ISSN 1027-5495. Functional Materials, 31, No.4 (2024), p. 495-500
doi:http://dx.doi.org/10.15407/fm31.04.495

On luminescent and scintillation properties of $CsMgCl_3$:Eu^{2+} crystals

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Received July 15, 2024

The paper reports results of pure $CsMgCl_3$ and $CsMgCl_3$:xEu^{2+} (x = 0.5, 1 and 1.5 mol. %, in the charge) single crystals growth and investigations of their functional properties. The crystals were grown by Bridgman method and the entry ratio of Eu^{2+} into $CsMgCl_3$ was determined as 0.021, i.e. in all the europium-activated samples the concentration of the activator was at the level of admixtures. The photoluminescence spectra of $CsMgCl_3$:Eu^{2+} show that Eu enters in the crystal both as Eu^{2+} form (main) and Eu^{3+} one (trace amounts). The shape of the spectra are dependent on excitation wavelength (λ_{ex}): at λ_{ex}=350 nm the shape of the spectra corresponds to those of Eu^{2+} activated halides (the maxima in 470–490 nm range) and at λ_{ex}=275 nm the shape of spectra corresponds to those of Eu^{3+}-activated phosphors. X-ray luminescence spectra include two bands with the maxima at 460 nm proper for Eu^{2+}- activated halides and at 545 nm which could be ascribed to the distortions of $CsMgCl_3$ crystal lattice due to entering of the slightly isomorphic Eu^{2+}. The X-ray luminescence decay time is estimated within 0.8–0.9 μs. $CsMgCl_3$:Eu^{2+} crystals possess the light yield of *ca.* 150 % *vs.* BGO ($Bi_4Ge_3O_{12}$) and it is impossible to determine the concentration dependence since only traces of the activator are incorporated inside $CsMgCl_3$:Eu^{2+} crystals. The best energy resolution is 18 %.

Keywords: cesium chloride, magnesium chloride, europium bromide, entry ratio, luminescence, scintillation, light yield.

Люмінесцентні і сцинтиляційні властивості кристалів $CsMgCl_3$:Eu^{2+}. *В.Л.Чергинець, В.Д. Алексєєв, К.Ю. Брильова, Т.В. Пономаренко, О.Л. Ребров, Т.П. Реброва, О.В. Сорокін, О.В. Зеленська, О.І. Юрченко, В.В. Соловйов*

В роботі наведено результати, що стосуються росту і дослідження функціональних параметрів кристалів неактивованого $CsMgCl_3$ і твердих розчинів $CsMgCl_3$:xEu^{2+} (x = 0,5, 1 and 1,5 мол. %, в шихті). Вирощування проводили методом Бріджмена. Коефіцієнт входження Eu^{2+} в матрицю $CsMgCl_3$ дорівнює 0,021, тобто, дійсна концентрація активатора у кристалах знаходиться на рівні домішок. Вивчення фотолюмінесценції $CsMgCl_3$:Eu^{2+} показало, що європій входить у кристал в формах Eu^{2+} (основна) і Eu^{3+} (сліди). Форма емісійних спектрів залежить від довжини хвилі збудження (λ_{ex}): при λ_{ex}=350 nm форма спектрів відповідає таким для галогенідів, активованих Eu^{2+}, з максимумами в інтервалі 470-490 нм і при λ_{ex}=275 nm форма спектрів аналогічна Eu^{3+}-активованим фосфорам.

Спектри рентгенолюмінесценції містять дві смуги з максимумами при 460 нм, притаманними для Eu^{2+}-активованих галогенідів, і при 545 нм, що можуть бути приписані викривленням кристалічної гратки $CsMgCl_3$ внаслідок входження слабко ізоморфного іону Eu^{2+}. Час загасання рентгенолюмінесценції для досліджених зразків оцінено в межах 0,8–0,9 мкс. Кристали $CsMgCl_3$:Eu^{2+} характеризуються світловиходом приблизно 150 % по відношенню до BGO ($Bi_4Ge_3O_{12}$) при відсутності концентраційної залежності внаслідок незначної концентрації активатора. Найкраще енергетичне розділення дорівнює 18 %.

