

04,13

***Ab initio* studies of structural, electronic and vibrational properties of crystals with the belousovite structure**

© Yu.N. Zhuravlev

Kemerovo State University,
Kemerovo, Russia

E-mail: zhur@kemsu.ru

Received June 5, 2024

Revised June 5, 2024

Accepted June 10, 2024

The methods of density functional theory in the generalized gradient approximation PBE with dispersion correction D3 and the basis of localized orbitals of the CRYSTAL program code were used to calculate the crystal, electronic and vibrational structure of belousovite and its synthetic analogues $AZn(SO_4)X$ ($A = K, Rb, Cs, Tl; X = Cl, Br, I$). Dependences of lattice constants, interatomic spacing on average radius of cations A and anions X are determined. Density distribution of electronic states is calculated, and their nature is determined. It is shown that structural features of crystals manifest themselves in infrared absorption spectra, where individual bands in region 1120–1170 and 940–970 cm^{-1} correspond to oscillations of atoms of sulfur and oxygen $[SO_4]$ with different spacings S–O. Oscillations of atoms Zn–O occur in region of wavenumbers 350 cm^{-1} , and Zn–X — from 310 cm^{-1} and below. Vibrational modes for A–O atoms have low intensity, and their wavenumbers are in region below 150 cm^{-1} . The obtained patterns can be used to interpret experimental spectra and identify belousovite, its synthetic analogues and their mixed compositions.

Keywords: density functional theory, synthetic crystals, crystal structure, density of states, chemical bonding, vibrational spectra, infrared absorption.

DOI: 10.61011/PSS.2024.08.59051.149

1. Introduction

Natural mineral belousovite was discovered on Tolbachik volcano, Kamchatka Peninsula, Russia [1]. It occurs in form of grains of irregular shape and microcrystalline masses associated with other minerals. In the Tolbachik fumaroles about 350 species of mineral are reliably identified, including 123 minerals first discovered here [2]. Belousovite empirical formula is $K_{0.97}Rb_{0.01}Zn_{1.00}S_{1.01}O_{4.03}Cl_{0.97}$, and ideal — $KZn(SO_4)Cl$. This is monoclinic crystal with space group $P21/c$, its structure if studied in detail in [3]. It comprises endless layers $[ZnSO_4Cl]$ and ions K^+ . Layers are formed by general corners of mixed ligand tetrahedra ZnO_3Cl and tetrahedra SO_4 . [4] shows that crystal structure of belousovite in fact is archetype for a large family of isostructural synthetic compounds $AZn(TO_4)X$ ($A = K, Rb, Cs, Tl, NH_4; T = S, Se; X = Cl, Br, I$), that form morphotropic series and were obtained by methods of melting and evaporation by reaction AX and $ZnTO_4$ either at high temperatures, or in hot aqueous solutions. From them only two synthetic compounds were described previously [5]. This is rather rare situation when great number of crystals with different radiuses of cations and anions have same structure, this ensures study of features of their electronic and vibratory structure, and based on this studying the dependence „structure-property“ between microscopic and macroscopic parameters.

As structures $AZn(SO_4)X$ are obtained relatively recently, there are no detailed experimental studies of their physical

properties. In this relation the methods *ab initio* of computer modeling are actual. Such approach ensures practical forecast of microstructures and macroproperties of the crystal materials due to its benefits. Firstly, it can determine the microscopic and internal atomic and electronic characteristics of materials to provide uniform description of their properties at deep level. Secondly, it ensures quick determination of large amount of information on material properties and effective modeling of extreme conditions that are difficult to achieve by experiments. During last ten years a great set of calculation programs was developed [6], they facilitate development of properties study of new crystalline systems and are reason for next experimental studies. The present paper objective is determination of patterns of feature manifestations of interactions of structural elements with physical properties of crystalline sulfates with the structure of belousovite $AZnSO_4X$ ($A = K, Rb, Cs, Tl; X = Cl, Br, I$).

2. Calculation method

The structure, electronic and vibratory properties of crystals were studied by density functional theory (DFT) methods in combination with the Hartree-Fock method in the CRYSTAL software package [7]. Crystalline orbitals are given by linear combinations of localized Gaussian atomic functions whose exponents and coefficients are determined from the all-electron set for atoms of oxygen

(8^2s)-($4^61^01^0sp$)-(1^01^0d) [8], sulfur (8^2s)-($6^83^61^01^0sp$)-(1^01^0d) [9], zinc (8^2s)-($6^84^81^21^01^0sp$)-(4^101^0d) [10], chlorine (8^2s)-($6^83^71^01^0sp$) [11], pseudopotential for bromine, iodine ($1^21^01^01^0s$)-($1^51^01^01^0p$) [12], for them also — all-electron DZVP [13], and for atoms of alkaline metals and thallium — pseudopotential DZVP and TZVP [14,15]. Here the following designations are used: digit indicates number of Gaussian functions in decomposition of the orbital type s , sp , p , d , and upperscript — numbers of their filling. Description of basis sets of double and triple zeta valence with polarization quality (DZVP and TZVP) can be found in referred publications.

Exchange-correlation functionals were used in the generalized gradient approximation DFT of one of the most common forms of the functional Perdew–Burke–Ernzerhof (PBE) [16], amended by empirical dispersion correction in the form D3(BJ) [17] and adapted for solid bodies PBEsol [18].

The thresholds controlling the accuracy of the Coulomb and exchange series are set to 8, 8, 8, 8, 16 [19]. The reciprocal space is discretized using the Monkhorst–Pack grid [20] $4 \times 4 \times 4$ with 30 independent k -points in the irreducible part of the Brillouin zone. Accuracy of the self-coupling procedure was not less than 10^{-9} a.u. (1 a.u. = 27.21 eV).

Frequency of harmonic oscillations of lattice atoms was calculated using procedure FREQCALC [21,22]. Harmonic frequencies ν_n of phonons at a point Γ ($k = 0$, center of first Brillouin zone) are obtained from diagonalization of the Hessian mass-weighted matrix W , which is determined by numerical differentiation of analytical gradients with respect to the Cartesian coordinates of atoms:

$$W_{\alpha i, \beta j}(\Gamma) = \frac{H_{\alpha i, \beta j}}{\sqrt{M_\alpha M_\beta}}.$$

Here $H_{\alpha i, \beta j}$ is the second derivative of energy that is calculated numerically from analytical gradients, M_α and M_β are atomic masses, Greek and Latin indices correspond to atoms and Cartesian coordinates, respectively. The IR absorption intensity for ν_n -oscillation is calculated using Born effective charge tensor, which characterizes the electronic configuration change upon atom displacement and serves as its dynamic characteristic [23].

To establish linear relationships between different values a correlation coefficient is used, which is calculated using the formula

$$K = \sqrt{\frac{\sum_{i=1}^N (y_i^{\text{fit}} - \bar{y}^{\text{fit}})^2}{\sum_{i=1}^N (y_i^{\text{data}} - \bar{y}^{\text{data}})^2}},$$

where average value $\bar{y} = \frac{1}{N} \sum_{i=1}^N y_i$, data — initial, fit — interpolated values, N — number of measurements.

