DOI 10.31489/2022PH1/117-122

UDC 538.9

N.A. Mazhenov[1], Z.R. Syzdykova[*1]

[1]*Karaganda Technical University, Kazakhstan*
[*]*E-mail: zika_0885@mail.ru*

The formation of the mixed anions $PAsO_7$ in solid solutions $Mg_2P_2O_7 — Mg_2As_2O_7$

The article presents structural features at formation of solid solutions of the isostructural $Mg_2P_2O_7$ and $Mg_2As_2O_7$ connections. In these compounds, complex $P_2O_7^{4-}$ anions, $As_2O_2^{4-}$, as well as the formation of complex $PAsO_7^{4}$ anions, is not natural. The formation of solid solutions is confirmed by the linear dependence of x-ray debaegram and optical refractive indices, depending on the concentration of P/As. In the article, phosphates are involved in energy processes in cells. For the first time, the formation of mixed anions in polyphosphates has been proven. The oscillatory spectra of pyro anions have intervals of localization of terminal and bridging groups of atoms that have no intersection regions. Strip at 662–670 cm^{-1} (between structures from P: As=0.8:0.2 to 0.1–0.9), located between v_sPOP frequency in $_\beta$ — $Mg_2P_2O_7$ at 737 cm^{-1} and the frequencies about 550 cm^{-1} characteristic of fluctuations of v_sAsOAs in alkaline pyroarsenates, is interpreted as a strip of fluctuations of v_sPOAs of the mixed $PAsO_7$ ions. In the area, the strip at 925–902 cm^{-1} is located between frequencies of fluctuations of v_{as}POP and v_{as}AsOAs. The fluctuations of mastic group P-O found in ranges of infrared absorption allow establishing knowledge of the adjacent anions $(PAsO_7)^{4-}$ that it is possible to confirm with quantum-chemical calculations in the subsequent.

Keywords: pyrophosphate, pyroarsenate, debaegram, empirical, refractometric, valence-force field, linear approximation.

Introduction

Solid solutions of Mg_2 (P, $As)_2O_7$ with molar contents of pyrophosphate and pyroarsenate varying in 10 % were obtained by thermal decomposition of the corresponding mixtures of $MgHPO_4$ and $MgHAsO_4$ at 900^{0}C and characterized by refractometric analysis. The obtained solid solutions are colorless, the refractive indices change linearly, with a composition from 1.585 for $Mg_2As_2O_7$ to 1.680 for α-$Mg_2P_2O_7$ (Figure 1). Debaegrams are characterized by clear reflexes, and the values of interplane distances change smoothly as the composition changes.

IR spectra of solid solutions (Specord-75 spectrometer, samples with a constant molar concentration for all compositions obtained by pressing powders with KVG) are shown in Figure 2. The assignment of frequencies in the $Mg_2P_2O_7$ spectrum has already been discussed in the literature [1, 2]. The spectrum of $Mg_2As_2O_7$ resembles that of isostructuredtorteuitite $Sc_2Si_2O_7$ [3] and the assignment of the frequencies of valence oscillations of a complex anion can be carried out by analogy with interpretating the latter spectrum (Table 1).

The structures of $Mg_2As_2O_7$ and α-$Mg_2P_2O_7$ are not identical: if the first is structurally quite similar to thortveitite [4], the second differs from it by “curved” groups of P_2O_7 ($P2_1/c$, Z=2), but already under 68^{0}C undergoes an α_β transformation, and the structure of the type of thortveitite for the $_\beta$ — form may be carried out by statistical averaging over the configurations of P_2O_7 groups, each of which separately may remain non — centrosymmetric [5]. Judging by the sharp broadening of the bands characteristic of the спектра-$Mg_2P_2O_7$ spectrum, it is possible to switch to this type of structure from α-$Mg_2P_2O_7$ already at 10 % arsenate content in solid solution (Figure 2).

