Calculation of Vibrational Spectra and Thermodynamic Functions of a Natural Zinc Silicate – Willemite

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Abstract

A zinc silicate is in a great demand in modern technology due to its fluorescent, optical and catalytic properties. However, its thermodynamic properties have been studied not sufficiently, and they are focused primarily in the geological and geochemical sciences. An attempt to calculate for a natural zinc silicate willemite (Zn_2SiO_4) its crystal structure, vibrational properties, phonon states and thermodynamic functions was made in this work. The force constants and vibrational states of the mineral have been calculated in this paper by a combination of the methods of quantum-chemical calculations (MOPAC) with semi-empirical method PM5 and the theory of crystal lattice dynamics (LADY program) with valence force field potential model. Theoretical infrared and Raman spectra of the mineral were simulated on the base of calculated vibrational states. A good agreement between the experimental and theoretical vibrational spectra of the mineral has been achieved. After that the Brillouin zone scanning of the mineral crystal structure was made which is necessary to obtain the information about the whole phonon spectrum in the lattice. Density-of-state function was determined by summation over all the phonon states and used for determination of energetics of the crystal. The values of the basic thermodynamic functions for willemite (heat capacity, entropy and change of enthalpy) over the range of (10-298.15) K have been obtained. The standard values of these functions are: $C_p(298.15)$ = 126 J/(mol•K) (PM5 calculation) and 122.5 J/(mol•K) (LADY calculation), $S^o(298.15)$ = 133.4 J/(mol•K) (LADY calculation), and $H^o(298.15)–H^o(0)$ = 21494 J/mol (PM5 calculation). The calculated heat capacity values are in satisfactory agreement with known experimental data.

Introduction

A natural zinc silicate willemite Zn_2SiO_4 is a relatively rare mineral, but sometimes it forms significant agglomerations in the oxidation zones of lead-zinc deposits in pseudomorphoses on hemimorphite. Traditionally willemite is regarded as a product of the secondary change of zinc sulfide sphalerite at usual temperatures. In natural conditions the formation of willemite also often proceeds at high temperatures and has a hydrothermal character [1], in this case willemite develops primarily on sphalerite ZnS, but not on zinc carbonate $ZnCO_3$ – smithsonite and a zinc hydrosilicate – hemimorphite $Zn_4Si_2O_7(OH)_2•H_2O$, which subsequently replaced willemite. Furthermore, willemite as well as sphalerite, has been proposed as an Rb–Sr geochronometer for a direct dating of non-sulfide ore deposits of lead and zinc [2].

In virtue of feature of its crystal structure a zinc silicate exhibits luminescence properties, especially in the presence of dope admixtures [3]. Due to this feature the compound is in a great demand in many fields of modern electronic industry: its use ranges from materials for the base of luminescent screens to light-emitting coating layers and devices [4]. The practical application of willemite spectral properties spreads to the protection against ultraviolet radiation [5].

The methods of obtaining luminophores based on zinc silicate are very diverse [6], the same as the methods of synthesis of nano-size forms of willemite. The method of sol-gel, the spray pyrolysis method, hydrothermal methods are presented among the relatively new methods of the synthesis of a zinc silicate. Methods of synthesis of the mineral are often based on the use of phase diagrams of willemite and compounds related to it [7]. As a rule, thermo-

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dynamic properties of the mineral are estimated or calculated ones [1].

Willemite also shows microwave dielectric properties [8] used in high-frequency hardware, mobile devices, etc. Another area of application of a zinc silicate both in a crystalline and amorphous form is its use as a catalyst of the reactions of ozonization, esterification and reesterification, the latter being promising in obtaining the diesel fuel from renewable plant raw materials [9].

Theory

In a first approximation, the ways of calculating the physical properties of minerals and inorganic substances having the crystal structure can be divided into two main groups. The methods of quantum-chemical calculation belong to the first group. They solve the problem of finding the minimum of energy of the atoms of the crystal structure by taking into account all the electronic and nuclear interactions. These methods are associated with a considerable amount of calculation. The second group includes the crystal-chemical methods and first of all it considers the energy of interatomic interactions in the crystal and dynamics of the atoms in the crystal lattice, which requires less complicated mathematical apparatus. However, in this case, the potential of interatomic interaction contains a number of parameters whose values are determined empirically, and sometimes even with the help of heuristic assumptions. Thus, to describe the dynamic properties of crystals better, in the theoretical calculations it is efficient to use basic parameters found by the quantum-chemical methods that significantly improves the reliability of calculations.

