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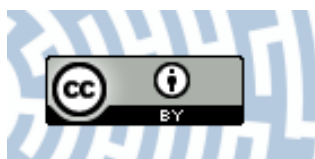
Detection of a ferroelastic phase transition in $Cs_x(NH_4)_{1-x}LiSO_4$ with the use of the DSC method

Piotr Czaja

Abstract In this paper the technology of producing solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ using the slow evaporation method is presented. Appropriate conditions were chosen to grow large samples. The ammonium ion content in the solid solutions was determined using the Kjeldahl method. It was found that the real ammonium ion concentration is twice lower than the one applied in the initial substances. At room temperature, the base crystal, lithium cesium sulfate ($CsLiSO_4$), is paraelastic, whereas lithium ammonium sulfate (NH_4LiSO_4) is ferroelectric. It is expected that as a result of substituting Cs^+ ions with NH_4^+ ions, instead of the Cs^+ ions, the modification of the ferroic properties of solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ will take place. Tests conducted with the use of the differential scanning calorimetry method (DSC) allowed the detection of the ferroelastic phase transition which takes place in these compounds. A gradual increase of temperature transition was observed from 202 K for the pure $CsLiSO_4$ to 203.8 K for $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ and 230.1 K for $Cs_{0.85}(NH_4)_{0.15}LiSO_4$ with the increase of NH_4^+ ions concentration. Using polarized light microscopy, a ferroelastic domain structure was detected in the examined solid solutions, which appeared below the structural phase transition temperature.

Keywords Solid solutions · Ferroelastic phase transition · DSC · Polarization microscopy · Kjeldahl method

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Introduction

Crystals of solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ belong to the family of double sulfates with general formula being $ALiSO_4$, where: $A = (Cs, NH_4, Rb, K, Na)$. The crystalline structure of these compounds may be considered as a small distortion of the prototype structure α-K_2SO_4 with $P6_3$/mmc symmetry [1]. For majority of compounds, this phase is not observed experimentally. However, the most widespread low-temperature implementation of the α-K_2SO_4 lattice is the β-K_2SO_4 structure which is characterized by a lattice of a rhombic symmetry [2]. These compounds have a characteristic skeletal structure, which is a derivative of the tridymite structure. It consists of two types of tetrahedrons: LiO_4 and SO_4 [3].

During lowering the temperature, the β-K_2SO_4 crystalline modification very often loses its stability and as a result of a single phase transition or a sequence of transitions, the crystals transform into: ferroelectric, ferroelastic, or incommensurate phases. The variety of phases is also largely influenced by the "chemical" pressure which may be changed by the replacement of cations and anions in the β-K_2SO_4 structure [4].

The base crystals of the solid solution of $Cs_x(NH_4)_{1-x}LiSO_4$: lithium cesium sulfate $CsLiSO_4$ (LCS) and lithium ammonium sulfate β-NH_4LiSO_4 (LAS) crystallize at room temperature in the rhombic system [3, 5]. In these compounds, depending on the size of the A cation, the structural phase transition from the rhombic phase to the ferroleastic monoclinic phase takes place directly as it happens in case of the $CsLiSO_4$ crystal [5–10] or via the ferroelectric phase as for the β-NH_4LiSO_4 crystal [4, 11–14].

The application of newly produced materials very often depends on possibilities of obtaining the desired properties at room temperature. This aim may be reached by obtaining

solid solutions of base compounds, modifying not only the values of the structural phase transition temperature but also their properties. Due to a series of very interesting physical properties, including the ferroic properties, solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ became recently an object of intensively developed research.

Crystals of solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$, where $0 \leq x \leq 1$ were object of investigations with the use of optical and calorimetric methods [4, 15]. Areas of crystalline structures of various symmetries were identified based on the tests results. Suitable data were presented in the phase diagram x–T in Fig. 1. The extreme points of the diagram correspond, respectively, to the β-LAS ($x = 0$) and LCS ($x = 1$) compounds and for $x = 0.4$ the triple point is visible, where phases with Pmcn, $P2_1cn$, and $P112_1/n$ symmetries come together. Optical tests have shown that even a slight replacement of far larger Cs^+ cations with NH_4^+ cations influences the optical properties of crystals and also the character of the phase transition; however, its ferroelastic nature remains unchanged. With growing content of the NH_4^+ ions concentration, the temperature of ferroelastic transition (for LCS $T_c = 202$ K) increases, as well as the rotation angle of the optical indicatrix, whereas the transition remains continuous. For the concentration of $x = 0.5$, the monoclinic ferroelastic phase becomes visible at room temperature but its stability decreases—during cooling, another phase transition appears, as a result of which, at the temperature of 220 K, the crystal transforms from the monoclinic ferroelastic phase to a ferroelectric polar phase of rhombic symmetry.

