LITHIUM AND AMMONIUM SELENATES

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Received November 29, 1994
Accepted March 16, 1995

The Li_2SeO_4–H_2SeO_4–H_2O and $(NH_4)_2SeO_4$–Li_2SeO_4–H_2O systems were studied at 30 °C to obtain data for determining the conditions of formation of the compound $(NH_4)_4LiH_3(SeO_4)_4$, whose characteristics correspond to those of substances possessing significant dielectric properties. The results were used to construct the pseudoternary $LiNH_4SeO_4$–NH_4HSeO_4–H_2O section in the quaternary system, which gave evidence that only $(NH_4)_3H(SeO_4)_2$ forms in the crystallization region of the compound sought. Attention was also paid to lithium ammonium selenate, which was characterized by its X-ray, spectral, and thermal analysis data.

Compounds of the $X_4LiH_3(SeO_4)_4$ type with X = K, Rb, or Cs have been studied recently[1], and a ferroelectric phase transition characteristic of ferroelectrics involving short hydrogen bonds has been observed for them[2]. The conditions of formation of such compounds are specified by the solubility diagram of the H_2SeO_4–Li_2SeO_4–X_2SeO_4–H_2O quaternary system, which can be depicted in the triangular pyramid or prism projection. The present study was devoted to the Li_2SeO_4–H_2SeO_4–H_2O and $(NH_4)_2SeO_4$–Li_2SeO_4–H_2O systems which, together with the $(NH_4)_2SeO_4$–H_2SeO_4–H_2O system examined by King[3] at 30 °C, form the sides of the quaternary phase diagram described in general terms above, specifying the conditions of formation of the compound $(NH_4)_4LiH_3(SeO_4)_4$.

From among the known ammonium selenates, the selenates NH_4HSeO_4 and $(NH_4)_3H(SeO_4)_2$ have been found in the above-mentioned solubility diagram[3]; the preparation and structure of ammonium hydrogen selenate have been described more recently in refs[4,5]; and the phase transitions and structure properties of the phases have been studied in refs[6–9]. For triammonium hydrogen bis(selenate), the structure has been determined by Kishimoto and coworkers[10]. In addition to those substances, whose conditions of existence are specified by the above solubility diagram to a sufficient extent, the structure of a phase whose composition is $(NH_4)_4H_2(SeO_4)_3$ has been determined by Kruglig and coworkers[11], who prepared it from aqueous solutions at 28 °C. Hence, if the solubility diagram presented by King has been measured with a sufficient accuracy, the compound described by Kruglig and coworkers must decompose at temperatures lower than 30 °C.

Only two lithium selenates are known, viz. the anhydrous Li_2SeO_4 and its monohydrate. Their preparation and conditions of existence have been dealt with in refs[12,13].

The preparation of lithium ammonium selenate has been attempted by Petrlik[14], viz. by a modified temperature gradient method in a Teflon-lined autoclave. However, crystals of anhydrous Li_2SeO_4 only emerged; their structure was determined. Nevertheless, lithium ammonium selenate has been prepared, its infrared spectrum studied[15], and structure determined[16].

EXPERIMENTAL

Solubility diagrams. The balance method was applied[17,18]. For some samples in the system, this method was supplemented with analysis of the liquid phase. Samples were thermostatted at 30 °C and agitated occasionally. The process of equilibrium establishing, which took 12–14 days, was monitored by refractive index measurements. For the Li_2SeO_4–H_2SeO_4–H_2O system, a segment of the diagram was constructed by applying the conventional Schreinemakers method[19].

Powder X-ray diffraction patterns. The X-ray diffractograms were obtained by the Debye–Scherrer method with the aim to identify solid phases forming in the systems studied. The photographs were evaluated visually on a comparator. The powder X-ray diffraction patterns of $LiNH_4SeO_4$ were obtained on a URD-6 diffractometer. The theoretical powder diffraction patterns of Li_2SeO_4, NH_4HSeO_4, $(NH_4)_4H_2(SeO_4)_3$, and $LiNH_4SeO_4$ were calculated by the “Lazy Pulverix” code based on structure data published in refs[4,10,11,14,16,20].

