New compound $Mg_3In_4V_6O_{24}$ and its physicochemical characteristic

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Abstract

A new compound of the formula $Mg_3In_4V_6O_{24}$ belonging to the family $M_3A_4V_6O_{24}$ [where M = metal(II), A = metal(III)] was obtained by the solid-state reaction method. The compound was synthesized by heating in air a mixture of $Mg_3(VO_4)_2$ and $InVO_4$ or MgV_2O_6 and In_2O_3 or In_2O_3 and V_2O_5, with a precursor of MgO. The new compound was characterized by XRD, SEM, IR, UV–Vis and DTA–TG methods. $Mg_3In_4V_6O_{24}$ was shown to crystallize in the triclinic system. Its unit cell parameters were calculated. The new compound is stable in air up to 1000 °C and is a semiconductor ($E_g \sim 3.3$ eV).

Keywords $Mg_3In_4V_6O_{24}$ · Ceramic compound · Solid-state reaction · Magnesium vanadate(V)

Introduction

Semiconductors have been for a long time fundamental to development of industry and are pivotal elements of many devices. Ceramic materials based on indium(III) orthovanadate(V) have been used for production of anodes because of their electrochemical stability and high electric capacity [1–3]. Recently, also $InVO_4$ admixtured with divalent metals has been found to be a suitable catalyst in the process of photocatalytic decomposition of water [4, 5].

The choice of a compound from the family $M_3A_4(VO_4)_6$ as the subject of the study was dictated first of all by the structure of this family compounds and interesting application possibilities of known vanadates(V) of divalent metals and indium(III) orthovanadates(V).

Literature data imply the existence of a series of compounds of the general formula $M_3Fe_4(VO_4)_6$ in the three-component metal oxide systems of $MO–Fe_2O_3–V_2O_5$ (M = Zn, Mg, Mn, Cu) [6–10]. What is more, also the compound of the formula $M_2FeV_3O_{11}$ has been reported to be formed in some of these systems [11–13]. The structures of $Mn_3Fe_4(VO_4)_6$ and $Cu_3Fe_4(VO_4)_6$ are known [7–9, 14]. These compounds crystallize in the triclinic system [7–9].

To the best of our knowledge, the ternary oxide system, i.e., $MgO–In_2O_3–V_2O_5$, has been previously examined to a very limited extend. According to the hitherto published scarce data on this system, as a result of the reaction of $Mg_2V_2O_7$ with $InVO_4$ in solid state, one compound $Mg_2InV_3O_{11}$ is formed [15]. The similarity of unit cell parameters of $Mg_2InV_3O_{11}$ and those of $Mg_2FeV_3O_{11}$ as well as the similarity of their IR spectra indicates that they are isostructural [15].

The ternary oxide systems $MO–In_2O_3–V_2O_5$, where M = Co, Cd, Cu, Ni, Pb, Sr have been already studied [16–22]. Results of the studies revealed the formation of a series of vanadates: $M_2InV_3O_{11}$ (M = Co, Pb, Sr) [17, 19, 22], but only in the system $CdO–In_2O_3–V_2O_5$ a compound of the formula $Cd_3In_4V_6O_{24}$ was formed [18]. The compound crystallizes in the monoclinic system, and it has not been isostructural with the family of compounds of the general formula $M_3A_4(VO_4)_6$.

The main aim of the presented work was to check whether in the system $Mg_3(VO_4)–InVO_4$ which is one of the cross-sections of the system $MgO–In_2O_3–V_2O_5$, any new compounds are formed and if so, to determine its some physicochemical properties.

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Experimental

The commercial reagents used for syntheses were:

- $3MgCO_3·Mg(OH)_2·3H_2O$ (a.p., POCh, Gliwice, Poland), as a precursor of MgO,

- In_2O_3 (a.p., Aldrich, Germany),
- V_2O_5 (a.p., Riedel-de Haën, Germany).