1. Introduction

The investigations of Eu^{2+}-doped complex compounds of $Me^IMe^{II}X_3$ composition (where Me^I alkali metal: Cs, Rb, K; Me^{II} alkaline earth metal: Ca, Sr, Ba and X halogen: Cl, Br, I) were performed in many works since the luminescence of Eu^{2+} (4f-5d transitions) gives the possibility to use corresponding solid solutions as scintillators [1], X-ray storage phosphors [2] etc.

Regarding the scintillation materials obtaining, the most favorable Me^I and Me^{II} are Cs which has no natural radioactive isotopes in contrast to K and Rb, and Sr, Ca, Ba (Sr^{2+} is perfectly isomorphic to Eu^{2+} and Ba^{2+} and Ca^{2+} are restrictedly isomorphic to Eu^{2+}) [3–8].

As for Me^IMgX_3-based materials, they are studied to considerably less extent. There are data on scintillation properties of undoped $CsMgCl_3$ material as cross-luminescence X-ray scintillator [9]. Luminescence properties of $CsMgCl_3$:0.5 mol.% Eu^{2+} material were studied in [10] and the authors made conclusion that the studied material can be a scintillator although the scintillation parameters such as light yield and energy resolution were not studied there.

The purpose of this work is to investigate the scintillation properties of $CsMgCl_3$:Eu^{2+} crystals with different content of Eu^{2+}.

2. Experimental

Reagents. CsCl (of extra pure quality), NH_4Cl and MgO (both of reagent quality) were used for the preparation of $CsMgCl_3$ charge. The charge was prepared by such a manner. Preliminary annealed MgO (2 h at 650 °C and 3 h at 720 °C) was dissolved at the heating in aqueous solution of NH_4Cl in such a proportion: 47.2 g of MgO, 188 g of NH_4Cl and 2 dm^3 of distilled water. After complete dissolution of MgO the solution was evaporated to the volume of 1 l and 197 g of CsCl was added to it. Then the solution was evaporated at 125 °C to the state of snow-like mass and dried under the vacuum up to complete removal of NH_4Cl. The remained powder was melted and was treated with CCl_4 vapor to remove oxygen-containing admixtures.

Anhydrous $EuBr_2$ (chemically pure) was used for the doping of the $CsMgCl_3$ matrix and it was added to the charge with the equivalent amount of CsCl.

Three compositions of charge were prepared for the growth of $CsMgCl_3$:Eu^{2+} crystals with the activator content of 0.5, 1 and 1.5 mol. %.

The growth procedure. The charge was placed in quartz ampoule of 12 mm diameter and of 500 mm height. Before the growth the ampoule with the charge was kept under vacuum of 1 Pa at 700 °C for 24 h.

The growth of the crystals was performed by Bridgman method in two-zone furnace, the difference of temperature between the zones was 80 °C, temperature gradient was 40 °C/cm, the rate of the dropping of the ampoule was 3.2 mm/h. The temperature at the diaphragm corresponded to the melting point of $CsMgCl_3$ – 612 °C. After the finishing of the ampoule broaching the furnace was cooled to room temperature during 72 h.

The cooled ampoule was placed in the glow box where it was broken down and the ingot was removed. The transparent part of the ingot was cut, polished and kept in polyethylene batch in the glow box. The cutting of the crystals was difficult since they are disposed to cracking. The samples presented cylinders of 6÷8 mm diameter and 1 mm height. The obtained samples were practically non-hygroscopic, therefore, they were not packed into hermetic containers.

Investigation of the obtained samples. Photoluminescence and luminescence excitation spectra were recorded with a Lumina spectrofluorimeter (ThermoScientific, USA).

A gamma-ray source of Cs-137 was used to measure the time characteristics of the samples. The scintillation setup for the time parameter measurement consists of a photomultiplier tube Hamamatsu R1307 and a digital oscilloscope Rigol DS 1302 CA (300 MHz, 2 GS/s, 8 bit), which is controlled by computer.