In the spectra of solid solutions, it is possible to distinguish only three bands that have no analogues in the spectra of the extreme members of the series: 925–902, 670–662, 625–623 cm^{-1}. The last of the bands is selected (despite the presence of a band with the same frequency in the spectrum of α-$Mg_2P_2O_7$, table) based on the dependence of its intensity on the concentration of the solid solution: this band appears when adding 10 % phosphate to the arsenate, and already with the composition of P: As=0.3:0.7 practically disappears: the band $_\beta$-$Mg_2P_2O_7$ with the same frequency appears at P: As=0.5:0.5 and then monotonously increases.

The band at 662–670 cm^{-1} (in the range of compositions from P: As=0.8:0.2 to 0.1–0.9), located between the v_sPOP frequency at $Mg_2P_2O_7$ at 737 cm^{-1} and frequencies of the order of 550 cm^{-1} characteristic of v_sAsOAs oscillations in alkaline pyroarsenates [6], is interpreted as the v_sAsOAs oscillation band of mixed

$RAsO_7$ ions. In the area between the vibration frequencies of v_sPOP and v_sAsOAs, the band at 925–902 cm^{-1} is located, which can be attributed to the antisymmetric oscillation of the ROAs bridge. It should be noted that the lower value of the frequency v_sAs 829 cm^{-1}, obtained earlier when calculating the oscillations of the $PAsO_7$ ion [7], can be explained by the excessively small value of the angle ROAs (120^0) adopted for the calculation, and by the rather low force constants of the P-O (As) and As-O (P) bonds.

Table 1

Anion vibration frequencies in the IR spectra of solid solutions$Mg_2P_2O_7$ _ $Mg_2As_2O_7$

Frequency assignment		Frequencies of absorption maxima in the IR spectrum (cm^{-1}) at various phosphorus contents							
Type of anion	Waveform	1,0	0,9	0,8	0,6	0,4	0,2	0,1	0,0
I, III	$v_{as}PO_3$	1206	1210	1210	1203	1200	1190	1190	1006
I, III	$v_{as}PO_3$	1185	1115	1108	1100	1090	1089	1089	900
		1136	1055	1050	1043	1042	1042	1000	879
II	$v_{as}AsOAs$	1101	1005	1003	1003	1002	1000	880	845
I	$v_{as}POP$	1080	985	970	975	975	910	845	820
III	$v_{as}POAs$	1040	975	921	916	902	883	623	505
II, III	$v_{as}AsO_3$	990	925	732	850	850	845	592	440
		970	735	620	727	665	660	505	406
II, III	$v_{as}AsO_3$	737	620	588	665	590	625	440	405
I	$v_{as}POP$	620	588	550	624	508	590	405	403
III	$v_{as}POAs$	600	550	510	590	402	505	402	405
II	$v_{as}AsOAs$	588	510	440	550	400	405	400	400

*I — P_2O_7; II — As_2O_7; III — $PAsO_7$.

Thus, the appearance of vibration bands v_sPOAs and $v_{as}POAs$ of mixed $PAsO_7$ ions convincingly proves their formation in solid solution.

It should be noted that the band at 737–727 cm^{-1} remains in the spectra of solid solutions up to the composition P: As=0.5:0.5, indicating the preservation of the curved configuration of pyrophosphate groups. The presence of this band in the spectra of compositions characterized, apparently, by the structure of the type β-$Mg_2P_2O_7$ allows us to presumably explain the appearance of a band about 625 cm^{-1} in the spectra of solid solutions with P contents from 10 to 20 % by activating the v_sAsOAs oscillation due to a violation of the statistical centrosymmetry of the $Mg_2As_2O_7$ structure. Thus, we can assume a curved configuration of the As_2O_7 groups individually and in pure $Mg_2As_2O_7$. Similarly, if the oscillation band of vAs-As is correctly identified in the spectra of solid solutions, then the comparison of its frequency with the frequency of vAs-As indicates (taking into account the results of calculating the oscillations of the $RAsO_7$ ion [8]) rather the curved shape of the p-O-As bridge in this ion, i.e. the uniformity of the structure of complex anions of any composition in the considered series of solid solutions.