Also, $InVO_4$, MgV_2O_6 and $Mg_3(VO_4)_2$ were used as reagents in the conducted studies, and their syntheses are reported in [16, 23, 24]. The syntheses were carried out by the standard method of calcinations, described, e.g., in paper [25]. The reacting substances were weighed in appropriate portions, thoroughly homogenized by grinding, shaped into pellets and heated in cycles in a syllite furnace, in air. After each heating stage the samples were cooled together with the furnace to ambient temperature, ground and subjected to DTA and powder X-ray diffraction (XRD) measurements. After shaping them again into pellets, they were further heated. This procedure was repeated until equilibrium samples were obtained.

The types of phases occurring in particular samples were determined with the use of XRD method. Powder X-ray diffraction patterns of the samples were recorded with a PANalytical Empyrean II diffractometer in the 2Θ range of $10°$–$60°$ with graphite monochromator and $CuK\alpha_{1,2}$ radiation ($\lambda = 0.15418$ nm) within the continuous scanning mode with a step of $0.013°$, generator voltage 40 kV, tube current 30 mA and divergence slit $1.0°$. The phases were identified on the basis of X-ray characteristics contained in PDF cards [26] and found in the literature [15].

The DTA-Tg measurements were conducted by using a derivatograph Q-1500 of Paulik-Paulik-Erdey (MOM, Budapest, Hungary). The samples to be examined by this method, in portions of 500 mg, were placed in corundum crucibles. All measurements were performed in air, within the temperature range 20–1300 °C, at a heating rate of $10°$ min^{-1}.

The density of the new compound was determined using a gas pycnometer Ultrapyc 1200e (Quantachrome Instruments USA) using argon of 5 N purity as pycnometric gas.

The unit cell parameters were calculated with the aid of the program POWDER [27] belonging to the crystallographic program library X-ray System 70. Accurate positions of the diffraction lines were established by the internal standard method. The internal standard was α-Al_2O_3. The parameters of the unit cell were refined by the Refinement program of DHN/PDS package.

The infrared spectra were recorded in the wavenumber range 1100–250 cm^{-1} using a spectrometer SPECORD M 80 (Carl Zeiss, Jena, Germany). The measurements were performed by mixing the investigated sample with KBr at the mass ratio of 1:300.

A sample of the new compound was examined using scanning electron microscope (JSM-1600, Joel, Japan).
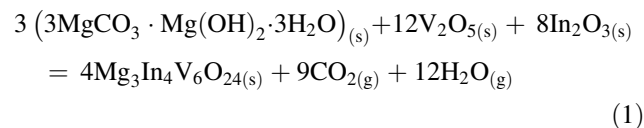
Optical absorption spectra of new phase were recorded at room temperature on UV–Vis–NIR JASCO-V670 spectrophotometer in the wavelength region of 180–1000 nm. The spectrophotometer was equipped with an integrating sphere assembly and $BaSO_4$ was a reference.
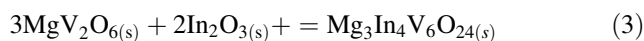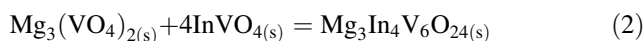
Results and discussion

Twelve samples were prepared from V_2O_5, In_2O_3 and $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ with compositions representing the whole range of the components concentrations of $Mg_3(VO_4)$–$InVO_4$ system. The compositions of all samples, in terms of the contents of $Mg_3(VO_4)_2$ and $InVO_4$, as well as oxides are shown in Table 1, which also gives the compositions of the initial mixtures of the samples, conditions of their heating and the phases detected after the last stage of heating.

Taking into account that the new set of XRD lines was recorded in the diffractogram of the sample whose initial mixture with V_2O_5 and In_2O_3 contained 37.50 mol % of MgO (Table 1, sample 10), the new compound was described by the stoichiometric formula $Mg_3In_4V_6O_{24}$. The diffraction pattern of the new compound contained, however, a set of diffraction lines at positions close to those of the lines characteristic of $Mg_3Fe_4V_6O_{24}$ [6]. It means that the new compound belongs to the family of the general formula $M_3A_4(VO_4)_6$ [where M = metal(II), A = metal(III)]. The new compound of the formula $Mg_3In_4V_6O_{24}$ was obtained as a result of the solid-state reaction:

$$3\left(3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O\right)_{(s)} + 12V_2O_{5(s)} + 8In_2O_{3(s)}$$
$$= 4Mg_3In_4V_6O_{24(s)} + 9CO_{2(g)} + 12H_2O_{(g)} \tag{1}$$