3. Crystal structure

For *ab initio* study of the crystal structure $AZnSO_4X$ ($A = K, Rb, Cs, Tl; X = Cl, Br, I$) (hereinafter — AZSX)

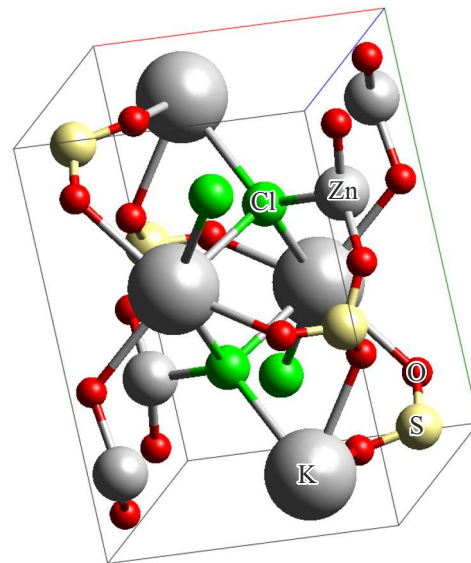


Figure 1. Lattice cell of crystal $KZn(SO_4)Cl$.

different basis sets and functionals are used. Accuracy was checked using relative standard deviation

$$\Delta = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{f_i^{\text{theor}} - f_i^{\text{exp}}}{f_i^{\text{exp}}} \right)^2}$$

by 27 structural parameters, including lattice constants a, b, c , monoclinic angle β , cell volume V ; four spacings R_{A-O} , four R_{S-O} , three R_{Zn-O} , two R_{A-X} , R_{Zn-X} and nine angles $\angle O-A-O$, $\angle O-Zn-X$, $\angle O-S-O$. Use of basis sets DZVP [13–15] for all atoms in combination with functional PBE-D3 resulted in Δ from 4.5 to 7.7% on different crystals. At that for some of them the set in experiment [4] sequence in spacings between atoms of metals A , Zn and oxygen O , halogen X was violated. This is due to that monoclinic angle β formed in calculations has value close to 90° , but in experiment is varies from 94° to 99° . The correct sequence of positions was achieved when for atoms of zinc, sulfur, oxygen and halogen the bases [8–12] were selected. Minimum values of mean-square deviations (below 2.9%) were achieved selecting DZVP [14] sets of atoms K, Rb and TZVP [15] for Cs, Tl . Somewhat better results showed functional PBEsol, but considering time costs the functional PBE-D3 was optimal, results with it are further used by default.

Table 1 shows experimentally measured and obtained as result of full optimization of geometry (lattice constants and atom coordinates structural data for crystals AZSX, and Figure 1 shows lattice cell.

It follows from Table 1 that the calculated and experimental data are in a satisfactory agreement. Minimum deviation $\Delta = 1.45\%$ is observed in $RbZn(SO_4)I$ (hereinafter referred to as — RZSI), where spacings R_{A-O} (0.80%) and spacings R_{Zn-O} (0.57%) are calculated most accurately. Also structural parameters were well determined in $RbZn(SO_4)Cl$

Table 1. Lattice constants a, b, c , angle β , volume V , short spacings $R_{A-O}, R_{Zn-O}, R_{Zn-X}$ for monoclinic crystals $AZn(SO_4)X$ indicating mean-square deviation Δ between calculated with functional PBE-D3 and measured by experiments in [4] (Exp).

Crystal; Δ , %	Method	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$\beta, ^\circ$	$V, \text{\AA}^3$	$R_{A-O4}, \text{\AA}$	$R_{Zn-O1}, \text{\AA}$	$R_{S-O4}, \text{\AA}$	$R_{Zn-X}, \text{\AA}$
KZn(SO ₄)Cl; 1.83	Exp	6.9324	9.606	8.2227	96.524	544.0	2.753	1.941	1.430	2.1871
	PBE-D3	6.9770	9.6655	8.2640	96.732	553.45	2.7658	1.9618	1.4712	2.2683
KZn(SO ₄)Br; 2.13	Exp	7.0420	9.7207	8.4233	98.201	570.71	2.736	1.955	1.435	2.3190
	PBE-D3	7.0759	9.7524	8.4468	98.391	576.64	2.7543	1.9741	1.4699	2.3921
RbZn(SO ₄)Cl; 1.78	Exp	7.2692	9.6261	8.3178	95.524	579.33	2.8998	1.9448	1.4337	2.1914
	PBE-D3	7.3817	9.7368	8.3623	94.831	598.90	2.9350	1.9618	1.4724	2.2714
RbZn(SO ₄)Br; 1.95	Exp	7.3 573	9.7091	8.5 753	97.820	606.86	2.905	1.9527	1.4330	2.3236
	PBE-D3	7.4831	9.7625	8.7012	98.079	629.35	2.9446	1.9767	1.4695	2.4044
RbZn(SO ₄)I; 1.45	Exp	7.5036	9.8981	8.8015	99.175	645.34	2.947	1.969	1.433	2.5148
	PBE-D3	7.5803	9.9704	8.8752	99.255	662.04	2.9802	1.9876	1.4684	2.5791
CsZn(SO ₄)Cl; 2.34	Exp	7.6854	9.6794	8.4492	95.303	625.85	3.089	1.9405	1.431	2.1938
	PBE-D3	7.8732	9.7065	8.2733	93.227	631.25	3.0859	1.9680	1.4753	2.2674
CsZn(SO ₄)Br; 1.85	Exp	7.7892	9.7910	8.7355	97.290	660.82	3.116	1.952	1.430	2.3294
	PBE-D3	7.8579	9.8412	8.8578	97.674	678.85	3.1404	1.9773	1.4708	2.4037
CsZn(SO ₄)I; 1.89	Exp	9.449	8.311	9.393	96.982	732.2	2.993	1.979	1.444	2.4859
	PBE-D3	9.5371	8.3104	9.4411	97.640	741.64	3.0364	2.0067	1.4760	2.5663
TlZn(SO ₄)Cl; 2.27	Exp	7.341	9.622	8.1632	94.012	575.2	2.906	1.942	1.451	2.220
	PBE-D3	7.5034	9.5621	8.0490	92.910	576.76	2.9555	1.9645	1.4762	2.2644
TlZn(SO ₄)Br; 2.88	Exp	7.3746	9.7060	8.3810	96.370	596.19	2.897	1.939	1.434	2.3323
	PBE-D3	7.5375	9.7782	8.6777	98.258	632.94	2.9628	1.9733	1.4707	2.3953

(hereinafter referred to as — RZSC), where $\Delta = 1.78\%$, and deviations in appropriate spacings are 1.11% and 0.55%. The situation is worse in TlZn(SO₄)Br (hereinafter referred to as — TZSB), where maximum deviations are available for lattice constants Δ_{abc} (3.46%) and spacings R_{A-O} (2.87%), R_{S-O} (3.19%). Mean-square deviation Δ_{abc} is also large (1.96%) for RbZn(SO₄)Br (hereinafter referred to as — RZSB), and the lower value is (0.55%) in KZn(SO₄)Br (hereinafter referred to as — KZSB) and (0.81%) in CsZn(SO₄)I (hereinafter referred to as — CZSI). Spacings R_{S-O} in sulfate ion are very overestimated compared to the experiment. The maximum deviations (3.34%) are observed in CsZn(SO₄)Cl (hereinafter referred to as — CZSC), 3.13% in CsZn(SO₄)Br (hereinafter referred to as — CZSB) and 3.08% in KZn(SO₄)Cl (hereinafter referred to as — KZSC). Angles between atoms are most worse (3.21%) in TlZn(SO₄)Cl (hereinafter referred to as — TZSC). Design structural deviations should be considered in analysis of other obtained data.