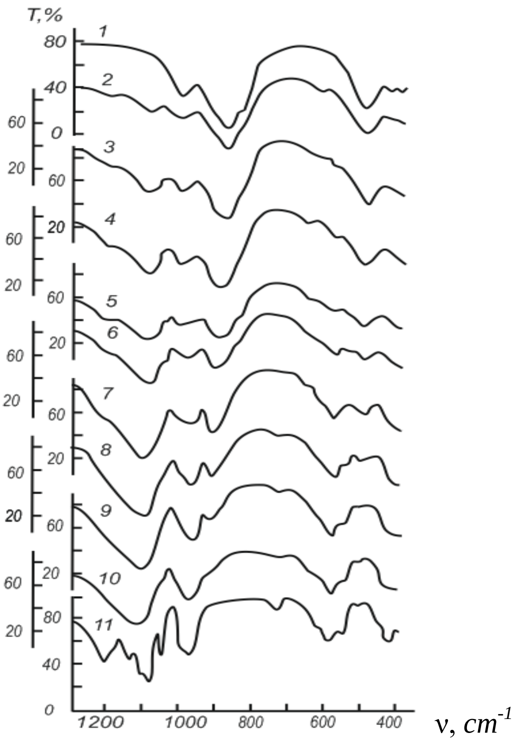

Figure 1. Change in light refraction index N of solid solution $Mg_2(P, As)_2O_7$

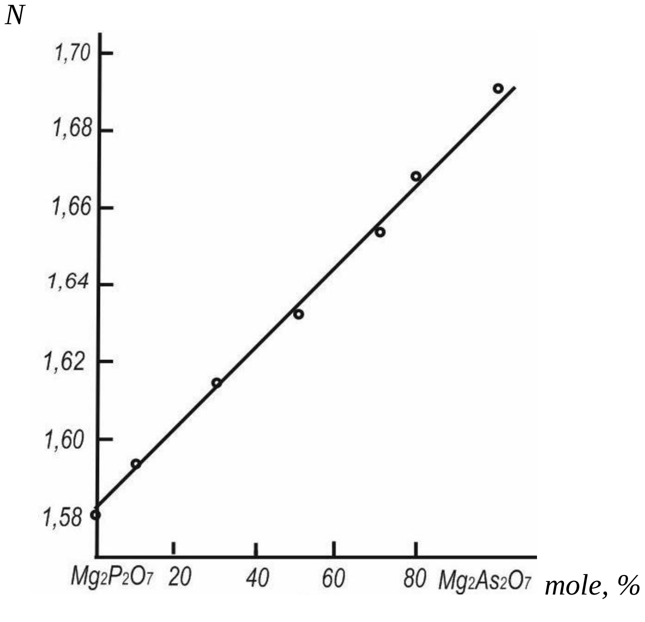

Figure 2. IR spectra of solid solutions in system $Mg_2P_2O_7$ — $Mg_2As_2O_7$

Relation P: As: 1–0,0:1,0; 2–0,1:0,9; 3–0,2:0,8; 4–0,3:0,7; 5–0,4:0,6; 6–0,5:0,5; 7–0,6:0,4; 8–0,7:0,3; 9–0,8:0,2; 10–0,9:0,1; 11–1,0:0,0

Oscillations of the crystal lattice and deformation properties of the crystal.

The structure of an ideal crystal with N atoms in a unit cell is described by specifying vectors a_1, a_2, a_3 that determine the size and shape of the unit cell, and N vectors r_i that specify the coordinates of the atoms in the cell. Homogeneous deformations are described by changes in the vectors and the increments of the vectors Δr_i form a basis convenient for describing the limit oscillations (long-wave) and the internal structural relaxation of the lattice caused by its homogeneous deformations under external influences.

For compactness of formula writing, generalized vectors are used. So, it is convenient to combine the coordinates of atoms in a cell into a 3N-dimensional vector r = (x_1, y_1, z_1, ...z_n), and describe small shifts of sub-lattices with the vector Δr.