The new compound $Mg_3In_4V_6O_{24}$ was obtained also as a result of the solid-state reaction between $Mg_3(VO_4)_2$ and $InVO_4$ mixed at the molar ratio 1:4 or MgV_2O_6 and indium(III) oxide, mixed at the molar ratio 3:2, heated in the following stages: 700 °C(12 h) + 850 °C(12 h) + 950 °C(12 h × 2):

$$Mg_3(VO_4)_{2(s)} + 4InVO_{4(s)} = Mg_3In_4V_6O_{24(s)} \tag{2}$$

$$3MgV_2O_{6(s)} + 2In_2O_{3(s)} + = Mg_3In_4V_6O_{24(s)} \tag{3}$$

$Mg_3In_4V_6O_{24}$ has a light yellow color. Figure 1 presents fragments of the diffractogram of a mixture of MgV_2O_6 and In_2O_3 (Fig. 1b) as well as the diffractogram of the new compound $Mg_3In_4V_6O_{24}$ (Fig. 1a).

The powder diffractograms of $Mg_3In_4V_6O_{24}$ was subjected to indexation, and the results are displayed in Table 2. The parameters of its triclinic elementary cell are: $a = 0.6649(8)$ nm, $b = 0.8231(4)$ nm, $c = 1.0349(8)$ nm, $\alpha = 103.06°$, $\beta = 103.45°$ $\gamma = 102.75°$, $Z = 1$; the X-ray density is $d_{rtg} = 3.95$ g cm^{-3}, while the pycnometric density is $d_{pic} = 4.00 \pm 0.05$ g cm^{-3}. The results of this part

Table 1 Compositions of initial mixtures for Mg$_3$(VO$_4$)$_2$–InVO$_4$ system, their heating conditions and XRD analysis results for samples after their final heating stage