The results of calculations of the vibrational states of a natural zinc silicate for the purpose of determining the temperature dependence of the heat capacity and other thermodynamic properties of the mineral using a combination of semi-empirical method of quantum-chemical calculation PM5 and the calculation according to the model of the valence force field (VFF) in terms of the theory of lattice dynamics are presented in this study. The fidelity criterion for determination of the vibrational states served the agreement between the calculated IR spectra and the experimental data known from literature. The force constants for valence angles and bonds of the minerals found by means of quantum-chemical calculations have been used to calculate the spectra according to the model of the valence force field.

On the basis of determined vibrational states the calculation of Brillouin zone and thermodynamic function of the compound is carried out. The heat capacities of the substance (more exactly, the cor-

responding phonon contribution) at temperatures T are calculated within the harmonic approximation as follows:

$$C(T) = \frac{1}{N_t} \sum_{n,k} \left[\frac{h\omega_n(k)/2k_B T}{2\sinh(h\omega_n(k)/2k_B T)} \right]^2$$

where $N_t=(2N+1)^3$ – number of points in Brillouin zone; ω_n – phonon frequencies at wave-vectors k; h – Planck constant; k_B – Boltzmann constant.

In quantum-chemical calculation, the heat capacity consists of vibrational, rotational, translational and internal contributions; the vibrational part for heat capacity is determined as follows:

$$C_{vib} = R(hc/k_B T)^2 \sum_i \left\{ \frac{\omega_i^2 e^{-\omega_i hc/k_B T}}{(1 - e^{-\omega_i hc/k_B T})^2} \right\}$$

where R – molar gas constant; c – speed of light in vacuum; ω_i – wave number of vibrational state, related to vibrational frequencies v_i for the normal modes of vibration as $\omega_i = v_i/c$.

Experimental

Willemite is referred to the compounds crystallizing in the structural type of phenacite Be_2SiO_4. In crystallographic terms willemite is referred to the trigonal system with point symmetry group $R\bar{3}$. The unit cell parameters in the hexagonal axes are: a = 13.948 Å, c = 9.315 Å; the number of formula units per cell is Z = 18 [10]. These parameters together with the crystallographic positions of the atomic set of willemite were used in calculating the full unit cell of willemite (Fig. 1) by means of the program for calculation of the crystal lattice dynamics LADY [11].
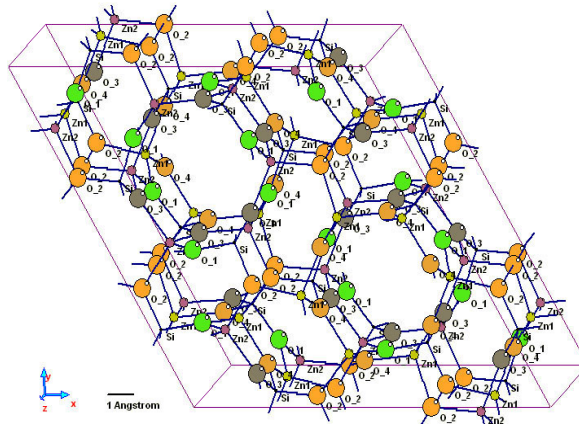

Fig. 1. The unit cell of willemite.

The atomic positions obtained were used in compiling the source files to calculate a set of force constants of the compound using a package of quantum-chemical calculation programs MOPAC. The total values of the force constants of valence bonds and angles corresponding to the positions of the absorption bands in the experimental spectrum are shown in Table 1.

Table 1
Force constants of valence bonds and angles of willemite

Bond or angle	Value of bond or angle (Å; degree)	Force constant (μ_{dyn}; $\mu_{dyn}/Å$)
Si – O(2)	1.6278	3.4
Si – O(4)	1.6288	3.4
Si – O(1)	1.6388	3.3
Si – O(3)	1.6431	3.2
Zn(1) – O(2)	1.9450	1.3
Zn(1) – O(1)	1.9493	1.2
Zn(1) – O(4)	1.9506	1.2
Zn(1) – O(4)	1.9531	1.2
Zn(2) – O(1)	1.9412	1.3
Zn(2) – O(2)	1.9530	1.1
Zn(2) – O(3)	1.9701	1.1
Zn(2) – O(3)	1.9800	0.9
O(2) – Si – O(4)	110.56	0.5
O(2) – Si – O(1)	106.11	0.5
O(2) – Si – O(3)	110.62	0.4
O(4) – Si – O(1)	108.35	0.5
O(4) – Si – O(3)	110.79	0.5
O(1) – Si – O(3)	110.27	0.03

The calculated force constants were used in calculating the vibrational states of the crystal lattice of willemite in the program LADY with valence force field model. As a fidelity criterion of the calculations an agreement between the calculated and experimental [5, 12-18] vibrational spectra of willemite was used, for this purpose a sequence variation of the force constants used in the calculation was performed. As a result a good agreement between the positions of the calculated lines in the theoretical spectrum and the absorption bands in the experimental infrared spectrum has been achieved (Table 2).

