.97	2.93	2.98
$\Delta\rho_{\min}/\Delta\rho_{\max}, \text{e}/\text{\AA}^3$	-1.38/1.42	-1.47/1.38	-1.33/1.16	-0.90/0.91	-0.42/0.33
Software	CrysAlis [7], Jana2006 [8]				

Table 2. Interatomic distances in the structures of $ZnWO_4$ (I), $Mg_{0.32}Zn_{0.68}WO_4$ (II), $Mg_{0.59}Zn_{0.41}WO_4$ (III), $Mg_{0.74}Zn_{0.26}WO_4$ (IV), and $MgWO_4$ (V) single crystals

Distances	I	II	III	IV	V
W1–O1 × 2	1.906(2)	1.907(2)	1.905(2)	1.905(2)	1.904(2)
–O1 × 2	2.136(2)	2.136(2)	2.135(2)	2.136(2)	2.133(2)
–O2 × 2	1.786(2)	1.786(2)	1.790(2)	1.783(2)	1.788(2)
Average	1.943	1.943	1.943	1.941	1.942
Zn,Mg–O1 × 2	2.026(2)	2.016(2)	2.024(2)	2.026(2)	2.044(2)
–O2 × 2	2.089(2)	2.088(2)	2.084(2)	2.086(2)	2.081(2)
–O2 × 2	2.227(2)	2.223(2)	2.208(2)	2.199(2)	2.169(2)
Average	2.114	2.109	2.105	2.103	2.098

parameters of the crystals were refined by the full-matrix least-squares method. The main crystallographic characteristics and parameters of the structure refinement for the single crystals under study are given in Table 1, and the main interatomic distances are

listed in Table 2. The obtained information about the investigated structures was deposited with the Cambridge Structural Database (CCDC no. @).

Raman spectra were measured in a Renishaw inVia microscope at a wavelength of 514 nm. Photolumines-

cence spectra were obtained on a laboratory setup of the Division of Physical Problems of Quantum Electronics (Skobeltsyn Institute of Nuclear Physics, Moscow State University) based on an LOT-Oriel MS-257 spectrograph operating in the spectrograph mode and a Marconi CCD detector. The excitation source was 150-W xenon lamp. All recorded luminescence spectra were normalized to the instrumental function of the recording system.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The search for unit cells in the single crystals under study was finished by a choice of monoclinic cells with the parameters listed in Table 1, which made it possible to index more than 70% of the measured reflections. Thus, it was established that each $Zn_xMg_{1-x}WO_4$ mixed crystal has an original crystal structure rather than is a mixture of two components.

Refinement of the structural parameters of the series of $Zn_xMg_{1-x}WO_4$ mixed single crystals ($x = 0, 0.26, 0.41, 0.68$ or 1) was performed within the anisotropic approximation of thermal atomic displacements within the sp. gr. $P2/c$ ($Z = 2$), established previously in [9–12]. A unit cell of the monoclinic modification of the lattice of $Zn_xMg_{1-x}WO_4$ single crystals contains four independent atoms: one Mg (Zn), one W, and two O. At the stage of refining their coordinates and thermal parameters within the anisotropic approximation, we refined the occupancies of Zn, Mg, W, and O atoms of intrinsic crystallographic sites. The site occupancy by Zn and Mg atoms was refined on the assumption that the site is 100% jointly occupied by zinc and magnesium atoms. Many uninterpretable peaks of the residual electron density were revealed in difference electron-density maps plotted near W and O atomic sites for all five samples (Table 1). It should be noted that the number of these peaks was minimum for the $MgWO_4$ single crystal. Tungsten atoms in the structures under study are in rather distorted octahedra (Table 2); therefore, it is possible that W atoms and surrounding oxygen atoms are structurally disordered over several positions. However, it does not seem possible to refine the W and O atomic distributions over several close positions because of the strong correlation between the structural parameters. In addition, the X-ray diffraction analysis did not make it possible to unambiguously determine the presence of vacancies at oxygen atomic sites in the structure containing heavy atoms, such as tungsten. The chemical formulas of the investigated single crystals, obtained by refining the site occupancies of Zn and Mg atoms in the structures, are presented in Table 1.

The structure of the monoclinic modification of $Zn_xMg_{1-x}WO_4$ mixed single crystals ($x = 0, 0.26, 0.41, 0.68$ or 1) is composed of WO_6 and $Mg(Zn)O_6$ octahedra (Table 2; Figs. 1, 2). Octahedra with one-type cat-

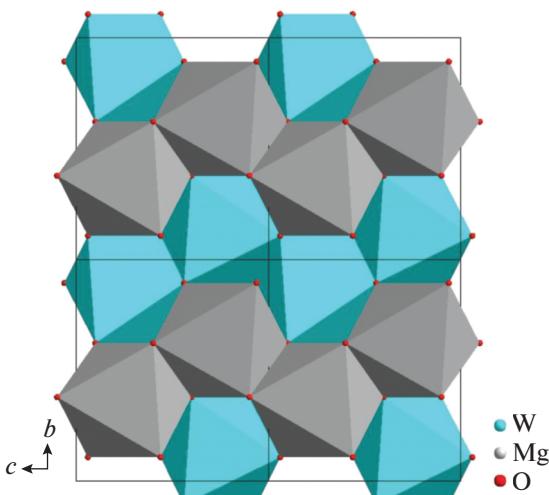


Fig. 1. Projection of the $MgWO_4$ structure on the (100) plane.