In crystals AZSX atoms of alkaline metal A, zinc Zn, sulfur S, halogens Cl, Br, I occupy in lattice unique positions,

and oxygen atoms — four: O1, O2, O3 and O4. In sulfate anion [SO₄] spacings S—O for four oxygen atoms differ. For all crystals R_{S-O4} is minimum. In KZSC further O1 follows at spacing 1.522 Å (1.479 Å in [4]), O3 — 1.527 (1.479) Å and O2 — 1.528 (1.48) Å. But already in KZSB this order is another: O1 — at 1.524 Å, O2 — 1.525 Å, O3 — 1.525 Å; in RZSI — third: O2 — at 1.526 Å, O1 — 1.527 Å, O3 — 1.537 Å. The angles between atoms of sulfur and oxygen also change in proportion to the spacings. In KZSC sequence of four angles $\angle O4-S-O, \dots, \angle O-S-O4$ will be 112.56, 102.84, 108.94, 109.43 °, and in KZSB 111.79, 109.65, 108.48, 113.08 °. So, in each of crystals the sulfate ion has distorted tetrahedral structure with different bond lengths S—O and angles $\angle O-S-O$.

Atom of alkaline metal is surrounded by atoms of oxygen and halogen, and configuration AO_nX_m is not common for all crystals in relation to values n and m . So, in KZSC according to design data the sequence A—O looks like: O4 at 2.766 Å (2.753 Å in experiment [4]), O4 — 2.781 (2.766) Å, O3 — 2.848 (2.879) Å, O2 — 2.925 (2.966) Å, O1 — 2.967 (2.994) Å, and sequence of spacings A—Cl —

3.2095, 3.2659, 3.2938 (3.2493, 3.2650, 3.3365) Å. So, in this crystal environment of potassium looks like KO_5Cl_3 . In KZSB in above sequence O2 and O1 change places, and one atom, O1, is added at 3.463 Å. So, here we have environment KO_6Br_3 . Also crystals RZSC, RZSB have such environment. For RZSI the oxygen environment does not change, and for R_{A-I} only two atoms of iodine precede sulfur atoms, and, thus the environment looks like RbO_6I_2 . For caesium compounds there are some differences between the design and experimental spacings between atoms of oxygen and caesium. According to [4] for CZSC is looks like CsO_6Cl_3 , and CZSB already CsO_7Br_3 , and in theoretical calculations, inversely, initially 7, then 6. In CZSI spacing Cs–S equal to 3.8369 Å (3.8213 Å [4]) becomes larger then Cs–I equal to 3.9139 (3.9213) Å, and environment is determined as CsO_7 , no other crystal from series AZSX has such. On thallium compounds the order of sequence of first four oxygen atoms coincides with KZSC, and two rest are after halogen atom so for them formula TlO_6Cl_3 and TlO_6Br_3 is also preserved.

The closest environment of zinc atom in all crystals stays same and is described by formula ZnO_3X ($X = \text{Cl}, \text{Br}, \text{I}$). But sequence of oxygen atoms with distance increasing from zinc atom will be different. Thus, in RZSC this sequence is: O1 (1.962 Å), O3 (1.971 Å), O2 (1.989 Å), in CZSB — O3 (1.960 Å), O1 (1.960 Å), O2 (1.988 Å), in TZSC — O1 (1.964 Å), O2 (1.963 Å), O3 (2.009 Å). These differences should manifest themselves in vibrational spectra of crystals.

Let's determine common dependences of structural parameters. To do this, you shall choose one universal value on which they will depend linearly. It is convenient to use ionic radii of ions [24] depending on coordination environment. For ions of alkaline metals and thallium considering the oxygen environment the radii R_A are chosen as 1.375 Å (KZSC), 1.38 Å (KZSB), 1.52 Å (RZSC, RZSB, RZSI), 1.67 Å (CZSC, CZSB), 1.705 Å (CZSI), 1.50 Å (TZSC, TZSB) and for halogens R_X are equal for chlorine 1.81 Å, bromine 1.96 Å, iodine 2.20 Å. For each crystal the mean radius is determined as $R_{AX} = (R_A + R_X)/2$. Then interpolation formula for parameter f will be $f = f_0 + f_1 \cdot R_{A-X}$, where coefficients f_0, f_1 are determined for all ten crystals under study. f_0 has dimension of value f , and f_1 — dimension f , divided by Å. The procedure accuracy if evaluated by correlation coefficient K . The formula can be used to make forecasts in other similar crystals and solid solutions based on them. For example, with correlation coefficient 0.91 we can calculate the lattice constant c , Å = 2.685 + 3.393 R_{A-X} . For constant a $K = 0.84$, whereas for constant b K is low due to drop-down value for CZSI. For volume of lattice cell we have V , Å³ = -255.3 + 507.1 R_{A-X} ($K = 0.98$). For experimental values of cell volume the correlation coefficient is somewhat lower 0.97. High coefficients K have dependences for interatomic spacings $R_{\text{Zn-O1}}$, Å = 1.77 + 0.112 R_{A-X} (0.93), $R_{\text{Zn-X}}$, Å = 0.74 + 0.942 R_{A-X} (0.86), R_{A-X} , Å = 0.092 + 1.951 R_{A-X} (0.99) and angles $\angle\text{O4-A-O4}^\circ = -83.46$

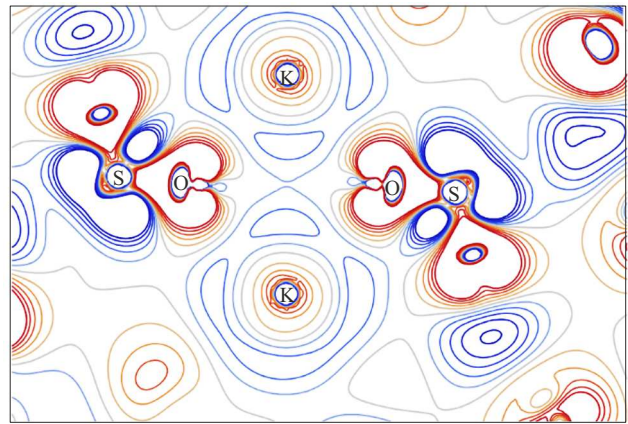


Figure 2. Deformation density of $\text{KZn}(\text{SO}_4)\text{Cl}$ in plane with shortest spacings K–O4.

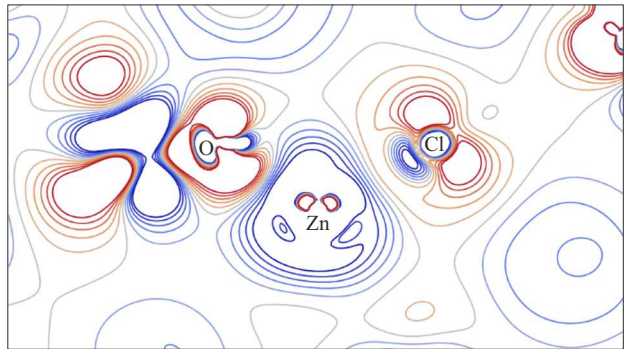


Figure 3. Deformation density of $\text{KZn}(\text{SO}_4)\text{Cl}$ in plane with shortest spacings Zn–O and Zn–Cl.

+ 98.94 R_{A-X} (0.84). Such dependences are set also for experimental crystallographic parameters. As it follows from formulas, with increase in mean radius of cation-anion the appropriate spacings increase, this is rather a natural result.