Thermal decomposition. The differential thermal analysis (DTA) and thermogravimetry (TG) techniques were employed by using a Derivatograph instrument (MOM, Budapest) over the temperature range of 20–600 °C in the linear temperature increase mode at a rate of 2.5 °C/min.

Infrared spectra. The spectra of Nujol mulls were scanned on a Perkin–Elmer 684 infrared spectrophotometer over the 470–4 000 cm^{-1} region at room temperature. Tripene mulls were also measured within the H_2O and NH_4^+ stretching and bending mode regions.

Raman spectra. A JRS-S1 laser Raman spectrometer (JEOL, Tokyo) was employed; excitation line 488 nm, scanning region 60–3 500 cm^{-1}.

Analytical methods. Selenic acid was determined alkalimetrically with a titrimetric solution of NaOH (0.1 mol/dm^3) using phenolphthalein as the indicator. Selenium was determined by a modified method after Blanka and coworkers[21], namely so that bromine liberated by reaction of hexavalent selenium with KBr was titrated with a solution of hydrazinium sulfate (0.1 mol dm^{-3}). Several drops of barium chloride were added before attaining the end point in order to make the color transition from deep yellow to colourless clearer. Lithium was quantitated by atomic absorption spectrometry on a Varian instrument at 670.8 nm. Nitrogen was determined with a Perkin–Elmer elemental analyzer.

Chemicals. Lithium selenate monohydrate was prepared by neutralization of lithium carbonate with selenic acid. Ammonium selenate was synthesized by neutralization of ammonia. The composition of the two compounds was verified analytically. All the other chemicals were of reagent grade purity.

RESULTS

Solubility Study

The solubility diagram of the Li_2SeO_4–$(NH_4)_2SeO_4$–H_2O system at 30 °C is shown in Fig. 1. The diagram exhibits crystallization fields of the starting substances (fields I and V) and the crystallization field of lithium ammonium selenate (field III). Fields II and IV correspond to the equilibrium between two solid phases and solutions whose composition corresponds to points E_1 and E_2, respectively. The composition corresponding to point E_1 is 24.16% Li_2SeO_4, 23.56% $(NH_4)_2SeO_4$, and 47.72% H_2O, that corresponding to point E_2 is 14.45% Li_2SeO_4, 40.60% $(NH_4)_2SeO_4$, and 45.11% H_2O. Lithium ammonium selenate is congruently soluble. For further investigation, this compound was prepared, based on the solubility diagram, by crystallization from an initially unsaturated solution with the stoichiometric composition, followed by recrystallization from

TABLE I
Composition of the pseudoternary system samples (%)

Sample	$LiNH_4SeO_4$	NH_4HSeO_4	H_2O
1	34.58	25.45	39.97
2	33.70	34.15	32.15
3	26.07	51.93	22.00
4	19.00	56.61	24.39
5	14.63	60.57	24.80

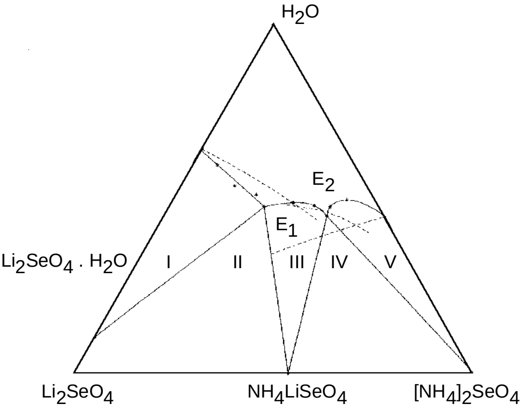

FIG. 1
Solubility diagram of the $(NH_4)_2SeO_4$–Li_2SeO_4–H_2O system at 30 °C. Description given in the text

