CESIUM AND CESIUM-LITHIUM SELENATES

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The Cs_2SeO_4–H_2SeO_4–H_2O and Cs_2SeO_4–Li_2SeO_4–H_2O systems were studied at 30 °C as a basis for determining the conditions for formation of the compound $Cs_4LiH_3(SeO_4)_4$, which has been observed to undergo a ferroelectric phase transition. The results of a solubility study were used to construct a pseudo-ternary cross-section for $CsLiSeO_4$–$CsHSeO_4$–H_2O in the quaternary system Cs_2SeO_4–Li_2SeO_4–H_2SeO_4–H_2O, which demonstrated that, in the region of crystallization of the compound of interest, a substance with the composition $Cs_4LiH_3(SeO_4)_4$ is actually formed. Attention was further paid to the following newly prepared compounds: cesium-lithium selenate hemihydrate, $CsLiSeO_4 \cdot 1/2\ H_2O$, tricesium-lithium bis(selenate) hemihydrate, $Cs_3Li(SeO_4)_2 \cdot 1/2\ H_2O$ and hydrogen tricesium bis(selenate) hemihydrate, $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$, which were characterized by X-ray, spectral and thermoanalytical data.

Key words: Cesium; Selenates; Solubility diagrams; Infrared spectra; Thermoanalytical properties; X-Ray diffraction.

Recently, compounds of the $X_4LiH_3(SeO_4)_4$ type (X = K, Rb, Cs)[1] have been studied, for which ferroelectric phase transitions have been observed and which are characteristic of ferroelectric substances with short hydrogen bonds[2]. The conditions for the formation of these substances are given by the solubility diagram in the four-component system H_2SeO_4–Li_2SeO_4–X_2SeO_4–H_2O. The aim of this work is to study the systems Cs_2SeO_4–H_2SeO_4–H_2O and Cs_2SeO_4–Li_2SeO_4–H_2O that, together with the Li_2SeO_4–H_2SeO_4–H_2O, which we studied[3] at a temperature of 30 °C, forms the faces of the quaternary phase diagram described in general above, giving the conditions for the formation of the compound $Cs_4LiH_3(SeO_4)_4$. Of the known acid selenates of cesium, the substances $CsHSeO_4$ (ref.[4]), $Cs_3H(SeO_4)_2$ (ref.[5]), $Cs_5H_3(SeO_4)_4 \cdot H_2O$ (ref.[6]) and $CsH_3(SeO_4)_2$ (ref.[7]) were described in the literature. $CsHSeO_4$ has a tetragonal scheelite structure[8]. Yokota[9] has stated that this substance is monoclinic with space group *P2/c* at laboratory temperature. A phase transition was found at 401 K by measuring temperature dependence of the

dielectric permittivity[10] and the thermal expansion[11]. Above this temperature, the substance is tetragonal[12]. More detailed research revealed the existence of a total of four phases[13–15] through a conductivity study. The existence of phase transitions and the symmetries of the individual phases were studied using the vibrational spectra[16–18]. The monoclinic phase of $CsHSeO_4$ is isostructural with $CsHSO_4$ (ref.[19]). Phase transitions also occur in $Cs_3H(SeO_4)_2$ and its deuterated crystals. The temperatures of the phase transitions have been found by measuring the relative permittivities[20]. The structure of "phase III" of this substance was determined in ref.[21]. The compound crystallizes in the *C2/m* monoclinic space group and is isostructural with $Ba_3(PO_4)_2$ (ref.[22]). Merinov *et al.*[6] described the preparation of $Cs_5H_3(SeO_4)_4 \cdot H_2O$ under stoichiometric conditions at laboratory temperature; however, it is apparent from the results of this work that this substance is not formed under the given equilibrium conditions at 30 °C or even at 6 °C. Pentacesium trihydrogentetrakis(selenate) is orthorhombic at laboratory temperature and changes to the hexagonal modification at 345 K. Troyanov *et al.*[7] for the first time prepared anhydrous cesium trihydrogenselenate ($CsH_3(SeO_4)_2$) by the reaction of cesium carbonate with 90% H_2SO_4 and studied its crystal structure. The compound crystallize in the $P2_1/c$ monoclinic space group and is isostructural with $KH_3(SeO_4)_3$ and with corresponding sulfates. Of the known lithium selenates anhydrous Li_2SeO_4, its monohydrate and $LiHSeO_4$ were described in the literature. The preparation and conditions for the existence of these substances are given in refs[3,23–25]. Cesium-lithium bis(selenates) have not yet been described.