4. Electronic structure

The crystal structure is determined by interactions between its forming elements. Their mechanisms, in turn, are described using electronic charge redistribution between atoms. If the charge is redistributed from one to another, then this is usually called an ionic bond, and if the electrons are more likely to be between them, then it is called a covalent bond. This is clearly demonstrated by the deformation density $\Delta\rho$, which is determined by the difference between the crystalline density of interacting atoms. Figure 2 shows deformation density of KZSC in plane with shortest spacings $R_{\text{K-O4}}$, and on Figure 3 — with $R_{\text{Zn-O1}}, R_{\text{Zn-Cl}}$. For rest crystals $\Delta\rho$ has qualitatively similar view.

From distribution $\Delta\rho$ it follows that the electronic charge decreases in region of alkaline metal and zinc, because

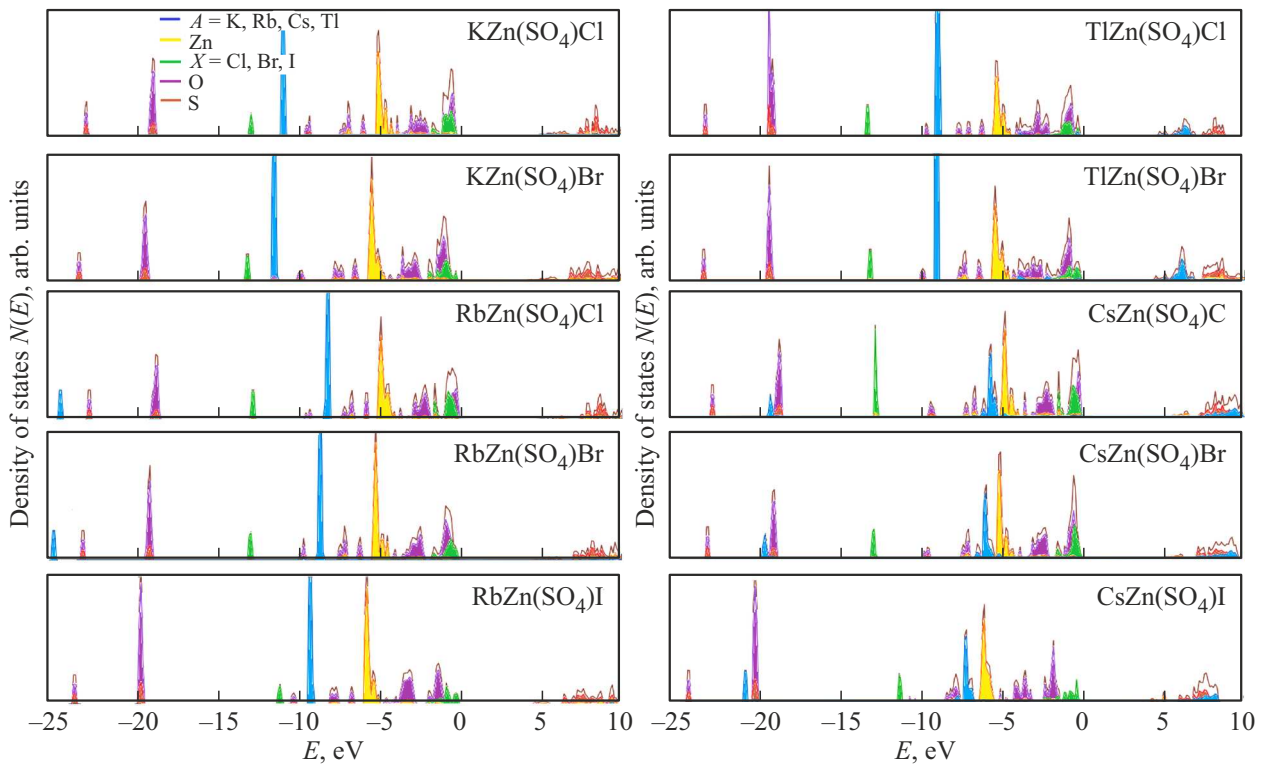


Figure 4. Full and partial density of electron states $N(E)$ of crystals $AZn(SO_4)X$.

potassium cations are formed with charge $+0.92|e|$, where e — charge of electron, and zinc $+0.87|e|$. Ion charge is calculated as difference of nucleus charge and population of all electron shells of atom PA, distributed as per Mulliken diagram. The first one do not differ greatly from the formal charge $+1$, and second one — differs significantly from $+2|e|$. Therefore, for potassium the chemical bond is predominantly ionic, and for zinc it is covalent in nature. Also sulfur atom has positive charge, it is equal to $+1.29|e|$. The deformation density near the nuclei of atoms of oxygen and chlorine is negative (electronic charge flows from this region), and positive in bond lines Zn–O, Zn–Cl and after nuclei in form of torus. Such its distribution for the chlorine, unlike halides of alkaline and alkaline earth metals, is untypical. Due to excessive electrons the charge of oxygen becomes equal to $-0.63|e|$, and of chlorine — $-0.53|e|$. Population of overlapping of electron shells of atoms in bond line Zn–O — $0.15e$, Zn–Cl — is even higher, $0.25e$, and in line S–O4 — $0.47e$. For other oxygen atoms it is lower, but increase with spacings change: $P_{S-O1} = 0.317e$, $P_{S-O3} = 0.322e$, $P_{S-O2} = 0.351e$.

Charge of metal atoms does not change in halogen family, and is for rubidium $+0.98|e|$, caesium $+0.92|e|$ and thallium $+0.95|e|$. For zinc it linearly decreases similarly to Q_{Zn} , $|e| = 1.16 - 0.172R_{A-X}(0.76)$. Charge of chlorine atom in family of metal $A = K, Rb, Cs, Tl$ changes as $-0.53, -0.57, -0.53, -0.52|e|$, bromine — $-0.51, -0.56, -0.53, -0.50|e|$, and of iodine — $-0.53, -0.47|e|$. Population of overlapping of bond Zn–O changes slightly depending on

compound; excluding CZSI, where it is $0.14e$. Population of overlapping of bond Zn–X predictably increases with R_{A-X} increasing with rate $0.148 e/\text{\AA}$, so in CZSI it achieves value $0.3e$. Population of overlapping in bond line S–O4 is maximum in $0.51e$ for rubidium compound, minimum for thallium $0.37e$.

Energy distribution of electrons in crystal is determined by zone spectrum — energy dependence on wave vector $E_n(k)$ and by density of states $N(E)$ — number of electron states in cell per unit of energy. Spectrum $E_n(k)$ in region of occupied states is characterized by present of individual bands of weakly dispersed zones, and in region of unoccupied states — by presence of two bands separated by forbidden section of energies and having different nature. Lower of four zones has anion nature, and top — cation nature. Density of electron states of all ten crystals is shown in Figure 4, colour separates partial contributions of individual atoms. The last filled state is taken as zero energy.

Narrow band of core s -states of alkaline metals is located in region approximately -27 eV for potassium, $(-25.3) - (-24.3)$ eV for rubidium, and $(-20.3) - (-19.0)$ eV for caesium. With increase from iodine to chlorine its width is $0.01 - 0.07$ eV. Band of p -states of potassium about 0.16 eV wide lies in region of $(-11.2) - (-10.6)$ eV, of rubidium about 0.22 eV wide in region $(-9.0) - (-8.0)$ eV and for caesium — 0.55 eV in region $(-6.7) - (-5.4)$ eV. For thallium zone of d -states is located approximately in region of energies

(-8.8) – (-8.7) eV. Width of d -zone of zinc decreases with increase in radius R_{A-X} from 0.95 eV in KZSC to 0.75 eV in CZSI by law $E_d, \text{ eV} = 1.85 - 0.54R_{A-X}(0.85)$. Its center of gravity is in region -5.56 eV in CZSI and -4.42 eV in KZSC. In caesium compounds it is partially overlapped with p -states of metal. The valence s -states of sulfur and oxygen in KZSC have width 0.07 and 0.27 eV with centers of gravity -22.6 and -18.6 eV. In other compounds they slightly change their energy parameters. s -zones of chlorine 0.12 eV wide are located in region -12.5 eV, of bromine 0.09 eV wide at -12.6 eV and iodine 0.22 eV wide at -10.8 eV.