No.	Composition of initial mixture in terms of the compositions of the study system [mol %]		Composition of initial mixtures in terms of oxides percentage [mol %]			Heating conditions	Phase composition of samples after their final heating stage
	Mg$_3$(VO$_4$)$_2$	InVO$_4$	MgO	In$_2$O$_3$	V$_2$O$_5$		
1.	90.00	10.00	72.90	1.40	25.70	550 °C(12 h) + 650 °C(12 h) + 750 °C(12 h) + 850 °C(12 h) + 950 °C(12 h) + 1000 °C(12 h) + 1050 °C(2 × 12 h)	Mg$_3$(VO$_4$)$_2$, β-Mg$_2$V$_2$O$_7$, In$_2$O$_3$
2.	80.00	20.00	70.60	2.90	26.50		
3.	70.00	30.00	67.80	4.80	27.40		
4.	60.00	40.00	64.30	7.10	28.60		
5.	50.00	50.00	60.00	10.00	30.00		β-Mg$_2$V$_2$O$_7$, In$_2$O$_3$
6.	40.00	60.00	54.50	13.60	31.80	550 °C(12 h) + 650 °C(12 h) + 750 °C(12 h) + 850 °C(12 h) + 950 °C (2 × 12 h)	Mg$_2$InV$_3$O$_{11}$, β-Mg$_2$V$_2$O$_7$, In$_2$O$_3$
7.	33.33	66.67	50.00	16.67	33.33		Mg$_2$InV$_3$O$_{11}$, In$_2$O$_3$
8.	30.00	70.00	47.40	18.40	34.20		Mg$_2$InV$_3$O$_{11}$, In$_2$O$_3$
9.	25.00	75.00	42.86	21.43	35.71	550 °C(12 h) + 650 °C(12 h) + 750 °C(12 h) + 850 °C(2 × 12 h) 900 °C(2 × 12 h)	Mg$_2$InV$_3$O$_{11}$, In$_2$O$_3$, Mg$_3$In$_4$V$_6$O$_{24}$
10.	20.00	80.00	37.50	25.00	37.50		Mg$_3$In$_4$V$_6$O$_{24}$
11.	15.00	85.00	31.03	29.31	39.66		Mg$_3$In$_4$V$_6$O$_{24}$, InVO$_4$
12.	10.00	90.00	23.08	34.61	42.31		Mg$_3$In$_4$V$_6$O$_{24}$, InVO$_4$
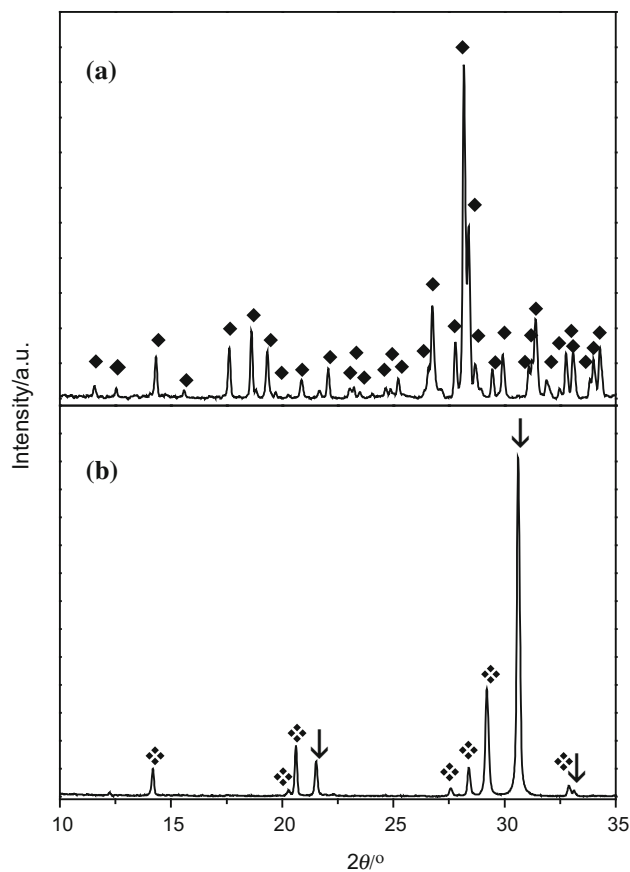
Fig. 1 X-ray diffraction patterns of **a** Mg$_3$In$_4$V$_6$O$_{24}$ (black diamond), **b** initial mixture of MgV$_2$O$_6$ (black diamond minus white x) and In$_2$O$_3$ (down arrow)

of the study revealed that Mg$_3$In$_4$V$_6$O$_{24}$ was isostructural with Mg$_3$Fe$_4$V$_6$O$_{24}$ [6]. A SEM image of Mg$_3$In$_4$V$_6$O$_{24}$ (Fig. 2) shows the presence of only one crystals' habit. The crystals of the new compound have different sizes, from larger ones of 4 μm to small ones of about 1 μm.
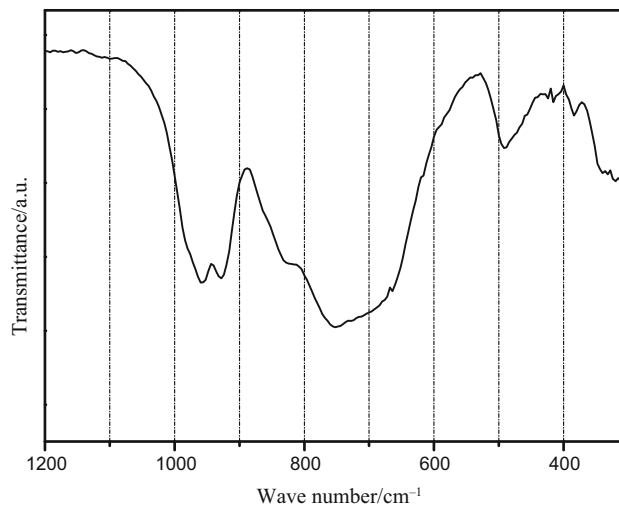
IR spectrum of Mg$_3$In$_4$V$_6$O$_{24}$ is shown in Fig. 3. The spectrum is very similar to that of Mg$_3$Fe$_4$V$_6$O$_{24}$ which is shown and described in [6]. Three ranges of absorption bands can be distinguished in the spectrum of Mg$_3$In$_4$V$_6$-O$_{24}$ (Fig. 3). The first one between 1050 and 880 cm^{-1} exhibits two distinct maxima occurring at 960 and 930 cm^{-1}. In this wavenumber range, the absorption is caused by the stretching vibrations of V–O bonds in the VO$_4$ tetrahedra [3, 28]. The second wide absorption band, in the wavenumber range 880–570 cm^{-1}, exhibits absorption maxima at 820 and 750 cm^{-1}. This band can be ascribed to stretching vibrations of the In–O bonds in InO$_6$ [29, 30]. In the last wavenumber range, i.e., 520–280 cm^{-1}, the band can be assigned to the stretching vibrations of Mg–O bonds in the MgO$_6$ octahedra [11, 31] as well as to the bending vibrations of the O–V–O bonds in the VO$_4$ tetrahedra. It cannot be excluded that the