ions form zigzag chains in the [001] direction (Fig. 1). Isolated chains of WO_6 octahedra with shared edges form layers oriented perpendicular to [100], which are alternated with layers of $Zn(Mg)O_6$ octahedra (Fig. 2). The W atom is surrounded by O1 atoms at distances of ~1.905 and 2.135 Å and by O2 atoms at a distance of ~1.788 Å. O1 atoms (which are most distant from the W atoms) belong simultaneously to two anion complexes WO_6^{6-} , being the so-called bridging oxygen ions. An analysis of Table 2 shows that incorporation of zinc atoms into the $MgWO_4$ structure changes only slightly the environment of tungsten cations. As one would expect, significant changes in the $Zn_xMg_{1-x}WO_4$ structure are observed in the $Mg(Zn)O_6$ octahedra: the average interatomic (Mg, Zn)–O distance increases after incorporation of zinc atoms into the $MgWO_4$ structure, which correlates with the ionic radii of Zn^{2+} (0.74 Å) and Mg^{2+} (0.66 Å) cations [13]. Changes in the $Mg(Zn)O_6$ octahedra lead to an increase of the unit-cell volume with the concentration of zinc atoms in the crystal (Table 1, Fig. 3).

Raman Spectroscopy

Raman spectroscopy also provides information about changes in the solid-solution composition. The spectra of $Zn_xMg_{1-x}WO_4$ mixed crystals ($x = 0, 0.26, 0.41, 0.68$ or 1) are shown in Fig. 4. According to [14–16], the group of bands from 300 to 900 cm⁻¹ corresponds to stretching vibrations of the W–O bonds in the WO_6 group, whereas the group of low-frequency bands below 300 cm⁻¹ is assigned to vibrations involving zinc and magnesium cations. Thus, the bands with frequencies 906 (A_g), 786 (B_g), 708 (A_g), 545 (A_g), 406 (A_g) and 340 (B_g) cm⁻¹, observed in the $ZnWO_4$ spectrum,

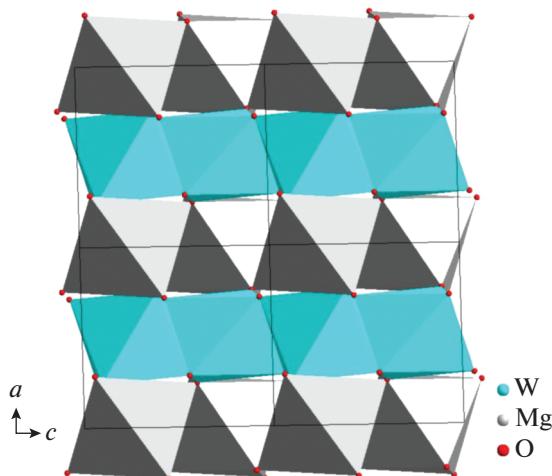


Fig. 2. Projection of the MgWO_4 structure on the (010) plane.

are internal modes, whereas the bands at 194 (A_g) and 122 (A_g) cm^{-1} are external modes. In the case of MgWO_4 , the A_g modes at 353, 420, 551, 710 and 917 cm^{-1} are internal and those at 154, 277 and 294 cm^{-1} are external.

Let us consider the behavior of Raman bands corresponding to the internal and external modes in dependence of the substitution-cation concentration in $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$. The strongest Raman band for all crystals is observed at $\sim 910 \text{ cm}^{-1}$, which is typical of wolframites and corresponds to symmetric internal vibrations of the WO_6 octahedron [16]. The band shifts to lower frequencies with an increase of x from zero to unity (Fig. 4, right-hand panel). A similar behavior is characteristic of the mode at $\sim 120 \text{ cm}^{-1}$ (Fig. 4, left-hand panel), which is related to external vibrations involving the Zn cation (this mode is absent in the case of MgWO_4).

The observed band shift is consistent with the increase in the unit-cell volume with a change of x . The profile of the band corresponding to the internal mode is independent of cation concentration (Fig. 4, right-hand panel). The band corresponding to the external mode arises and significantly narrows with an increase of x , which indicates gradual substitution of Zn cations for Mg cations (Fig. 4, left-hand panel). The presented results also indicate that each $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ crystal has an original structure and cannot be considered as a mixture of macroscopic inclusions of the components of solid solutions of ZnWO_4 and MgWO_4 crystals. This statement is based on the observed gradual displacement of the maxima of vibrational modes. If the mixed crystal is a mixture of phases (i.e., ZnWO_4 and MgWO_4), one would expect the presence of two peaks characteristic of finite compositions, which would manifest themselves