In the valence-force field (VFF) model, so-called natural coordinates defined as small increments of valence bond lengths, angle values there between, etc. are selected as a coordinate basis for setting a potential function and for describing deformation. The whole set of translational — non-equivalent natural coordinates q_n , is described by the generalized vector $q_n = \left(q_1, q_2, ..., q_M\right)$. The dimension of this vector M is generally chosen to be greater than 3N, allowing the proposed nature of interatomic interactions in the VFF model and taking into account the symmetry properties of natural coordinates with respect to crystal factor-group operations.

The calculation of normal coordinates in the VFF model is based on the linear approximation between q and Δr, described using the matrix B:

$$q = B\Delta r$$

The potential energy of the lattice in the valence-force field model in natural coordinates is expressed as a quadratic form:

The elements of the matrix F are force constants-fitting parameters for solving the inverse spectral problem.

The elements of which determine the relative amplitudes of changes in individual natural coordinates in different normal oscillations.

From the above definitions, the relationship between the force constants, frequencies, and forms of normal oscillations follows,

$$\Lambda = Q_l^{+} F Q_l,$$

which is necessary for the analysis of various contributions to the elasticity of normal vibrations.

The elastic constants of the crystal are described by a matrix C (6 x 6), whose elements are defined as the second derivatives of the energy density for various components of the vector of homogeneous deformations: where Ω is the volume of the unit cell.

The expression for elastic constants can be obtained by directly differentiating the expression for energy if we introduce the concept of the uniform deformation form described in the linear approximation by the Q_u matrix:

$$q = Q_u u.$$

To calculate IR intensities and piezoelectric constants, information is needed about the change in the polarization of the crystal under various lattice deformations. To do this, depending on the nature of the structure of the object, different model representations are used (rigid or deformable ions, variable charges on atoms, a valence-optical scheme, etc.), which describe the dependence of the dipole moment of the cell P on the deformations Δr and u.

Conclusions

Structural features at formation of solid solutions of the isostructural $Mg_2P_2O_7$ and $Mg_2As_2O_7$ connections are considered. In these compounds, there are complex $P_2O_7^{4-}$ anions, $As_2O_2^{4-}$, as well as the formation of complex $PAsO_7^{4-}$ anions, is not natural.

Infrared absorption spectra depend on the composition of P/As. For removal of IR spectrums of solid $Mg_2P_2O_7$ solutions — $Mg_2As_2O_7$ was used the modern Specord-75 spectrophotometer, samples with constant molar concentration for all structures are received by pressing of powders with KBR. The oscillatory spectra of pyro anions have intervals of localization of terminal and bridging groups of atoms that have no intersection regions. Strip at 662–670 cm^{-1} (in the range of structures from P: As=0,8:0,2 to 0,1–0,9), located between v_sPOP frequency in β — $Mg_2P_2O_7$ at 737 cm^{-1} and the frequencies about 550 cm^{-1} characteristic of fluctuations of v_sAsOAs in alkaline pyroarsenates, is interpreted as a strip of fluctuations of v_sPOAs of the mixed $PAsO_7$ ions. The strip at 925–902 cm^{-1} is located between frequencies of fluctuations of v_{as}POP and v_{as}AsOAs. The fluctuations of mastic groups P-O found in ranges of infrared absorption — As allow to establish reliably education the adjacent anions $(PAsO_7)^4$-that it is possible to confirm with quantum-chemical calculations in the subsequent.

In the $Mg_2P_2O_7$-$Mg_2As_2O_7$ system, a continuous series of solid solutions is formed, whose IR spectra indicate the presence of mixed $[RAsO_7]^{4-}$ions, characterized by a nonlinear configuration of P-O-As bridges.

References

1 SuFuhai, Ma Balei. Luminescence temperature and pressure studies of Zn_2SiO_4 doped by with Mn^{3+} and Eu^{3+} ions / Fuhai Su, Balei Ma // Lett. Journal Luminescence, 2006. — Vol. 116, No. 1–2. — P. 117–126.

2 Лазарев А.Н. Колебательные спектры и строение силикатов / А.Н. Лазарев. — Л.: Наука, 2001 — 348 с.