The light yield and the energy resolution of the obtained samples were determined by the method of comparison [11]. The measurements were recorded using a pulse processing

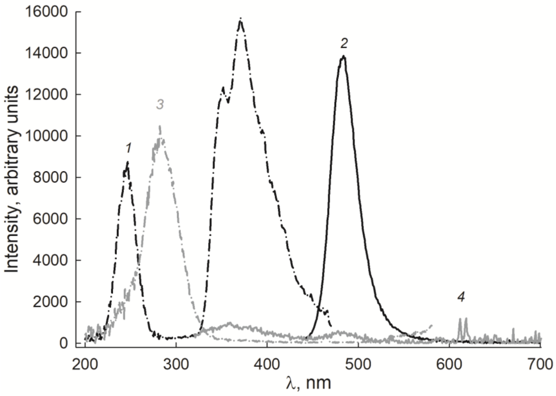

Fig. 1. The photoluminescence spectra of $CsMgCl_3$:1.5 mol.% Eu^{2+} crystal: 1 – excitation spectrum (λ_{em}=490 nm), 2 – emission spectrum (λ_{ex}=350 nm), 3 – excitation spectrum (λ_{em}= 614 nm), 4 – emission spectrum (λ_{ex}=275 nm)

chain consisting of an R1307 SU 0192 PMT (Hamamatsu, Japan), a charge-sensitive preamplifier BUS 2-95, a custom shaping amplifier and a multichannel analyzer AMA-03F. Relative light yield was determined by comparing the peak position (abscissa) of the grown crystals and that of a BGO ($Bi_4Ge_3O_{12}$) crystal (10,000 photons/MeV and energy resolution of 10 %). All measurements were done under the same conditions using the shaping time of 8 µs. The studied crystals were placed on the PMT window without optical contact. The error of the light yield and energy resolution measurements was less than 5 %.

3. Results and discussion

Let us consider an example of photoluminescence spectra of the obtained materials ($CsMgCl_3$:1.5 mol.% Eu^{2+}) presented in Fig.1.

The excitation spectrum 1 and the luminescence spectrum 2 are proper to the luminescence of Eu^{2+}, although there is a ‘gap’ between bands with the maxima at 250 and 350 nm. Additionally two other spectra are caused by the presence of Eu^{3+} traces that is common for Eu-activated chlorides: the traces of Eu^{3+} decompose slowly at temperatures above 700 °C and the process runs via a series of intermediate compounds of n $EuCl_2$·m $EuCl_3$ compositions [12].

As for the luminescence spectra, the maxima can be explained using the results of [13].

The emission at 613 nm (614 nm in the present work) corresponds to $^5D_2\rightarrow{}^7F_2$ transition of Eu^{3+}. The band with the maximum at 275 nm in the excitation spectrum was ascribed by the authors of [13] to the of charge transfer (CT) transitions from matrix to activator.

The X-ray luminescence spectra of the $CsMgCl_3$ matrix and obtained Eu^{2+}-doped materials are presented in Fig.2. As is seen, the integral intensity of the doped samples exceeds considerably that of the pure matrix. The X-ray luminescencespectra of all the doped samples are practically coincided and the main maxima of the main band lies in 470–490 nm range. We did not observe the directed shift of the maxima of X-ray luminescence band with the change of the activator concentration. This can be argument that the entry ratio (k_L) of both Eu^{2+} and Eu^{3+} in $CsMgCl_3$ matrix is too low since ionic radii of Eu^{2+} and Mg^{2+} differ essentially: 0.117 and 0.072 nm for the coordination number of 6, respectively [14]. The difference (38 % with respect to Eu^{2+}) is considerably higher than the predicted by the Goldschmidt rule value of 15 %. Indeed, the analysis of the crystal boule samples gives the value of k_L as 0.021. This means that after introducing 0.5 mol.% of Eu^{2+} we obtain crystal doped with *ca.* 0.01 mol.% of Eu^{2+} and for doping with 1 and 1.5 mol.% of the activator its actual concentrations in the