EXPERIMENTAL

Solubility diagrams. The solubility study was carried out by determining the analytical composition of the liquid phase in a phase complex with known composition. Phase complexes were kept at the temperature of the isotherm under consideration and occasionally shaken. Establishment of equilibrium taking about 20 days was monitored by measuring the refractive index.

Powder X-ray patterns. X-Ray patterns were measured on a URD-6 diffractometer (Freiberg, Germany) in the 2θ range 10–50° using CuKα radiation for the purpose of identification of the solid phases formed in the studied systems. The theoretical powder X-ray patterns of Li_2SeO_4, $Cs_3H(SeO_4)_2$, $CsHSeO_4$ and $Cs_5H_3(SeO_4)_4 \cdot H_2O$ were calculated from the published structural data[4,6,20,24] using the "Lazy pulverix" program[26].

Thermal decomposition. The thermal decomposition was studied on a Derivatograph OD-102 MOM instrument (MOM Budapest) in the 20–700 °C range with a heating rate of 1.25 °C min^{-1}.

Infrared spectra. Infrared spectra were measured on a Perkin–Elmer 684 and Genesis (ATI Mattson) instruments in the 400–4 000 cm^{-1} range. The spectra were measured at laboratory

temperature in a Nujol suspension and, for $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$, also at temperatures of 230, 140 and 90 K.

Analytical methods. Selenic acid was determined alkalimetrically using of NaOH with a concentration of 0.05 mol dm^{-3} and phenolphthalein indicator. Selenium was determined by a modification of the Blanka method[27] by titration of the bromine released by the reaction of Se(VI) and KBr with a volumetric solution of hydrazinium sulfate with a concentration of 0.01 mol dm^{-3}, with controlling the equivalence point potentiometrically. Lithium and cesium were determined by the AAS on a Varian SpectrAA 300/400 instrument at a wavelengths of 670.8 and 852.1 nm, respectively.

Chemicals. Lithium selenate monohydrate and cesium selenate were prepared by neutralization of selenic acid with Li_2CO_3 and Cs_2CO_3, respectively. The compositions of both substances were verified analytically. Cesium carbonate was prepared from cesium bromide according to Brauer[28]. The other chemicals were of analytical grade purity.

RESULTS

The solubility diagram in the Li_2SeO_4–Cs_2SeO_4–H_2O system is depicted in Fig. 1. The crystallization fields of the initial substances (I and VII) are apparent in the diagram, along with that of newly prepared tricesium-lithium bis(selenate) hemihydrate (field III) and the crystallization field of also newly prepared cesium-lithium selenate hemihydrate (field V). The equilibrium between the two solid phases and solutions with compositions corresponding to points E_1, E_2 and E_3 corresponds to fields II, IV and VI. Point E_1 corresponds to the composition 6.57% Li_2SeO_4, 63.98% Cs_2SeO_4 and 29.44% H_2O, point E_2 to the composition 13.11% Li_2SeO_4, 52.08% Cs_2SeO_4