water. The composition matched the calculated values (calculated: 47.02% Se, 4.13% Li, 8.34% N; found: 47.32% Se, 4.05% Li, 8.11% N). The solubility diagram for the Li_2SeO_4–H_2SeO_4–H_2O system at 30 °C is shown in Fig. 2, exhibiting the crystallization fields of the starting lithium selenate monohydrate (field I) and anhydrous lithium selenate (field III). Field II is associated with the equilibrium between the two solid phases and the solution whose composition corresponds to the peritonic point P, where the composition is 16.64% Li_2SeO_4, 41.49% H_2SeO_4, and 42.17% H_2O. Anhydrous lithium selenate is incongruently soluble and, as the solubility diagram documents, can only be prepared from strongly acidic aqueous solutions. The dashed region of the diagram near the selenic acid point was not examined experimentally.

The $LiNH_4SeO_4$–NH_4HSeO_4–H_2O Pseudoternary System

The composition of samples 1–5 of the pseudoternary system is given in Table I. The composition range was chosen so as to cover the entire system. The establishment of equilibrium was monitored as described earlier. The equilibrium solid phases were identified by X-ray diffraction measurement.

Infrared and Raman Spectra of Lithium Ammonium Selenate

The spectral data are given in Table II. The vibrational mode assignment and references are given in Discussion.

Thermal Decomposition of Lithium Ammonium Selenate

The thermal analysis curve is evaluated in Table III. For effects on the DTA curve, their ends are tabulated. The intermediate and final thermal decomposition products

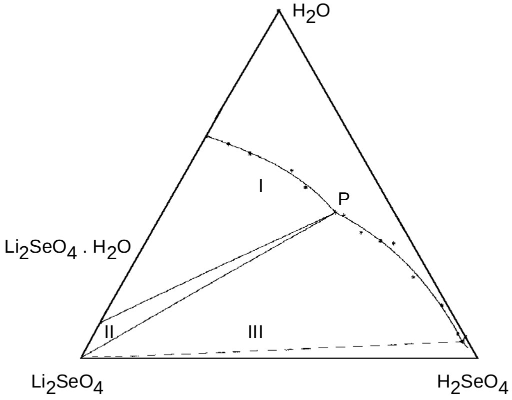

FIG. 2
Solubility diagram of the Li_2SeO_4–H_2SeO_4–H_2O system at 30 °C. Description given in the text

were identified by X-ray diffraction measurement. The assignment of the effects and references are given in Discussion.

DISCUSSION

Solubility Diagrams

No lithium hydrogen selenate was found based on the solubility diagram of the Li_2SeO_4–H_2SeO_4–H_2O system at 30 °C. The diagram also exhibits conditions in which anhydrous lithium selenate can be prepared in a straightforward manner from aqueous

TABLE II
Bands in the infrared and Raman spectra[a] of $LiNH_4SeO_4$

Raman spectrum		Infrared spectrum	
cm^{-1}	assigment	cm^{-1}	assigment
125 vw	lattice vibrations		
150 vw			
210 vw			
340 m	$\nu_2(SO_4^{2-})$		
355 m			
455 w	$\nu_4(SO_4^{2-})$	450 m	$\nu_4(SO_4^{2-})$
850 vs	$\nu_1(SO_4^{2-})$		
870 m		870 s	$\nu_1(SO_4^{2-})$ and
910 m	$\nu_3(SO_4^{2-})$		$\nu_3(SO_4^{2-})$
925 m			
1 435 m	$\nu_4(NH_4^+)$	1 431 s	$\nu_4(NH_4^+)$
1 635 w	δ H_2O (moisture)	1 676 w	δ H_2O (moisture)
1 700 w	$\nu_2(NH_4^+)$		
1 715 w		1 720 m	$\nu_2(NH_4^+)$
2 820 w	2 $\nu_4(NH_4^+)$		
2 875 w		2 869 m	2 $\nu_4(NH_4^+)$
2 980 w	$\nu_1(NH_4^+)$ and		
3 110 w	$\nu_3(NH_4^+)$	3 000 – 3 060 vs	$\nu_1(NH_4^+)$ and
3 175 w	ν H_2O (moisture)	3 200 vs	$\nu_3(NH_4^+)$