Top valence region is formed mainly by p -states of oxygen. For optical spectra in visible region we are interested in nature of the top valence band. In all compounds it has different nature. In sulfate-chlorides upper valence bands of p -states of chlorine and oxygen are overlap each other, in sulfate-chlorides p -bromides prevail, and with iodine form its upper portion. As in rubidium compounds the portion of p -states of halogen X increases as 11, 88, 94%, and portion of oxygen decreases to reverse in reverse direction. In caesium compounds the same values are 17, 85, 96%. For potassium compounds the contribution of chlorine is 52%, of bromine 89%, and for thallium 43 and 65%, respectively. Feature of these compounds is also the fact that contribution to upper valence regions is made by s -states of thallium, its portion in TZSC and TZCB was 25 and 20%, respectively. The established features should be confirmed in the photoelectron spectra of crystals.

Differences in crystallographic position of oxygen atoms O1–O4 resulted in their different contributions to partial density of states. Thus, in upper valence region of KZSC contribution of atoms O4 equal to 16%, O2 below 10%, O3 below 9% prevail. Same situation will be in, where portion of O4 will be 29%, and in TZSC — 12%.

Width of bottom unoccupied zinc of crystals with chlorine is maximum, and it decreases in family of alkaline metals K, Rb, Cs as 2.32, 2.21, 1.92 eV; for bromides it is lower — 2.18, 2.08, 1.84 eV, and more lower for iodides: 1.85, 1.64 eV. Bottom unoccupied state are formed by s -states of zinc, p -sulfur, and by very small participation of p -halogen. In thallium compounds there is no break in spectrum of unoccupied state, and conduction band is continuous energy spectrum. This is due to the fact that the portion of zinc here is in TZSC and TZSB 15 and 19%, respectively, the portion of sulfur — 348 and 35%, of s -thallium — 45 and 41%. Thus, optical spectra in visible region for thallium compounds will differ from other crystals AZSX. The nature of the electronic transition is also important here: direct, when the top of the valence band and the bottom of the unoccupied band are realized at one Brillouin point, and indirect, when they are realized at different points. In alkaline metal compounds the top of valence band is in point B with coordinates (1, 0, 0) in units of reciprocal lattice, and bottom of conduction band in point Γ (0, 0, 0) — center of Brillouin zone. In thallium

compounds, in both cases, this is point B, and, consequently, the transition here is direct.

Band gap E_g is calculated as difference between bottom unoccupied and upper filled states. In family of chlorides and bromides E_g increases with increase in radius of alkaline metal, and in iodides — decreases. In family of alkaline metal E_g decreases with increase in radius of halogen. For two thallium compounds E_g it is 4.36 and 4.38 eV. There is linear dependence $E_g, \text{ eV} = 8.51 - 2.41R_{A-X}$, simultaneously correlation coefficient is not so high: 0.73. For example, as per formula for CZSC we have 4.32 eV; accurate calculation — 4.73 eV. Such dependence agrees with nature of states of unoccupied zone. When evaluating number numerical results consider that functional PBE decreases actual values of band gap.

5. Vibrational spectra

Infrared spectroscopy is a powerful method to study details of structure and nature of chemical bond of sulfates of alkaline and alkaline earth metals by experimental [25,26] and theoretical [27] methods. It is widely used to determine presence of functional groups and other fragments. It was previously determined that in studied crystals AZSX stable sulfate ion $[\text{SO}_4]$, fragments ZnO_3X , AO_nX_m are distinguished. It is interested to plot theoretical spectra of infrared absorption and to determine how they demonstrate these structural features. Such data will be predictive for next experimental studies.

Theoretical IR spectra (IRS) are obtained by Gaussian broadening of intensities of normal longwave ($k = 0$) oscillations. Figure 5 shows IR absorption spectra of all ten crystals AZSX. For easy comparison the intensity I is given and arbitrary units, and its maximum value in each case is 3000 km/mol. Interval in wavenumbers μ is everywhere set as 0–1250 cm^{-1} . In IRS oscillations of symmetry will be active A_u and B_u , $A_u + 2B_u$ — acoustic and $23A_u + 22B_u$ — optical. Number before irreducible representation indicates the number of modes. Oscillations A_u are polarized for light along axis b , and B_u , respectively, a , c . The polarization vectors of oscillations determine the directions of displacement of atoms and their amplitude. Relative squares of amplitudes A_s , expressed in percents, determine the contribution of these atoms to one or another vibrational mode. In Figure 5 contributions of atoms are designated by squares, diamonds, circles and triangles, and with weight below 5% are not shown.

If the electron spectra of crystals are determined by the filling of the electron shells of their constituent atoms, then the vibrational spectra will depend on their atomic masses M . In family of metals $A = \text{K, Rb, Cs, Tl}$ they increase as 38.96, 84.91, 132.915, 204.97 amu, for halogens $X = \text{Cl, Br, I}$ — 34.97, 78.92, 126.90 amu, for zinc — 63.939 amu, sulfur — 31.97 amu, and oxygen — 16.00 amu. So, oscillations, in which A_s oxygen atoms prevail (have larger contribution), will be located in region