3 Sheludko V.I. Post-annealing green luminescence of sulphate crystals / V.I. Sheludko, S.G. Nedilko, V.V. Bojko // Lett. Functional Materials, 2003. — 10, 1. — P. 93–97.

4 Wang J. The atteanuation peak and elastic anomaly of $LiKSO_4$ crystal under low temperature / J.Wang, R.Wang, L. Zhang., F.Li, S.Lin // Lett. Journal Low Temperature Physics, 2002. — Vol. 11, 2. — P. 135–140.

5 Лазарев А.Н. Колебательные спектры сложных окислов / А.Н. Лазарев, А.П. Миргородский, И.С. Игнатьев. — Л.: Наука, 2000. — 296 с.

6 Alybakov A.A. Optical absortion and EPR spectra of Cu^{2+} ions in $LiKSO_4$ single crystals / A.A. Alybakov, V.A. Gubanova, K. Kudabaev, K. Sharsheev // Lett. Physica Status Solidi (b), 1988. — Vol. 146. — P. 135–139.

7 Маженов Н.А. Расчет колебаний иона $[(P, As)2O_7]$ методом нормальных координат / Н.А. Маженов, О.А. Маженова, З.М. Мулдахметов // Изв. АН СССР. Неорганические материалы. — 2002. — Т. 13, № 2. — С. 391, 392.

8 Kityk I.V. Band energy calculation and optical constans of K_2SO_4 single crustals/ I.V. Kityk, B.V. Andrievckii, V.O. Yuvchenco // Lett. Physica Status Solidi (b), 1994. — Vol. 182. — P. 79–83.

Н.А. Маженов, З.Р. Сыздыкова

$Mg_2P_2O_7$ — $Mg_2As_2O_7$ қатты ерітінділерде $PASO_7$ аралас аниондарының пайда болуы

Мақалада $Mg_2P_2O_7$ және $Mg_2As_2O_7$ изоқұрылымдық қосылыстарының қатты ерітінділерінің түзілуіндегі құрылымдық ерекшеліктер қарастырылған. Олардың құрамында $P_2O_7^{4-}$ мен $As_2O_2^{4}$ күрделі аниондар бар, ал $PAsO_7^{4}$ аниондарының түзілуі табиғи емес. Қатты ерітінділердің түзілуі P/As концентрациясының функциясы ретінде рентгендік дебаеграммалардың және оптикалық сыну көрсеткіштерінің сызықтық тәуелділігімен расталады. Мақаланың өзіндік ерекшелігі мынада: фосфаттардың жасушалардағы энергетикалық процестерге қатысуы. Авторлар алғаш рет полифосфаттарда аралас аниондардың түзілуін дәлелдеген. Пироаниондардың тербелмелі спектрлерінде қиылысу аймақтары жоқ атомдардың соңғы және көпірлік топтарының локализация аралықтары болады. 662–670 см$^{-1}$ жолағы (аралық құрамы P: As=0,8:0,2-ден 0,1–0,9-ға дейін) v_sPOP в $_{\beta}$–$Mg_2P_2O_7$ у 737см$^{-1}$ жиілік аралығында және 550 см$^{-1}$ жиілік ретімен орналасқан, сілтілі пироарсенаттардағы v_sAsOAs тербелістеріне тән, $PAsO_7$ аралас иондарының v_sPOAs тербелістерінің жолағы ретінде түсіндіріледі. v_{as}POP және v_{as}AsOAs тербеліс жиіліктері арасындағы ауданда 925–902см$^{-1}$ жолағы орналасқан. Инфрақызыл сіңіру спектрлерінде анықталған P—O—As көпірлік топтарының тербелістері іргелес аниондардың $(PAsO_7)^{4-}$ түзілуін сенімді түрде анықтауға мүмкіндік береді, оны кейіннен кванттық химиялық есептеулермен растауға болады.

Кілт сөздер: пирофосфат, пироарсенат, дебаеграмма, эмпирикалық, рефрактометриялық, валенттік-күш өрісі, сызықтық жуықтау.