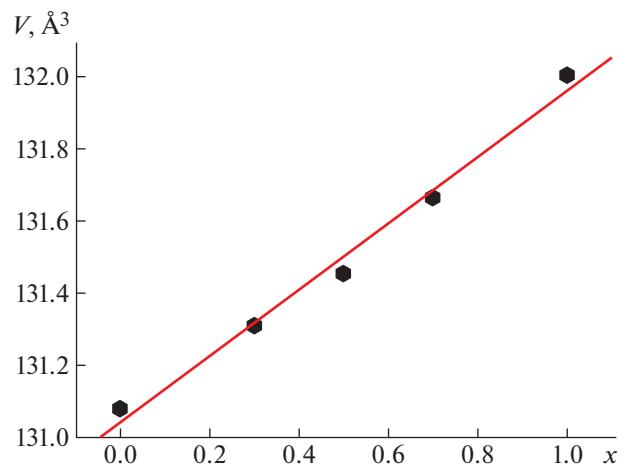


Fig. 3. Dependence of the unit-cell volume of $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ crystals on the content x .

with a relative intensity determined by the x value, as was observed in the case of $\text{CdW}_{1-x}\text{Mo}_x\text{O}_4$ [17].

Luminescence Spectroscopy

Single broad band at 2.5 eV (495 nm) was observed in the luminescence spectra of $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ (Fig. 5); this band is related to radiative decay of excitons self-trapped at WO_6^{6-} complexes [18]. The peak position and shape of the band slightly depend on the x value. The peak position shifts by only 0.04 eV to high energies with an increase of x from zero to unity. A weak dependence of the photoluminescence of the investigated mixed crystals on the cation concentration is in good agreement with the X-ray diffraction data, because the incorporation of zinc atoms into the

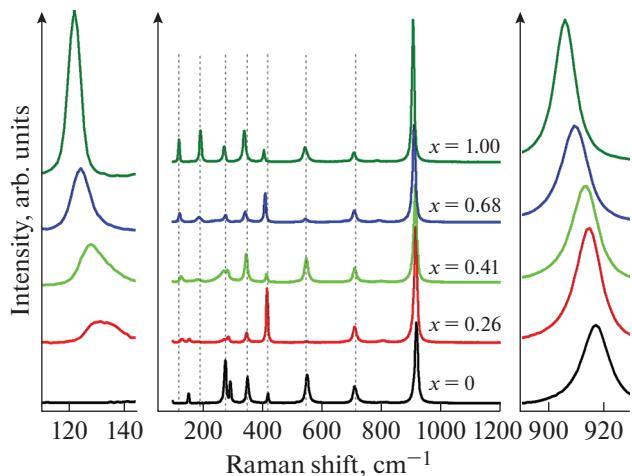


Fig. 4. Raman spectra of the $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ crystals. Changes in the bands at ~ 120 (on the left) and 910 cm^{-1} (on the right) are given on an enlarged scale.

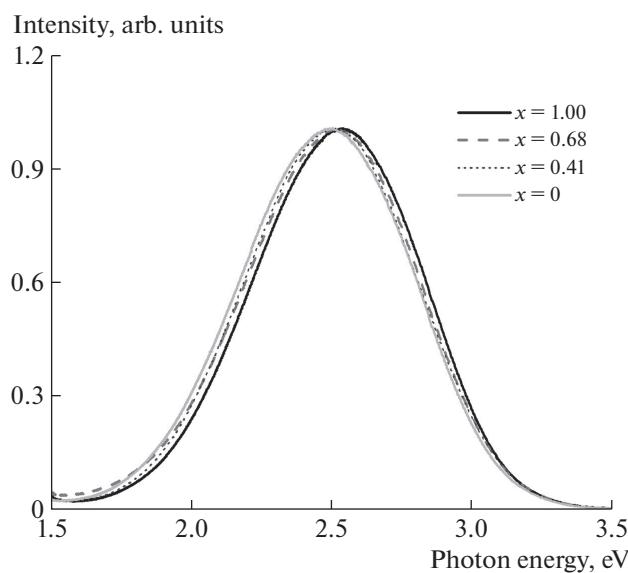


Fig. 5. Luminescence spectra of the $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ crystals at $\lambda_{\text{exc}} = 300 \text{ nm}$ and $T = 300 \text{ K}$.

MgWO_4 structure changes only slightly the geometry of the WO_6^{6-} complexes, which are luminescence centers.

CONCLUSIONS

It was established based on the X-ray diffraction data that all $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ crystals ($x = 0, 0.26, 0.41, 0.68$ or 1) are crystallized in a wolframite-type structure. An analysis of their structural features revealed a dependence of the unit-cell volume on the Zn and Mg atomic ratio in the crystal. The volume increases with an increase in the zinc atomic concentration in the crystal. Incorporation of zinc atoms into the MgWO_4 structure changes only slightly the coordination of tungsten cations. It was shown that W atoms are located in distorted oxygen octahedra. The $\text{Zn}_x\text{Mg}_{1-x}\text{WO}_4$ luminescence spectra exhibited one broad band related to radiative decay of excitons self-trapped at WO_6 complexes. A weak dependence of the peak position of the luminescence band on the concentration of Zn and Mg substitution cations is in good agreement with the slight changes in the coordination of tungsten cations with an increase in the concentration of Zn atoms in the MgWO_4 structure.

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