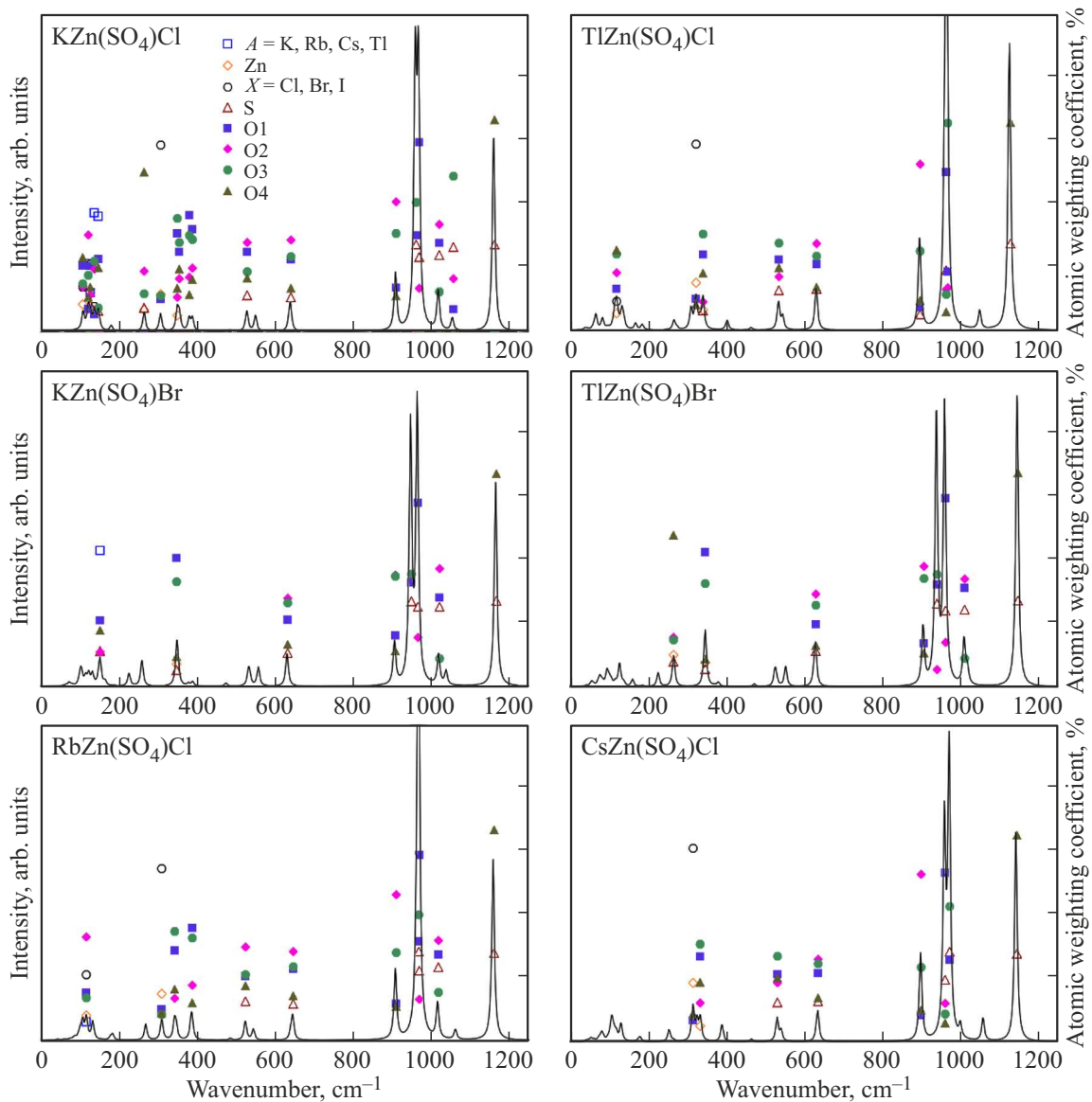


Figure 5. Spectra of infrared absorption of crystals with belousovite structure.

of high values of ν , and metal atoms — in region of lower values. Value characterizing width of the vibration spectrum — energy of zero oscillations $E_0 = \sum_{i=1}^N \frac{h\nu_i}{2}$ with correlation coefficient 0.89 fits into a linear relationship $E_0, \text{kJ/mol} = 264.22 - 34R_{A-X}$.

In KZSC the most intensive oscillations are three modes of symmetry — B_u, B_u, A_u with wavenumbers 1161.5, 968.5, 960.6 cm^{-1} , formed by intramolecular oscillations of atoms of sulfate-ion. Contributions of oxygen atoms differ by weighing coefficients A_s . Thus, for the most high-frequency mode, the contribution of the sulfur atom is 27%, and that of O4 atom 67%. For two other modes these values are 23% for sulfur, 59% for O1, 14% for O2 for symmetry B_u , and for symmetry A_u-S — 27%, O1 — 30%, O3 — 41%. For region of valence ν_3 -oscillations of sulfate-ion [28] the oscillation of symmetry A_u will be also

active with wavenumber 1019.5 cm^{-1} with contribution of sulfur 24%, O2 — 34%, O1 — 27% and O3 — 12%. For region of valence oscillations ν_1 oscillation of symmetry B_u will be also active at 910.0 cm^{-1} , formation will contain mode of symmetry B_u with wavenumber 640.8 cm^{-1} with contribution of atoms of sulfur 11%, O1–O3 from 23 to 28% and below 14% for O4 atoms. And finally, deformation oscillations of type ν_2 of symmetry B_u are observed at 529.8 and 550.8 cm^{-1} and of B_u at 356.4 and 381.3 cm^{-1} . They are formed by approximately 10% of sulfur atoms, by atoms O1, O2 (each 26%), and by O3, O4 (each 17%).

Atom oscillations in structure ZnO_3Cl should include the mode of symmetry B_u with wavenumber 307.8 cm^{-1} and contribution 59% from chlorine atoms, 12% from zinc, and 10% from atoms O1, O3, as well as of symmetry A_u at 350.8 cm^{-1} with contribution 6% from zinc, 90% from

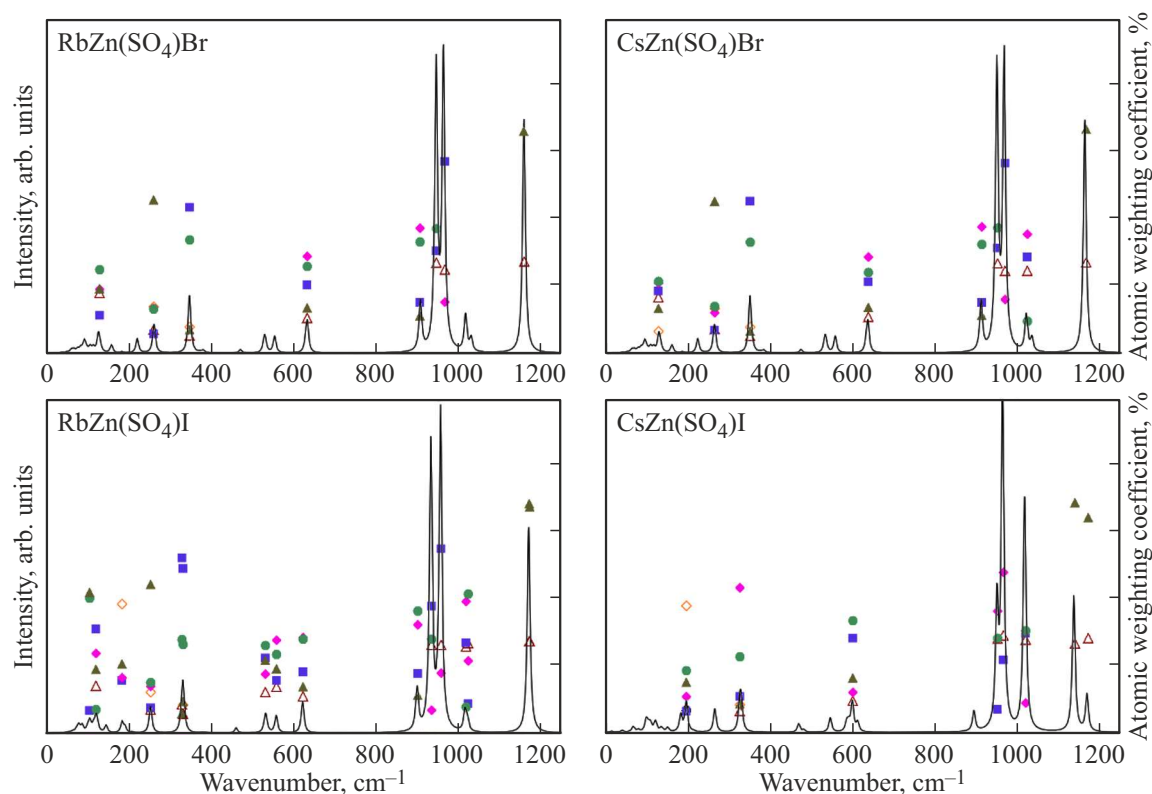


Figure 5 (continued).