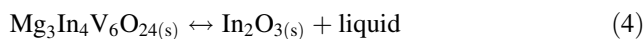**Table 2** Results of indexing powder diffractogram of $Mg_3In_4V_6O_{24}$

No.	d_{exp}/Å	d_{calc}/Å	h k l	I/I_0/%
1.	7.6650	7.6779	0 1 0	9.0
2.	7.0872	7.0985	0 − 1 1	2.5
3.	6.1930	6.1925	1 0 0	10.0
4.	5.6963	6.6880	1 − 1 0	2.3
5.	5.0401	5.0231	− 1 1 1	14.4
6.	4.7734	4.7800	1 − 1 1	8.7
7.	4.7300	4.7505	0 − 1 2	3.3
8.	4.6000	4.6201	1 0 1	17.4
9.	4.5149	4.5042	− 1 0 2	2.4
10.	4.2653	4.2573	1 1 0	6.6
11.	4.0316	3.9978	− 1 − 1 2	11.0
12.	3.8441	3.8389	0 2 0	7.0
13.	3.7898	3.7887	1 − 2 0	2.0
14.	3.6561	3.6609	1 − 2 1	1.5
15.	3.6143	3.6286	0 1 2	3.4
16.	3.5809	3.5758	1 − 1 2	3.4
17.	3.5349	3.5492	0 − 2 2	4.6
18.	3.3473	3.3483	1 0 2	9.8
19.	3.3363	3.3267	0 − 1 3	17.3
20.	3.2849	3.2743	− 1 0 3	1.0
21.	3.2147	3.2107	2 − 1 0	16.0
22.	3.1710	3.1840	− 1 − 1 3	100.0
23.	3.1473	3.1443	1 − 2 2	48.4
24.	3.1174	3.1130	− 1 − 2 1	11.1
25.	3.0400	3.0490	− 2 0 2	9.3
26.	2.9990	3.0119	− 1 − 2 2	13.2
27.	2.8731	2.8873	2 − 1 1	7.5
28.	2.8699	2.8711	− 1 1 3	11.5
29.	2.8499	2.8482	2 − 2 0	23.8

Fig. 3 IR spectra of $Mg_3In_4V_6O_{24}$
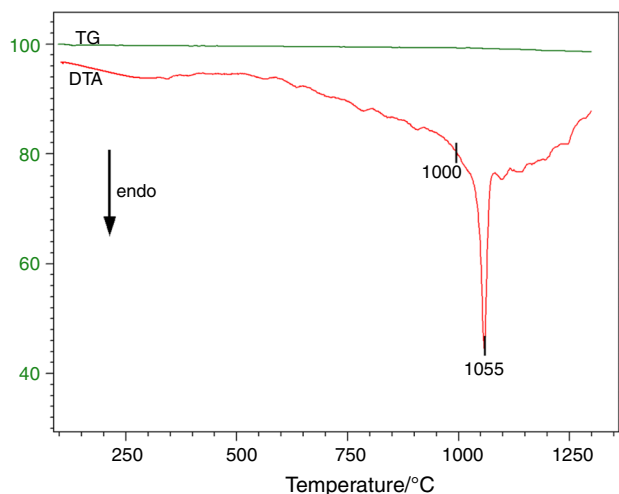
Fig. 4 DTA and TG curves of $Mg_3In_4V_6O_{24}$