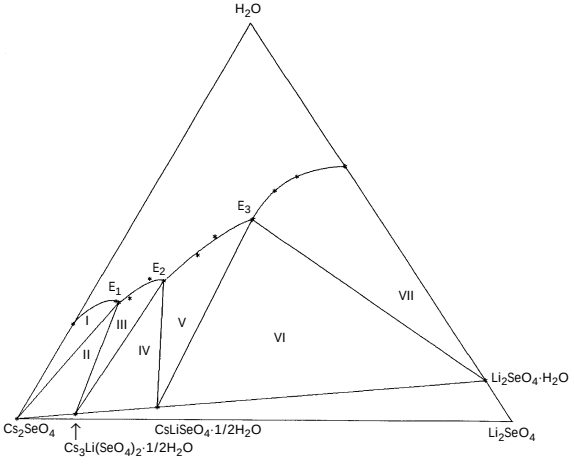

FIG. 1
Solubility diagram of the Cs_2SeO_4–Li_2SeO_4–H_2O system at 30 °C

and 34.81% H_2O and point E_3 to the composition 23.67% Li_2SeO_4, 26.94% Cs_2SeO_4 and 50.39% H_2O. Both the cesium-lithium selenates are congruently soluble. These substances were prepared for further study on the basis of the solubility diagram by crystallization from the originally unsaturated solutions with stoichiometric composition and recrystallization from water. The composition corresponded to the calculated values. Elemental analysis (calculated for $CsLiSeO_4 \cdot 1/2\ H_2O$ (291.8)): 26.59% (27.06%) Se, 2.41% (2.38%) Li, 43.92% (45.54%) Cs, 3.22% (3.08%) H_2O. Elemental analysis (calculated for $Cs_3Li(SeO_4)_2 \cdot 1/2\ H_2O$ (700.6)): 22.04% (22.54%) Se, 0.94% (0.99%) Li, 56.64% (56.91%) Cs, 1.65% (1.28%) H_2O.

The solubility diagram on the Cs_2SeO_4–H_2SeO_4–H_2O system at 30 °C is depicted in Fig. 2. The crystallization field of cesium selenate (Cs_2SeO_4 – field I) is apparent from the diagram, along with the crystallization field of tricesium hydrogenbis(selenate) (field III), cesium hydrogenselenate (field V) and, in all probability, also cesium trihydrogenbis(selenate) (field VII). Equilibrium between the two solid phases and a solution with a composition corresponding to eutonic points E_1, E_2 and E_3 corresponds to fields II, IV and VI. Point E_1 corresponds to the composition 64.81% Cs_2SeO_4, 7.59% H_2SeO_4 and 27.60% H_2O, point E_2 to the 52.95% Cs_2SeO_4, 19.66% H_2SeO_4 and 27.38% H_2O and point E_3 to the composition 37.66% Cs_2SeO_4, 50.96% H_2SeO_4 and 11.39% H_2O. Tricesium hydrogenbis(selenate) is congruently soluble and can be prepared by crystallization from a solution with the stoichiometric composition. However, a slight excess of H_2SeO_4 is of advantage for preparation of cesium hydrogenselenate from aqueous solution at

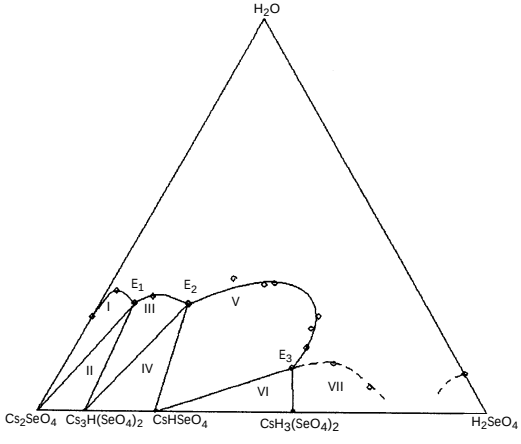

FIG. 2
Solubility diagram of the Cs_2SeO_4–H_2SeO_4–H_2O system at 30 °C

30 °C, as follows from the solubility diagram. The identities of both substances were confirmed by measuring the powder X-ray patterns, which were compared with the X-ray patterns calculated from the structural data. Both these substances have been described extensively in the literature and their properties have been studied in detail (see the literature[1–25]). The existence of cesium trihydrogenbis(selenate) can be expected on the basis of study of the solubility diagram and according to the published data; however, the substance could not be isolated from highly viscous solutions with high contents of selenic acid. The hatched part of the diagram in the vicinity of the point corresponding to selenic acid was not studied experimentally in details.

A part of the solubility diagram in the Cs_2SeO_4–H_2SeO_4–H_2O system was studied at 6 °C in the region of the expected crystallization field of $Cs_5H_3(SeO_4)_4 \cdot H_2O$. Part of the crystallization field of $CsHSeO_4$ is apparent from the diagram, as is the part of the crystallization field of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$, which is not formed at 30 °C and has not yet been described in the literature. Equilibrium between these two solid phases corresponds to the invariant composition of the liquid phase (eutonic point): 65.8% Cs_2SeO_4, 19.8% H_2SeO_4 and 14.4% H_2O. Tricesium hydrogenbis(selenate) hemihydrate is congruently soluble at 6 °C and can be prepared by crystallization from a solution with stoichiometric composition at this temperature. The identity of this new phase was confirmed analytically (calculated: 22.8% Se, 57.6% Cs, 1.3% H_2O; found: 22.4% Se, 57.0% Cs, 1.5% H_2O) and the powder X-ray pattern was measured, which is different from the corresponding anhydrous salt and from cesium hydrogen selenate, crystallization field of which being adjacent to the hemihydrate.