Table 2. Wavenumbers (cm^{-1}) of intramolecular vibrational modes ν_{1-4} of symmetry A_u and B_u , of large (b, > 1000 km/mol), moderate (m, > 300 km/mol) and low (l, < 300 km/mol) intensity

Crystal	ν_3		ν_1		ν_4	ν_2	
	A_u	B_u	A_u	B_u	B_u	A_u	B_u
KZn(SO ₄)Cl	1019.5 ^m	1161.5 ^b , 1055.5 ^l	960.6 ^b	968.5 ^b , 909.9 ^m	640.8 ^m	527.7 ^l	529.8 ^l , 550.9 ^l
KZn(SO ₄)Br	1019.7 ^m	1165.8 ^b , 1038.6 ^l	947.7 ^b	964.7 ^b , 906.7 ^m	631.6 ^m	532.6 ^l	557.8 ^l , 535.6 ^l
RbZn(SO ₄)Cl	1016.1 ^m	1158.6 ^b , 1061.8 ^l	966.1 ^b	967.3 ^b , 907.8 ^m	644.5 ^l	543.9 ^l	523.2 ^l
RbZn(SO ₄)Br	1018.3 ^l	1170.3 ^b , 1034.7 ^l	945.8 ^b	965.6 ^b , 905.4 ^m	632.4 ^m	531.0 ^l	557.4 ^l
RbZn(SO ₄)I	1017.0 ^l	1171.7 ^b , 1023.0 ^l	934.3 ^b	957.7 ^b , 901.0 ^m	623.1 ^m	532.1 ^l	558.7 ^l
CsZn(SO ₄)Cl	1001.9 ^l	1144.4 ^b , 1060.1 ^l	973.0 ^b	960.9 ^b , 899.6 ^b	636.2 ^m	542.0 ^l	531.6 ^l
CsZn(SO ₄)Br	1018.4 ^m	1160.7 ^b , 1031.9 ^l	946.8 ^b	964.7 ^b , 908.6 ^m	633.1 ^m	528.5 ^l	553.7 ^l , 531.2 ^l
CsZn(SO ₄)I	1137.8 ^b	1169.8 ^m , 1018.3 ^b	951.2 ^b	964.9 ^b , 895.1 ^l	612.6 ^l	586.1 ^l	546.0 ^l
TlZn(SO ₄)Cl	1126.8 ^l	1123.7 ^b , 1047.3 ^l	963.1 ^b	959.1 ^b , 893.4 ^b	628.5 ^m	542.2 ^l	531.5 ^m
TlZn(SO ₄)Br	1010.2 ^m	1146.3 ^b , 1019.0 ^l	939.5 ^b	960.5 ^b , 905.4 ^m	629.5 ^m	525.7 ^l	553.1 ^l , 528.7 ^l

oxygen, mainly O1, O3. Fragment KO_5Cl_3 can be characterized using oscillations with wavenumbers 138.2, 148.8 cm^{-1} with contribution of potassium 36%. In first one atoms of chlorine (8%) and O1–O3 participate, in second one — atoms of sulfur (6%) and oxygen O1, O3, O4.

In other crystals IRS structure in region of intramolecular oscillations is similar to belousovite — Table 2.

The outermost maximum, formed by oscillations of atoms of O4 and sulfur, for all crystals, except CZSI, TZSC, TZSB, obeys a linear dependence on the distance R_{S-O4} like

$\nu_{3B_u}, \text{cm}^{-1} = 7009.1 - 3969.9R_{S-O4}(0.98)$. Such dependence can be set also for the same type of oscillations, but of symmetry A_u : $\nu_{3A_u}, \text{cm}^{-1} = 3030.5 - 1317.6R_{S-O2}(0.92)$, but on spacings between atoms of sulfur and oxygen O2. Oscillations of type ν_1 split to two intensive maxima, but in some compounds they are located so close that merge into one, for example, in RZSC, TZSC. As these modes are formed due to oscillations of atoms of sulfur, O1 and O3, then for symmetry A_u there is linear dependence for all ten crystals: $\nu_{1A_u}, \text{cm}^{-1} = 4358.8 - 2226.3R_{S-O3}(0.92)$. It follows from it that for CZSC the obtained using formula value is 971.0 cm^{-1} , and accurately calculated — 973.0 cm^{-1} . From a practical point of view, it is convenient to use the inverse formula, $R_{S-O3}, \text{Å} = 1.895 - 3.84 \cdot 10^{-4}\nu_{1A_u}$ to calculate interatomic spacings using IRS data. Mode ν_4 is formed by oscillations of all oxygen atoms of sulfate group, so it has no clear dependence on spacings.

As already noted, the crystal structure CZSI differs from other compounds, and this is reflected in IRS. Modes ν_3 have two expressed maxima at 1137.7 and 1169.7 cm^{-1} , and they are formed by oscillations of atoms of sulfur and oxygen O4. In another mode of this type at 1018.4 cm^{-1} mainly oscillations of atoms O1, O3 participate, and, on the contrary, atoms O4 do not participate.

IRS in region below 400 cm^{-1} have different structure. For example, compounds with chlorine RZSC, CZSC, TZSC will contain active modes Zn–Cl of oscillations with wavenumbers $308.7, 316.1, 319.6 \text{ cm}^{-1}$, and here Cl weight exceeds 60%. For compounds with bromine and iodine oscillations of such types have lower intensity and lower wavenumbers. The same region contains oscillations Zn–O. For example, for atom O1 in AZSB wavenumbers are $348.6, 347.1, 346.3, 346.8 \text{ cm}^{-1}$ and approximately 260 cm^{-1} for atoms O4. Oscillations A–O with relatively low intensity will be located in region below 150 cm^{-1} . In Figure 5 for heavy metals they practically are not identified.

6. Conclusion

Crystal structures of belousovite and its synthetic analogues $AZn(SO_4)X$ ($A = K, Rb, Cs, Tl; X = Cl, Br, I$) contain one symmetrically located group $[SO_4]$, in which the minimum spacing is obtained for atoms S–O4, maximum for S–O2 in sulfate chlorides AZSC, S–O3 in sulfate bromides AZSB and sulfate iodides AZSI. Atoms Zn have tetrahedral coordination ZnO_3X , where shortest spacings are for Zn–O1 (KZSC, RZSC), Zn–O2 (CZSC, TZSC), Zn–O3 in AZSB, AZSI. Spacings Zn–X increase with increase in ionic radius of halide X. Polyhedra of atoms of metal A have environment AO_5X_3 in KZSC, AO_6X_3 in RZSC, AZSB, AO_7X_3 in CZSC, TZSC, and unique RbO_6I_2, CsO_7 in iodides. In all AZSX the shortest spacing is for A–O4, and in family X it increases with increase in ionic radius of cation, as well as spacing A – X in family of halide.

Populations of overlapping of electronic shells calculated according to Mulliken diagram ensure evaluation of cation

charges of potassium $+0.92|e|$, thallium $+0.95|e|$, rubidium $+0.98|e|$ and caesium $+0.92|e|$. Positive charge of zinc in family of each cation A decreases with increase in radius of halogen, as well as negative charge of halogen by absolute value. Population of overlapping of electronic shells in bond line Zn–O is for all AZCX $0.15e$, except CZSI, TZSC, where it is $0.14, 0.16e$; in line Zn–X changes from 0.24 (TZSC) to $0.3e$ (CZSI), and in line S–O — from 0.36 (TZSX) to $0.51e$ (RZSX).