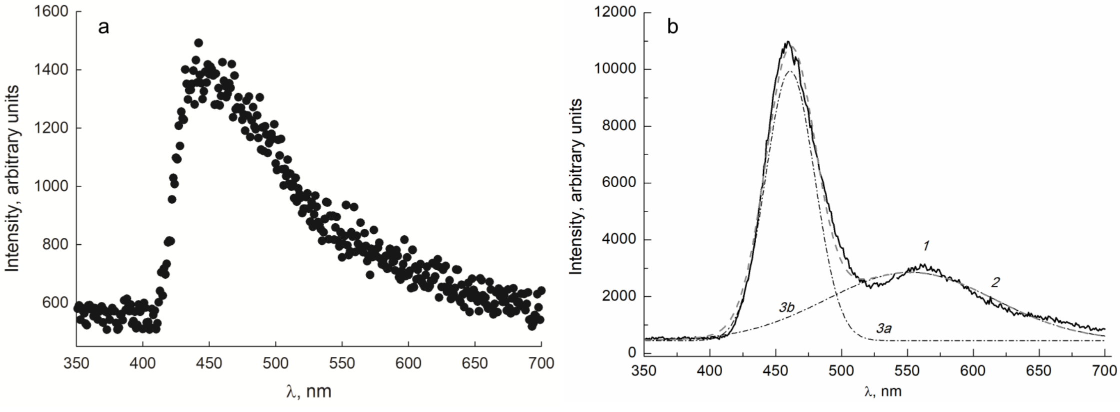

Fig. 2. The X-ray luminescence spectra of: a) pure $CsMgCl_3$, b) $CsMgCl_3$:1.5 mol.% Eu^{2+}: 1 – X-ray spectrum (solid line), 2a, 2b – components (dash-dot line), 3 – approximation line (grey line)

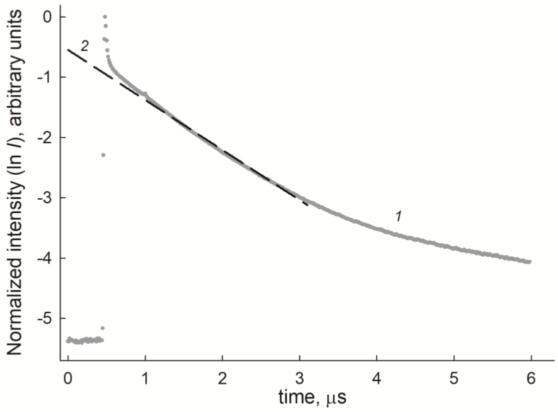

Fig. 3. The X-ray luminescence decay curve for the crystal of $CsMgCl_3$:1 mol.% Eu^{2+} composition: 1- the curve itself, 2 – the section chosen for the decay constant estimation.

grown crystals will be 0.02 and 0.03 mol.%, respectively. Such small actual concentrations of Eu^{2+} (near the level of admixtures) gives the possibility to understand the closeness of the luminescent characteristic of the grown doped materials.

As for the decomposition into the components of X-ray spectrum of the Eu^{2+}-doped sample, it can be described using two components with the maxima at *ca.* 460 nm and *ca.* 545 nm. The first component can be undoubtedly ascribed to Eu^{2+} and the nature of the second one is unclear. Eu^{3+} luminescence results in appearance of three specific groups of bands: in the 580–590 nm range, 610–630 nm range and 680 nm range. The maximum positions do not coincide with that of any of these groups. The component with the maximum at 545 nm can be caused by distortion of the crystal lattice of the matrix due to the entering of Eu^{2+} similarly to the data of [15] where the similar maxima arose at the entering of Ba^{2+} in SrI_2 matrix at the growing of BaI_2-SrI_2 crystal doped with Eu^{2+}.

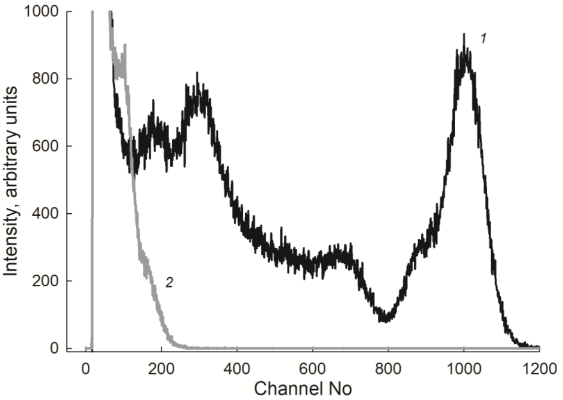

Fig. 4. Pulse height spectra of the grown crystals vs. BGO ($Bi_4Ge_3O_{12}$): a) 1 – BGO, 2 – $CsMgCl_3$ matrix; b) $CsMgCl_3$ doped with Eu^{2+}: 1 – 0.5 %, 2 – 1 %, 3 – 1.5 %.

To estimate the light yield of the obtained crystals the value of the scintillation light decay is required. An example of the curve of the X-ray luminescence decay for Eu^{2+} doped material is presented in Fig.3.