TABLE I
Composition of the phases in pseudo-ternary system

Sample	$LiCsSeO_4$, %	$CsHSeO_4$, %	H_2O, %	Solid phase
1	16.39	68.64	14.97	$CsHSeO_4$
2	20.25	61.76	17.99	$CsHSeO_4$
3	29.03	47.98	22.99	$Cs_4LiH_3(SeO_4)_4$
4	46.18	31.93	21.89	$Cs_4LiH_3(SeO_4)_4$ + $CsLiSeO_4 \cdot 1/2\ H_2O$
5	57.49	14.52	27.99	$CsLiSeO_4 \cdot 1/2\ H_2O$

Table I gives the composition of samples 1–5 of the above pseudo-ternary system. The range of compositions was selected to cover the whole system. Establishment of equilibrium was monitored as set forth above. The equilibrium solid phases were identified by X-ray measurements.

All the spectra are given in Tables II and III. Assignment of the vibration modes and the cited references are given in the discussion. The temperature dependence of the infrared spectra of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$ in the range 90–298 K is given in Fig. 3. The thermal decomposition of cesium-lithium selenates was studied only for the purpose of determination of the water of crystallization and the results are given in the part on the properties of these substances. The thermal decomposition of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$ is given in Table IV.

DISCUSSION

Solubility Diagrams

The study of the solubility diagram in the Li_2SeO_4–Cs_2SeO_4–H_2O system at 30 °C demonstrated the existence of two so-far not described congruently sol-

TABLE II
Infrared spectra of $CsLiSeO_4 \cdot 1/2\ H_2O$ and $Cs_3Li(SeO_4) \cdot 1/2\ H_2O$

Wavenumber, cm^{-1}	Assigment	Wavenumber, cm^{-1}	Assigment
$CsLiSeO_4 \cdot 1/2\ H_2O$		$Cs_3Li(SeO_4)_2 \cdot 1/2\ H_2O$	
3 414 m	$\nu_1(H_2O)$	3 419 m	$\nu_1(H_2O)$
3 463 m	$\nu_1(H_2O)$	3 412 m	$\nu_1(H_2O)$
1 649 m	$\delta(H_2O)$	3 164 m	$\nu_1(H_2O)$
1 151 w	?	1 649 m	$\delta(H_2O)$
902 s	$\nu_3(SeO_4)$	1 150 w	?
862 s	$\nu_1(SeO_4)$	905 w	$\nu_3(SeO_4)$
484 s	$\rho(H_2O)$	859 s	$\nu_1(SeO_4)$
452 s	$\nu_4(SeO_4)$	519 m	$\nu_4(SeO_4)$
442 s	$\nu_4(SeO_4)$	479 m	$\rho(H_2O)$
411 s	$\nu_4(SeO_4)$	409 s	$\nu_4(SeO_4)$
370 m	$\nu_1(SeO_4)$	354 m	$\nu_4(SeO_4)$

uble compounds, cesium-lithium selenate hemihydrate, $CsLiSeO_4 \cdot 1/2\ H_2O$, and tricesium-lithium bis(selenate) hemihydrate, $Cs_3Li(SeO_4)_2 \cdot 1/2\ H_2O$. The conditions under which these substances can be prepared and isolated are also apparent from the diagram.