[a] Band intensities: vs very strong, s strong, m medium, w weak, vw very weak.

solutions. Its crystallization field is large indeed, and so there is no problem in determining the composition of a solution from which the compound can be obtained by crystallization. In this context, the preparation by hydrothermal reaction in an autoclave[14] appears to be unnecessarily complicated. The diagram is also interesting from another aspect: although not very rare in general, the fact that the action of acids at higher concentrations results in a dehydration of hydrates to give anhydrous salts is rather unusual for the lithium salt.

In the $(NH_4)_2SeO_4$–Li_2SeO_4–H_2O system, only one double salt, viz. $LiNH_4SeO_4$, forms at 30 °C. This salt is congruently soluble, with a sufficiently large crystallization field. No other double salt was detected. The anhydrous salt of the corresponding composition has been described in literature. The shapes of the solubility curves in this system can be calculated following ref.[22] based on the idealizing assumption that the activity coefficients of the components are constant. The calculated solubility curves are shown as dashed lines in Fig. 1. The experimental solubility curve of ammonium selenate lies higher than the calculated curve, which means that its actual solubility in the ternary system is lower than the theoretical value. Such differences are typical of systems where lithium salts are the second components because by withdrawing water, lithium – a strongly hydrating cation – induces a decrease in the solubility of the first component (ammonium selenate in this case). For lithium selenate the solubility curve lies lower than the calculated curve, which implies that the actual solubility of this salt is lower than the calculated solubility.

Tentative investigation of the $LiNH_4SeO_4$–NH_4HSeO_4–H_2O pseudoternary section in the quaternary system mentioned in the introductory part showed that this section is not stable. The equilibrium solid phases were studied by X-ray diffraction, and the following solid phases were found to correspond to the samples whose numbering is given in Table I: 1, 2 $LiNH_4SeO_4$, and 3, 4, 5 $(NH_4)_3H(SeO_4)_2$. The above facts indicate that although the imaging point of the expected compound $(NH_4)_4LiH_3(SeO_4)_4$ lies on this

TABLE III
Thermal decomposition of $LiNH_4SeO_4$

T, °C	DTA	TG	$-\Delta m$, % found	Assignment	$-\Delta m$, % theory
230	*exo*	–	–	liberation of NH_3, oxygen and water	
260–290	–	plateau	25.62	$Li_2Se_2O_5$	25.03
360	*endo*	–	–	liberation SeO_2	
410–445	–	plateau	56.13	Li_2SeO_3	58.07
470	*endo*	–	–	melting	

section (the substance can be formally written as 3 $NH_4HSeO_4 . LiNH_4SeO_4$), only triammonium hydrogen bis(selenate), whose imaging point does not lie on the section, crystallizes at a composition near to that of the above point. Although those facts do not provide unambiguously evidence that the compound cannot exist, its crystallization field in the quaternary system would have to lie beyond the pseudoternary section studied, which is very improbable.

Properties of Lithium Ammonium Selenate

Based on the structure determined[16], the theoretical powder X-ray patterns were calculated and compared with the observed data; the agreement was very good.

Thermal decomposition of lithium ammonium selenate involves reduction of the compound at 230 °C and its transformation to lithium diselenite accompanied by liberation of ammonia and oxygen, as described by the equation

$$2\ LiNH_4SeO_4 \longrightarrow 2\ NH_3 + O_2 + Li_2Se_2O_5 + H_2O\ . \qquad (A)$$

The identity of lithium diselenite was confirmed by X-ray diffractometry[23]. The process is first accompanied by blackening of the substance due to the separation of some elemental selenium; in a time, however, lithium diselenite remains as the only solid present. This compound decomposes further to lithium selenite at 360 °C, in accordance with published data[23].