Н.А. Маженов, З.Р. Сыздыкова

Образование смешанных анионов в $PAsO_7$ в твердых растворах $Mg_2P_2O_7$ — $Mg_2As_2O_7$

В статье рассмотрены структурные особенности приобразования твердых растворов изоструктурных соединений $Mg_2P_2O_7$ и $Mg_2As_2O_7$. В них существуют сложные анионы $P_2O_7^{4-}$, $As_2O_2^{4-}$, и образование сложных анионов $PAsO_7^{4-}$ не является закономерным. Образование твердых растворов подтверждено линейной зависимостью рентгеновских дебаеграмм и оптических коэффициентов преломления в зависимости от концентрации P/As. Оригинальность статьи заключается в том, что фосфаты участвуют в энергетических процессах в клетках. Авторами впервые доказано образование смешанных анионов в полифосфатах. Колебательные спектры пироанионов имеют интервалы локализации концевых и мостиковых групп атомов, которые не имеют областей пересечения. Полоса у 662–670см$^{-1}$ (в интервале составов от P: As=0,8:0,2 до 0,1–0,9), расположенная между частотой v_sPOP в $_{\beta}$–$Mg_2P_2O_7$ у 737см$^{-1}$ и частотами порядка 550 см$^{-1}$, характерными для колебаний v_sAsOAs в щелочных пироарсенатах, с оче-

видностью интерпретируется как полоса колебаний v_sPOAs смешанных ионов $PAsO_7$. В области между частотами колебаний v_{as}POP и v_{as}AsOAs расположена полоса у 925–902 $см^{-1}$. Обнаруженные в спектрах инфракрасного поглощения колебания мостиковых групп P–O–As позволяют установить надежно образование смеженных анионов $(PAsO_7)^{4-}$, что можно подтвердить квантовохимическими расчетами в последующем.

Ключевые слова: пирофосфат, пироарсенат, дебаеграмма, эмпирический, рефрактометрический, валентно-силовое поле, линейная приближения.

References

1 Su Fuhai, Ma Balei (2006). Luminescence temperature and pressure studies of Zn_2SiO_4 doped by with Mn^{3+} and Eu^{3+} ions.Lett., *J. Luminescence, 116, 1–2,* 117–126.

2 Lazerov, A.N. (2001). *Kolebatelnye spektry i stroenie silikatov [Oscillatory spectra and structure of silicates].* Moscow: Nauka [in Russian].

3 Sheludko, V.I., Nedilko, S.G., & Bojko, V.V. (2003). Post-annealing green luminescence of sulphate crystals. *Lett., Functional Materials, 10,1,* 93–97.

4 Wang, J., Wang, R., Zhang, L., Li, F., & Lin, S. (2008). The atteanuation peak and elastic anomaly of $LiKSO_4$ crystal under low temperature. Lett., *Journal Low Temperature Physics, 11,2,* 135 — 140.

5 Lazerev, A.N., Mirgorodski, A.P., & Ignatev, I.S. (2000). Kolebatelnye spektry slozhnykh okislov [Oscillatory spectra of complex oxides]. Leningrad: Nauka, 5, 270–354 [in Russian].

6 Alybakov, A.A., Gubanova, V.A., Kudabaev, K., & Sharsheev, K. (1988). Optical absortion and EPR spectra of Cu^{2+} ions in $LiKSO_4$ single crystals. *Lett. Physica Status Solidi (b), 146,* 135 — 139.

7 Mazhenov, N.A., Mazhenova, O.A., & Muldahmetova, Z.M. (2002). Raschet kolebanii iona [(P, As)$2O_7$] metodom normalnykh koordinat [Calculation of vibrations of the [(P, As)$2O_7$] ion by the normal coordinate method]. *Izvestiia AN SSSR. Neorganicheskie materialy — Bulletion of ANSSSR. Inorganic materials, 13,* 391 [in Russian].

8 Kityk, I.V., Andrievckii, B.V., & Yuvchenco, V.O. (1994). Band energy calculation and optical constans of K_2SO_4 single crustals. Lett. *Physica Status Solidi (b), 182,* 79–83.