Results and Discussion

The calculated bands in the vibrational spectra of willemite over the range of 860-970 cm⁻¹ correspond to the valence vibrations of Si−O in the tetrahedral silicate-ion. The band at 861 cm⁻¹ refers to symmetric valence vibrations, and the bands at 954, 960 and 968 cm⁻¹ belong to the antisymmetric valence vibrations. The bands near 600, 612 and 622 cm⁻¹ are an-

tisymmetric valence vibrations of Zn−O bonds in a tetrahedral fragment of the structure of ZnO_4, and the bands at 568 and 587 cm⁻¹ are symmetric valence vibrations of Zn−O. In the spectral range of 350-460 cm⁻¹ there are bands of deformation vibrations of the valence angles of O−Si−O in the silicate-ion. The bands in the range 200-350 cm⁻¹ belong to deformation vibrations of the valence angles of O−Zn−O and Zn−O−Zn. The bands below 200 cm⁻¹ belong to the crystal lattice vibrations.

Thus, all absorption bands in calculated spectra of willemite are assigned to real atomic vibrations in the lattice of the mineral. Therefore, the correlation of spectra and assignment of bands allows to obtain the form of phonon spectrum which is close to the true one. This fact provides ability to achieve better accuracy in description of thermodynamic functions.

Based on a set of vibrational states of willemite, the calculation of the phonon states of the mineral in the Brillouin zone has been made using the program LADY with methods of the crystal lattice dynamics theory. Then the phonon states were used to calculate the thermodynamic functions of the compound, its heat capacity and entropy over the temperature range of 10-300 K.

The calculation of thermodynamic functions of willemite was also performed by means of the quantum-chemical calculation method PM5. The calculation was made on an atomic cluster containing one unit cell of the mineral; thus, the calculation involved 126 atoms. The smallest lateral dimensions of the cluster were 12×12×9.3 Å, what satisfied the compliance of the Born-Karman boundary conditions and ensured the correctness of the performed quantum-chemical calculation of the compound.

As a result of the quantum-chemical calculation the tabulated values (over the temperature range of 10-320 K) of the following thermodynamic quantities of the mineral have been obtained: the heat capacity, changes of enthalpy and heat of formation. The magnitude of the calculated values of the molar heat capacity of the compound at standard temperature was 126 J/(mol•K) (calculation PM5) and 122.5 J/(mol•K) (calculation LADY) (Table 3).

Robie and Hemingway [19] reported data on willemite $C_{p(298.15)}$ = 123.3 J/(mol•K), what differs from the values of the quantum-chemical calculation by 1.52 J/(mol•K). The maximum discrepancy of the calculated values of the heat capacity of willemite in comparison with the experimental data [20] is observed at temperatures of about (90-120) K and does not exceed 4 J/(mol•K) (Fig. 2). Molar entropy in [20] has been estimated as sum Debye and Einstein functions below 51 K, and standard entropy $S_{298.15}$ was given: 131.4±1.2 J/(mol•K), which agree with our value within 2 J/(mol•K).

Table 2
Experimental [5, 12-18] and calculated frequencies of IR and Raman spectra of willemite