In the Cs_2SeO_4–H_2SeO_4–H_2O system, two substances described in the literature are formed at 30 °C, $Cs_3H(SeO_4)_2$ and $CsHSeO_4$. Their identity was confirmed by their powder X-ray patterns, which are in good agreement with the X-ray diffraction patterns calculated from the structural data for

TABLE III
Infrared spectrum of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$

Wavenumber, cm^{-1}		Assigment
90 K	293 K	
3 516 vs	3 515 m	$\nu(H_2O)$
3 464 vs	3 464 m	$\nu(H_2O)$
2 311 s	2 356 m	ν(SeO–H)
2 179 m	–	ν(SeO–H)
2 044 m	–	ν(SeO–H)
1 758 sh	–	$\delta(H_2O)$
1 702 m	–	$\delta(H_2O)$
1 639 s	1 635 m	$\delta(H_2O)$
1 612 sh	–	$\delta(H_2O)$
1 352 s	1 349 m	δ(Se–O–H)
1 319 m	1 302 m	δ(Se–O–H)
1 287 m	1 274 m	δ(Se–O–H)
1 200 w	–	δ(Se–O–H)
1 169 w	1 169 w	δ(Se–O–H)
1 154 w	1 156 w	δ(Se–O–H)
935 vs	–	$\nu_{as}(SeO_3)$
926 vs	926 vs	$\nu_{as}(SeO_3)$
917 vs	915 vs	$\nu_{as}(SeO_3)$
872 s	870 s	$\nu_s(SeO_3)$
868 s	–	$\nu_s(SeO_3)$

TABLE IV
Data for the thermal decomposition of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$

T, °C	TG decrease % found	Weight decrease % calculated	DTA	Assigment
80	0	0	*endo*	phase transition
200	1.5	1.3	*endo*	$-0.5\ H_2O$
260	2.1	2.0	*endo*	$-0.25\ H_2O$
305	2.8	2.6	*endo*	$-0.25\ H_2O$
480	18.8	20.6	*endo*	$-SeO_2$; $-0.5\ O_2$
575	19.0	20.6	*endo*	phase transition Cs_2SeO_4

both substances. The existence of the $CsH_3(SeO_4)_2$ phase can also be assumed; however, even after long standing in a desiccator, this could not be isolated in a state in which it could be characterized. The compound was mentioned in the literature[7].

The above system was also studied at a lower temperature (6 °C) because Merinov *et al.*[6] described the preparation of the $Cs_5H_3(SeO_4)_4 \cdot H_2O$ phase

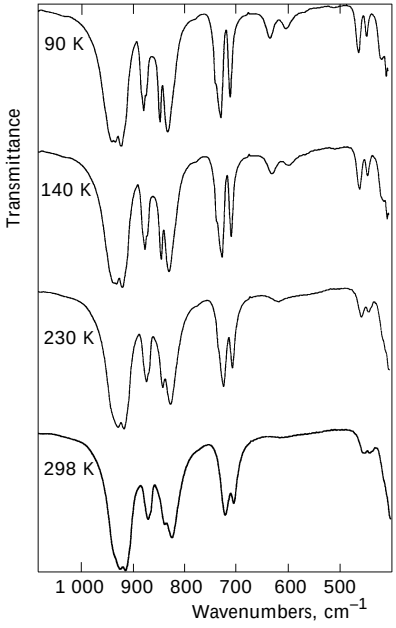

FIG. 3
Part of infrared spectra of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$ at various temperatures

and studied its structure. However, even at the low temperature, we did not manage to find the solubility field of this compound in the solubility diagram. The powder X-ray patterns of the studied solid phases in the region of their fields in the diagram always corresponded to a mixture of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$ and $CsHSeO_4$. This fact can most probably be explained by the metastability of the $Cs_5H_3(SeO_4)_4 \cdot H_2O$ phase. When this substances primarily crystallized, during the three weeks when the system is approaching equilibrium, it decomposes to the thermodynamically stable phases consisting of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$ and $CsHSeO_4$. The study of the solubility diagram in the Cs_2SeO_4–H_2SeO_4–H_2O system at 6 °C, however, led to the discovery of a phase, not described in the literature consisting of tricesium hydrogenbis(selenate) hemihydrate, whose crystallization field appears in the place of the crystallization field corresponding to the anhydrous salt. Thus, at 6 °C, the hemihydrate with stoichiometric composition crystallizes from solution, while the anhydrous salt crystallizes out at 30 °C.