Structural features AZSX are observed in spectra of infra red absorption. For sulfate ion intensive region ν_3 is identified with wavenumbers $1120–1170 \text{ cm}^{-1}$, formed by oscillations of mainly atoms of sulfur and oxygen O4; intensive ν_1 $940–970 \text{ cm}^{-1}$ — of sulfur, oxygen O1, and O1, O3, average intensity ν_4 $630–645 \text{ cm}^{-1}$ and low intensive ν_2 in region $525–560 \text{ cm}^{-1}$ with participation of all oxygen atoms. The wavenumbers of vibrational modes ν_3, ν_1 have linear dependence on spacing S–O4 and S–O3. Oscillations of atoms Zn–O occur in region of wavenumbers $250–350 \text{ cm}^{-1}$, Zn–X — from 310 cm^{-1} and below. The obtained patterns can be used to interpret experimental spectra and identify belousovite, its synthetic analogues and mixed compositions.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] O.I. Siidra, E.V. Nazarchuk, A.N. Zaitsev, E.A. Lukina, K.R. Aayukov, L.P. Vergasova, S.K. Filatov, G.A. Karpov, V.V. Shilovskikh. IMA 2016-047. CNMNC Newslett. 33, 1139 (2016); Mineral. Mag. **80**, 6, 1135 (2016).
- [2] I.V. Pekov, A.A. Agakhanov, N.V. Zubkova, N.N. Koshlyakova, N.V. Shchipalkina, F.D. Sandalov, V.O. Yapaskurt, A.G. Turchkova, E.G. Sidorov. Russ. Geol. Geophys. **61**, 5–6, 675 (2020). <https://doi.org/10.15372/RGG2019167>.
- [3] O.I. Siidra, E.V. Nazarchuk, E.A. Lukina, A.N. Zaitsev, V.V. Shilovskikh. Mineral. Mag. **82**, 5, 1079 (2018). <https://doi.org/10.1180/minmag.2017.081.084>
- [4] A.S. Borisov, O.I. Siidra, D.O. Charkin, K.A. Zagidullin, R.K. Burshtynovich, N.S. Vlasenko. Acta Cryst. B **78**, 3–2 Part 1, 499 (2022). <https://doi.org/10.1107/S2052520622003535>
- [5] B. Bosson. Acta Cryst. B **32**, 7, 2044 (1976). <https://doi.org/10.1107/S0567740876007073>
- [6] V. Gavini, S. Baroni, V. Blum, D.R. Bowler, A. Buccheri, J.R. Chelikowsky, S. Das, W. Dawson, P. Delugas, M. Dogan, C. Draxl, G. Galli, L. Genovese, P. Giannozzi, M. Giantomassi, X. Gonze, M. Govoni, F. Gygi, A. Gulans, J.M. Herbert, S. Kokott, T.D. Kühne, K.-H. Liou, T. Miyazaki, P. Motamari, A. Nakata, J.E. Pask, C. Plessl, L.E. Ratcliff, R.M. Richard, M. Rossi, R. Schade, M. Scheffler, O. Schütt, P. Suryanarayana, M. Torrent, L. Truflandier, T.L. Windus, Q. Xu, V.W.-Z. Yu, D. Perez. Modelling Simul. Mater. Sci. Eng. **31**, 6, 063301 (2023). <https://doi.org/10.1088/1361-651X/acdf06>

- [7] R. Dovesi, A. Erba, R. Orlando, C.M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, B. Kirtman. *WIREs Comput. Mol. Sci.* **8**, 4, e1360 (2018). <https://doi.org/10.1002/wcms.1360>
- [8] L. Valenzano, F.J. Torres, K. Doll, F. Pascale, C.M. Zicovich-Wilson, R. Dovesi. *Z. Phys. Chemie* **220**, 7, 893 (2006). <https://doi.org/10.1524/zpch.2006.220.7.893>
- [9] T. Bredow, P. Heitjans, M. Wilkening. *Phys. Rev. B* **70**, 11, 115111 (2004). <https://doi.org/10.1103/PhysRevB.70.115111>
- [10] J.E. Jaffe, A.C. Hess. *Phys. Rev. B* **48**, 11, 7903 (1993). <https://doi.org/10.1103/PhysRevB.48.7903>
- [11] E. Apra, M. Causa, M. Prencipe, R. Dovesi, V.R. Saunders. *J. Phys.: Condens. Matter* **5**, 18, 2969 (1993). <https://doi.org/10.1088/0953-8984/5/18/019>
- [12] K. Doll, H. Stoll. *Phys. Rev. B* **57**, 8, 4327 (1998). <https://doi.org/10.1103/PhysRevB.57.4327>
- [13] D.V. Oliveira, J. Laun, M.F. Peintinger, T. Bredow. *J. Computat. Chem.* **40**, 27, 2364 (2019). <https://doi.org/10.1002/jcc.26013>
- [14] J. Laun, D.V. Oliveira, T. Bredow. *J. Computat. Chem.* **39**, 19, 1285 (2018). <https://doi.org/10.1002/jcc.25195>
- [15] J. Laun, T. Bredow. *J. Comput. Chem.* **42**, 15, 1064 (2021). <https://doi.org/10.1002/jcc.26521>
- [16] J.P. Perdew, K. Burke, M. Ernzerhof. *Phys. Rev. Lett.* **77**, 18, 3865 (1996). DOI: <https://doi.org/10.1103/PhysRevLett.77.3865>
- [17] S. Grimme, S. Ehrlich, L. Goerigk. *J. Computat. Chem.* **32**, 7, 1456 (2011). <https://doi.org/10.1002/jcc.21759>
- [18] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke. *Phys. Rev. Lett.* **100**, 13, 136406 (2008). <https://doi.org/10.1103/PhysRevLett.100.136406>
- [19] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, P. D'Arco, M. Llunell, M. Causá, Y. Noël, L. Maschio, A. Erba, M. Rerat, S. Casassa. *CRYSTAL17 User's Manual*. University of Torino, Torino (2017).
- [20] H.J. Monkhorst, J.D. Pack. *Phys. Rev. B* **13**, 12, 5188 (1976). <https://doi.org/10.1103/PhysRevB.13.5188>
- [21] F. Pascale, C.M. Zicovich-Wilson, F. Lopez Gejo, B. Civalleri, R. Orlando, R. Dovesi. *J. Computat. Chem.* **25**, 6, 888 (2004). <https://doi.org/10.1002/jcc.20019>
- [22] C.M. Zicovich-Wilson, F. Pascale, C. Roetti, V.R. Saunders, R. Orlando, R. Dovesi. *J. Comput. Chem.* **25**, 15, 1873 (2004). <https://doi.org/10.1002/jcc.20120>
- [23] X. Gonze, C. Lee. *Phys. Rev. B* **55**, 16, 10355 (1997). <https://doi.org/10.1103/PhysRevB.55.10355>
- [24] R.D. Shannon. *Acta Cryst. A* **32**, 5, 751 (1976). <https://doi.org/10.1107/S0567739476001551>
- [25] M.D. Lane. *Am. Mineralogist* **92**, 1, 1 (2007). <https://doi.org/10.2138/am.2007.2170>
- [26] T.P. Myasnikova, A.É. Myasnikova. *Phys. Solid State* **49**, 10, 1903 (2007).
- [27] D.V. Korabel'nikov, Yu.N. Zhuravlev. *J. Phys. Chem. Solids* **119**, 114 (2018). <https://doi.org/10.1016/j.jpcs.2018.03.037>
- [28] K. Omori. *Mineralogical J.* **5**, 5, 334 (1968).

Translated by I.Mazurov