	Infrared spectrum									Raman spectrum			
vibra-tion type	v_{exp}, cm^{-1} [5]	v_{exp}, cm^{-1} [12]	v_{exp}, cm^{-1} [13]	v_{exp}, cm^{-1} [14]	v_{exp}, cm^{-1} [15]	v_{exp}, cm^{-1} [16]	v_{exp}, cm^{-1} [17]	v_{calc}, cm^{-1}	dP/dQ, e	vibra-tion type	v_{exp}, cm^{-1} [18]	v_{calc}, cm^{-1}	dP/dQ, e
A_u								90	0.01	$2E_g$	74	88	0.5
										A_g		95	0.3
$2E_u$								99	0.09	$2E_g$		96	0.8
										A_g		104	0.0
$2E_u$								111	0.07	$2E_g$		106	0.9
A_u								122	0.03	A_g		114	0.4
$2E_u$								128	0.02	A_g		121	0.7
A_u								142	0.04	A_g		133	0.1
A_u								150	0.06	$2E_g$		136	0.6
$2E_u$								151	0.06	$2E_g$		145	1.3
A_u								158	0.02	A_g		166	2.2
$2E_u$								191	0.74	$2E_g$		192	2.3
A_u								199	0.88	A_g		194	0.4
$2E_u$								206	0.31	A_g		205	0.2
$2E_u$								220	0.72	$2E_g$		219	2.4
A_u								223	1.02				
A_u								236	0.09	A_g		230	0.2
$2E_u$								239	1.26	$2E_g$		240	2.1
A_u								263	0.00	$2E_g$		260	1.8
										A_g		268	0.6
$2E_u$								279	0.10	$2E_g$		281	3.8
$2E_u$								325	0.25	A_g		335	0.1
A_u								334	0.11	$2E_g$		340	3.8
$2E_u$								354	0.07	$2E_g$		359	2.4
A_u		380				407		367	0.35	A_g		362	3.7
A_u		396				412		374	0.12	$2E_g$		368	1.5
$2E_u$	460	462	460	460	461	457	460	376	0.47	A_g		380	0.7
A_u	580	580	573	577	577	575	572	568	0.27	$2E_g$		577	1.4
$2E_u$								587	0.32	A_g		594	3.1
A_u								598	0.97	A_g		598	2.4
$2E_u$	602	600					591	599	0.65	$2E_g$		600	4.8
A_u								607	1.33	$2E_g$		614	6.3
$2E_u$		617	613	614	612	610	617	612	1.28	A_g		616	4.8
A_u								622	0.93	$2E_g$		619	7.0
$2E_u$								622	0.54	A_g		622	7.0
A_u	872	872	866	868	867	869	869	861	0.15	A_g	864	861	3.3
$2E_u$								863	0.17	$2E_g$		861	1.4
$2E_u$	907	905	901	901	897	891	913	954	1.54	A_g	908	953	1.6
A_u								956	0.15	$2E_g$		955	5.0
$2E_u$	935	934	931	932	932	929	942	959	0.72	A_g	941	959	4.0
A_u								960	1.81	$2E_g$		960	4.9
A_u	980	978	977	980	978	976	980	968	1.10	$2E_g$		968	4.1
$2E_u$								968	1.31	A_g		970	5.4

Table 3
Calculated thermodynamic functions of willemite

| T, K	$C_p^{o}{}_{exp}$ [20], J/(mol·K)	LADY calculation		MOPAC PM5 calculation	
		C_p, J/(mol·K)	$S^{o}{}_T$, J/(mol·K)	C_p, J/(mol·K)	$H^{o}{}_T - H^{o}{}_0$, J/mol
10		0.23	0.07	2.89	23.38
30		7.33	2.45	9.44	128.38
50	20.68	22.19	9.56	22.67	445.7
70	34.29	37.30	19.46	36.51	1038.8
90	46.85	50.602	30.48	49.20	1898.2
110	58.07	61.94	41.76	60.57	2998.1
130	68.24	71.68	52.92	70.79	4313.5
150	77.31	80.20	63.79	79.99	5822.8
170	85.44	87.79	74.30	88.32	7507.3
190	92.85	94.64	84.44	95.88	9350.6
210	99.68	100.87	94.23	102.73	11337.7
230	105.99	106.56	103.66	108.94	13455.5
250	111.72	111.76	112.76	114.57	15691.5
270	116.88	116.52	121.55	119.65	18034.5
290	121.55	120.87	130.03	124.25	20474.4
298.15	123.37	122.54	133.40	125.99	21494.2
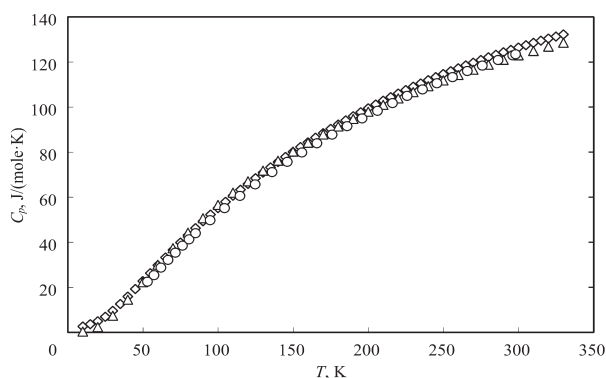
Fig. 2. Temperature dependence of the heat capacity of willemite: ◊ – calculation of MOPAC PM5; ○ – calculation LADY; Δ – experiment (Todd, 1951) [20].

Conclusions

Thus, the vibrational states of a natural mineral willemite have been calculated and its basic thermodynamic functions have been determined by means of a combination of the methods of quantum-chemical calculations and the theory of crystal lattice dynamics. As a result of the calculation a good agreement between the theoretical vibrational spectra and the experimental data has been obtained, and hence the values of thermodynamic functions have been found with sufficient accuracy.

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