Vibrational spectra of lithium ammonium selenate are consistent with published data of the ammonium cation and selenate anion[24,25]. Comparing the Raman spectrum with that published in ref.[15], the wavenumbers of the ν_1 and ν_3 vibrations are found identical to within ±4 cm^{-1}. The ν_2 and ν_4 vibrations are split to a lower degree in our spectrum than in ref.[15]. This also applies to the infrared spectra, except for the ν_2 vibrations which lie beyond the IR measuring region. In the ammonium cation vibration range, both spectra exhibit a band at 2 870 cm^{-1} corresponding to the ν_4 overtone.

This work was supported by Grant No. 203/93/0154 of the Grant Agency of the Czech Republic.

REFERENCES

1. Pietraszko A., Lukaszewicz K.: Z. Kristallogr. *185*, 564 (1988).
2. Brezina B., Glogar P.: *Ferroelektrika*, p. 112. Academia, Praha 1973.
3. King G. B.: J. Phys. Chem. *41*, 797 (1937).
4. Aleksandrov K. S., Kruglig A. I., Misyul S. V., Simonov M. A.: Kristallografiya *25*, 1142 (1980).

5. Sukhovskii A. A., Aleksandrova I. P., Mokvich Yu. N., Rozanov O. V.: Phys. Status Solidi A *105*, 145 (1988).
6. Czapla Z., Lis T., Sobczyk Z.: Phys. Status Solidi A *51*, 609 (1979).
7. Krasikov V. S., Kruglig A. I.: Fiz. Tverd. Tela *21*, 355 (1984).
8. Czapla Z., Pykacz H., Sobczyk L.: Ferroelectrics *769*, 291 (1981).
9. Kroupa J., Czapla Z.: Phys. Status Solidi A *61*, 117 (1981).
10. Kishimoto T., Osaka T., Komutue M., Makita Y.: J. Phys. Soc. Jpn. *56*, 2070 (1989).
11. Kruglig A. I., Simonov M. A.: Kristallografiya *22*, 1082 (1977).
12. Orlyanski Yu. N., Dmitrenko S. L.: Zh. Neorg. Khim. *26*, 291 (1981).
13. Pistorius J.: J. Phys. Chem. Solids *28*, 1811 (1967).
14. Petrlik F.: Acta Crystallogr., C *45*, 158 (1989).
15. Sankaranarayanan V. N., Krishnan R. S.: Proc. Indian Acad. Sci., A *76*, 267 (1972).
16. Waskowska A., Allman R.: Cryst. Struct. Commun. *11*, 2029 (1982).
17. Eysseltova J., Kovarova B.: Chem. Papers *39*, 607 (1985).
18. Eysseltova J., Micka Z., Walzelova M.: Chem. Papers *46*, 218 (1992).
19. Schreinemakers F. A. H.: Z. Phys. Chem. *11*, 75 (1993).
20. Lukaszewicz K., Pietraszko A., Augustyniak M. A.: Acta Crystallogr., C *49*, 430 (1993).
21. Blanka B., Hudec P., Mosna P., Touzin J.: Collect. Czech. Chem. Commun. *28*, 3434 (1963).
22. Vojtisek P., Havlicek D., Ebert M.: Electrochim. Acta *31*, 1609 (1986).
23. Micka Z., Ebert M., France P., Ptacek P.: Chem. Papers *40*, 309 (1986).
24. Horak M., Papousek D.: *Infracervena spektra a struktura molekul*, pp. 241, 775. Academia, Praha 1976.
25. Nakamoto K.: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, pp. 131, 138. Wiley, New York 1978.