The decay times were estimated as 0.93, 0.83 and 0.91 for $CsMgCl_3$:Eu^{2+} samples doped with 0.5, 1 and 1.5 % of activator respectively. The values of the decay constants give the possibility to choose the time of life collection as 8 μs.

Let us consider results of the scintillation properties investigations of the obtained crystals. The pulse-height spectra of the grown crystals of undoped $CsMgCl_3$ and $CsMgCl_3$:Eu^{2+} vs. BGO ($Bi_4Ge_3O_{12}$) etalon with the light yield of ca. 10000 photons per MeV (the abscissa of the photopeak is 1011) are presented in Fig.4.

Table 1. The data necessary for the calculation of relative light yield (L, %) and energy resolution (R, %) of undoped and Eu^{2+}-doped $CsMgCl_3$ crystals, the time of the light collection is 8 μs.

Crystal	Eu^{2+} concentration, mol.%	L, %		R, %
		Channel	LY *vs.* BGO	
BGO		1011	100.0	11.50
$CsMgCl_3$ matrix	-	170	16.8	–
$CsMgCl_3$:Eu^{2+}	0.5 (0.01 in the crystal)	1470	145.4	–
$CsMgCl_3$:Eu^{2+} (1)	1.0 (0.02 in the crystal)	1489	147.3	18.5
$CsMgCl_3$:Eu^{2+} (2)	1.0 (0.02 in the crystal)	1557	154.0	–
$CsMgCl_3$:Eu^{2+} (3)	1.0 (0.02 in the crystal)	1440	142.4	24.6
$CsMgCl_3$:Eu^{2+}	1.5 (0.03 in the crystal)	1459	144.3	—

The numeric data are presented in Table 1.

The presented data show that the light yield of Eu^{2+}-doped $CsMgCl_3$ single crystals achieves 150 % *vs*. BGO at the best energy resolution of 18 % (measured without pedestal). Comparing these results with those obtained for $Cs_3ZnCl_5:Eu^{2+}$ [16] it should be noted that the light yield of $Cs_3ZnCl_5:Eu^{2+}$ is equal to only 5.8 % against BGO.

So, the results of both studies lead to conclusion that for Eu^{2+}-doped materials the worsening of M^{II}-Eu^{2+} degree of isomorphism results in worsening of the light yield (comparing with Eu-doped $CsCaCl_3$ or $CsSrCl_3$) if the difference of the electronegativity is small (in the Mg-Eu case [17]).

In the case when M^{II}-Eu^{2+} not only differ in ionic radii but also essentially differ in the electronegativity (1.65 for Zn vs. 1.2 for Eu) this leads to the absence of excitation energy transfer from the matrix to the activator.

4. Conclusions

The crystals of undoped $CsMgCl_3$ and $CsMgCl_3:Eu^{2+}$ with Eu^{2+} concentration in the growth charge of 0.5, 1 and 1.5 mol. % were grown by Bridgman method. The entry ratio of Eu^{2+} into $CsMgCl_3$ was determined as 0.021 that allowed to calculate the actual concentration of the activator in the grown crystal as *ca.* 0.01, 0.02 and 0.03 mol. %, respectively.

The photoluminescence spectra of $CsMgCl_3:Eu^{2+}$ showed that Eu enters in the crystal in forms of Eu^{2+} (main) and Eu^{3+} (traces). The shapes of the spectra are dependent on excitation wavelength (λ_{ex}): at λ_{ex}=350 nm the shapes of the spectrum corresponds to those of Eu^{2+} activated halides with the maxima in 470-490 nm range and at λ_{ex}=275 nm the shapes of spectra corresponds to those of Eu^{3+}-activated phosphors with the corresponding maxima.

X-ray luminescence spectra of $CsMgCl_3:Eu^{2+}$ include two bands with the maxima at 460 nm proper for Eu^{2+}- activated halides and at 545 nm which could be ascribed to the distortions of $CsMgCl_3$ crystal lattice due to entering of the slightly isomorphic Eu^{2+}.

The measurements of the light yield showed that all the Eu^{2+} doped samples possessed the light yield of *ca.* 150 % *vs.* BGO ($Bi_4Ge_3O_{12}$) and the concentration dependence of the light yield was not observed due to negligible actual concentrations of activator in the obtained $CsMgCl_3:Eu^{2+}$ crystals. The best energy resolution is 18 %.