The DTA curve of $Mg_3In_4V_6O_{24}$ up to 1350 °C reveals only one endothermic effect with its onset temperature equal to 1000 ± 5 °C (Fig. 4). In order to determine the kind of process beginning at this temperature, monophasic sample containing $Mg_3In_4V_6O_{24}$ was heated at 1050 °C for 1.5 h and subsequently cooled down rapidly to room temperature (at the moment of removing the sample from the furnace it was melted) and subjected to tests by XRD method. Phase composition analysis of this sample showed the presence of In_2O_3 (PDF card no. 06-0416) as well as a small amount of $Mg_3In_4V_6O_{24}$. The obtained results indicate that the endothermic effect recorded in the DTA curve is due to incongruent melting of $Mg_3In_4V_6O_{24}$ in accordance with the reaction:
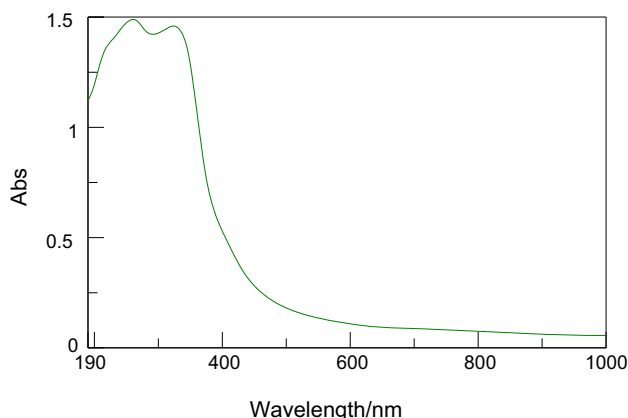
$$Mg_3In_4V_6O_{24(s)} \leftrightarrow In_2O_{3(s)} + liquid \tag{4}$$

Fig. 2 SEM image of $Mg_3In_4V_6O_{24}$

absorption in this wavenumber range has a combined nature.

Fig. 5 UV–Vis–NIR spectra of the $Mg_3In_4V_6O_{24}$

In the next step, the new compound $Mg_3In_4V_6O_{24}$ was investigated using UV–Vis–NIR method. Figure 5 shows the optical absorption spectra of $Mg_3In_4V_6O_{24}$ at room temperature recorded between 180 and 1000 nm. The spectrum permitted determination of the energy gap for the compound. The approximate value of E_g was found according to the Kubelka–Munk transformation. The energy gap determined in this way for $Mg_3In_4V_6O_{24}$ was $E_g \sim 3.3$ eV, which means that this compound is semiconductor.

Conclusions

The results obtained in the study have shown that in the ternary oxide system $MgO–In_2O_3–V_2O_5$ a new compound of the formula $Mg_3In_4V_6O_{24}$ is formed. This new compound was obtained as a result of the reaction in solid state between the oxides In_2O_3 and V_2O_5 with the precursor of magnesium oxide, i.e., with $3MgCO_3·Mg(OH)_2·3H_2O$, between $Mg_3(VO_4)_2$ and $InVO_4$ or MgV_2O_6 with In_2O_3. $Mg_3In_4V_6O_{24}$ crystallizes in the triclinic system with the unit cell parameters: $a = 0.6649(8)$ nm, $b = 0.8231(4)$ nm, $c = 1.0349(8)$ nm, $\alpha = 103.06°$, $\beta = 103.45°$ $\gamma = 102.75°$, $Z = 1$ and it is isostructural to $Mg_3Fe_4V_6O_{24}$. The new compound has a light yellow color. It melts incongruently at 1000 ± 5 °C with deposition of solid In_2O_3. On the basis of the energy gap calculated for $Mg_3In_4V_6O_{24}$ ($E_g \sim 3.3$ eV), it was classified as a semiconductor.

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