The study of the solid phases of the pseudo-ternary system $CsHSeO_4$–$CsLiSeO_4$–H_2O in the quaternary system given above led to the following results: The powder X-ray patterns of the solid phases of samples 1 and 2 (in Table I) correspond to $CsHSeO_4$. The X-ray pattern of the solid phase of sample 3 (in Table I) corresponds to another chemical species. Elemental analysis corresponds to the composition $Cs_4LiH_3(SeO_4)_4$, *i.e.* a substance that has been described in ref.[1] (calculated: 47.8% Cs, 28.4% Se, 0.62% Li; found: 47.5% Cs, 27.7% Se, 0.67% Li). The X-ray pattern of sample 4 (in Table I) corresponds to a mixture of the solid phase from sample 3 and $CsLiSeO_4 \cdot 1/2\ H_2O$. The X-ray pattern of the solid phase from sample 5 (in Table I) corresponds to $CsLiSeO_4 \cdot 1/2\ H_2O$. It follows from this study that the cross-section for $CsHSeO_4$–$CsLiSeO_4$–H_2O in the Cs_2SeO_4–H_2SeO_4–Li_2SeO_4–H_2O quaternary system is probably a stable diagonal and that the crystallization field of the expected compound $Cs_4LiH_3(SeO_4)_4$ occurs on it; this compound is incongruently soluble and can probably be prepared by heterogeneous reaction in water according to the equation:

$$3\ CsHSeO_4 + CsLiSeO_4 \rightarrow Cs_4LiH_3(SeO_4)_4\ .$$

The Properties of $CsLiSeO_4 \cdot 1/2\ H_2O$ and $Cs_3Li(SeO_4)_2 \cdot 1/2\ H_2O$

Both substances crystallize quite well; however, attempts to carry out X-ray structural analyses have not been successful because of twinning. Cesium-

lithium selenate loses its water of crystallization above 140 °C and decomposition is complete at 260 °C with maximum weight loss at 190 °C (by DTG); tricesium-lithium bis(selenate) also loses its water of crystallization from 140 to 260 °C with maximum loss at 185 °C and both substances are converted to the corresponding anhydrous salts. The infrared spectra showed the stretching vibration modes of water in the range 3 416–3 164 cm^{-1}, deformation modes at 1 649 cm^{-1} and libration vibrations in the range 484–479 cm^{-1}. The stretching and deformation vibrations of the selenate anion are in good agreement with the published data[29,30].

The Properties of $Cs_3H(SeO_4)_2 \cdot 1/2\ H_2O$

The presence of water of crystallization in the compound is confirmed by the infrared spectrum (see below) and thermoanalytical properties. A total of six *endo*-effects appear on the DTA curve. The first (at 80 °C) apparently corresponds to a phase transition. The second (at 200 °C) corresponds to a loss of water of crystallization. Further two *endo*-effects (at 260 and 305 °C) correspond to gradual decomposition of the hydrogen selenate anion in the original salt with an overall loss of 0.5 mol of water per mol of the original salt, with the formation of 0.5 mol of diselenate and 1 mol of cesium selenate. The fifth *endo*-effect at 485 °C corresponds to complete decomposition of the diselenate with the loss of selenium(IV) oxide and oxygen (selenium(VI) oxide no longer exists at this temperature[31]) and the formation of cesium oxide. At 575 °C cesium selenate undergoes a polymorphic conversion[32] (the sixth *endo*-effect).

The infrared spectra of tricesium hydrogenbis(selenate) hemihydrate at all temperatures from 90 to 298 K contain stretching (3 516–3 464 cm^{-1}) and deformation (1 612–1 758 cm^{-1}) vibrations of hydrated water, which are split into multiple peaks at lower temperatures. The spectrum further shows bands corresponding to the stretching (2 311–2 044 cm^{-1}) and deformation (1 349–1 154 cm^{-1}) vibrations of the Se–OH groups. The symmetrical stretching vibration of Se–OH lies at 598–721 cm^{-1}, and this vibration is also split into multiple peaks at lower temperatures. The spectrum also contains the stretching and deformation vibrations of selenate and hydrogenselenate ions to an extent corresponding to the literature data[33,34].

However, no marked changes occur in the overall character of the spectrum at low temperatures, which would indicate any rearrangement of protons in hydrogen bonds between the anions. In addition to temperature effects, the observed changes can be assigned to certain structural changes associated with a decrease in the local symmetry of the hydrogen selenate

anion. Thus, it is not possible to exclude a structural phase transition; however, a change in the proton dynamics in the hydrogen bonds apparently does not play any role in its mechanism.

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