References

1. K. Yang, M. Zhuravleva, C.L. Melcher, *Phys. Status Solidi RRL*, **5**(1), 43 (2011). https://doi.org/10.1002/pssr.201004434.
2. M. Suta, P. Larsen, F. Lavoie-Cardinal, C. Wickleder, *J. Lumin*, **149**(1), 35 (2014). https://doi.org/10.1016/j.jlumin.2013.12.040.
3. M. Zhuravleva, B. Blalock, K. Yang, M. Koschan, C. L. Melcher, *J. Cryst. Growth*, **352**(1), 115 (2012). https://doi.org/10.1016/j.jcrysgro.2012.02.025.
4. V.L. Cherginets, A.Yu. Grippa, T.P. Rebrova, Yu.N. Datsko, T.V. Ponomarenko, N.V. Rebrova, N.N. Kosinov, O.A. Tarasenko, Yu.I. Dolzhenko, O.V. Zelenskaya, *Funct. Mater.*, **19** (2), 187-191 (2012).
5. M. Koshimizu, N. Yahaba, R. Haruki, F. Nishikido, S. Kishimoto, K. *Asai, Opt. Mater.*, **36**, 1930 (2014). https://doi.org/10.1016/j.optmat.2014.04.004.
6. V. L. Cherginets, N. V. Rebrova, A. Yu. Grippa, Yu. N.Datsko, T. V.Ponomarenko, V. Yu. Pedash, N. N. Kosinov, V. A. Tarasov, O.V. Zelenskaya, I.M. Zenya, A.V. Lopin, *Mater. Chem.Phys.*, **143**(3), 1296 (2014). https://doi.org/10.1016/j.matchemphys.2013.11.037.
7. M. Zhuravleva, B. Blalock, K. Yang, M. Koschan, C.L. Melcher, *J. Cryst. Growth.*, **352**(1), 115 (2012). https://doi.org/10.1016/j.jcrysgro.2012.02.025.
8. N. V. Rebrova, A. Yu. Grippa, A. S. Pushak, T. E. Gorbacheva, V. Yu.Pedash, O. G. Viagin, V. L. Cherginets, V. A. Tarasov, V. V. Vistovskyy, A.P. Vas'kiv, S.V. Myagkota, J. *Cryst. Growth*, **466**, 39 (2017). https://doi.org/10.1016/j.jcrysgro.2017.03.016.
9. G. Shwetha, V. Kanchana, G. Vaitheeswaran, *J. Solid State Chem.*, **227**, 110 (2015). https://doi.org/10.1016/j.jssc.2015.03.024
10. M. Suta, F. Lavoie-Cardinal, J. Olchowka, K. Wickleder, *Phys. Rev. Appl.*, **9**, 064024 (2018). https://doi.org/10.1103/PhysRevApplied.9.064024.
11. Sysoeva E.; Tarasov, V.; Zelenskaya, O., *Nucl. Instr. Meth. Phys. Res. A.*, **486** (1-2), 67 (2002). https://doi.org/10.1016/S0168-9002(02)00676-9.
12. Oppermann H., Hennig C., *Z. Anorg. Allg. Chem.*, **626**, 450 (2000). DOI: 10.1002/(SICI)1521-3749(200002)626:2<450::AID-ZAAC450>3.0.CO;2-M.
13. Mua Z., Song E., Zhu D., Feng J., Yang Y., *Displays*, **43**, 18 (2016). DOI: https://doi.org/10.1016/j.displa.2016.04.001.
14. http://abulafia.mt.ic.ac.uk/shannon/radius.php (Last visited July 8 2024).

15. Rebrova N.V., Cherginets V.L., Kosinov N.N., Ponomarenko T.V., Rebrova T.P., Vjunnik I. N., Zelenskaya O.V., *Funct. Mater.*, **16**(4) 501 (2009).
16. Cherginets V., Rebrov O., Rebrova T., Ponomarenko T., Boyarintseva Ia., Zelenskaya O., Yurchenko O. Growth and investigation of functional parameters of Cs_3ZnCl_5-based scintillators, Abstr. XXI Int. Conf. Inorg. Chem. Ukraine 2024, 3-6.06.2024, Uzhhorod. P.84.
17. https://sciencenotes.org/list-of-electronegativity-values-of-the-elements/ (Last visited July 8 2024).