For $x = 0.39$, the monoclinic phase $P112_1/n$ exists only in a very narrow range of temperatures of ca. 25 K. Birefringence examination for a concentration of $x = 0.39$ in the temperature range of $300 \div 350$ K showed that the first transition is of a continuous nature, while the second phase transition is discontinuous with quite a high-temperature hysteresis ($\Delta T = 30$ K). It was also found that for the range of cesium ions concentration of $0.35 < x \leq 1$, the ferroelastic phase $P112_1/n$ in $Cs_x(NH_4)_{1-x}LiSO_4$ is present up to the temperature of liquid nitrogen. Calorimetric and optical tests (of optical double refraction) of solid solutions for the concentration scope x ($x = 0$; 0.045; 0.065; 0.09; 0.125; 0.15; 0.22) closer to the left, extreme point of the phase diagram have shown that the temperatures of both phase transitions in LAS ($T_{1LAS} = 460.5$ K ($x = 0$); 453 K (0.045); 449 K (0.065); 445 K (0.09); 431.5 K (0.15); 414.6 K (0.22) and $T_{2LAS} = 289$ K ($x = 0$); 280 K (0.045); 268.5 K (0.065); 260 K (0.09); 229, 241 K (0.15)) decrease significantly along with the increase of cesium concentration, the nature of the high-temperature transition remaining unchanged. It was noted that significantly larger influence
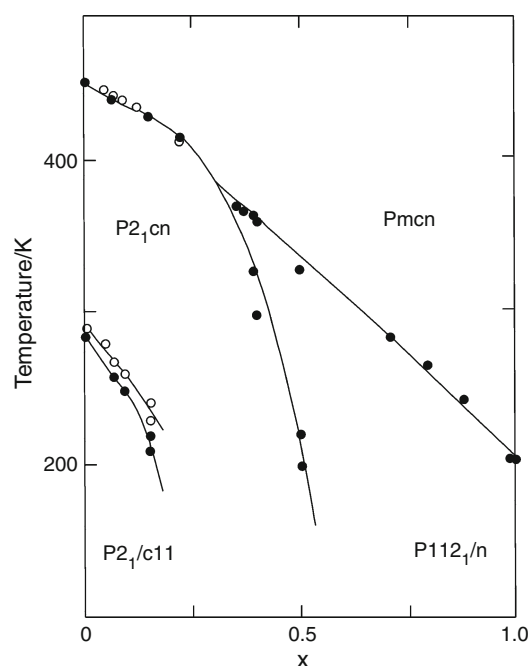
Fig. 1 Phase diagram x–T for the solid solution of $Cs_x(NH_4)_{1-x}LiSO_4$, obtained in the heating process during DSC tests (*unfilled circles*); in the cooling process during optical tests (*filled circles*)— according to papers [15, 16]

of change of concentration x is observed for the temperature of the second phase transition; the area of the presence of the ferroelectric phase widens and for $x = 0.22$, the phase can be observed until the temperature reaches 77 K. A replacement of cations, $NH_4^+ \rightarrow Cs^+$, results in an abrupt increase of double refraction δ_n and temperature hysteresis ΔT_2 in the phase transition from the ferroelectric phase $P2_1cn$ to the ferroelastic phase $P2_1/c11$. Hence, for $x = 0$; 0.065; 0.15 the values of δ_n and ΔT equal, respectively: $\delta_n = 10 \cdot 10^{-4}$, $\Delta T = 2$ K; $\delta_n = 12 \cdot 10^{-4}$, $\Delta T = 8.5$ K; $\delta_n = 15 \cdot 10^{-4}$, $\Delta T = 18$ K [15].

Ferroic phase transitions in crystals from the family of double sulfates are connected with gradual ordering of the orientation of structural units SO_4 and LiO_4, with the leading role played by SO_4 tetrahedrals [2, 5, 17]. Since isostructural compounds with an identical chemical formula, $ALiSO_4$, show different sequences of ferroic phase transitions within quite a wide temperature range, research on their solid solutions has been taken [4, 15, 16, 18–20] in order to explain the subtle mechanisms determining the ordering processes in different compounds in this family. This paper is focused on the compounds of $Cs_x(NH_4)_{1-x}LiSO_4$ for $x = 0.90$ and 0.85.

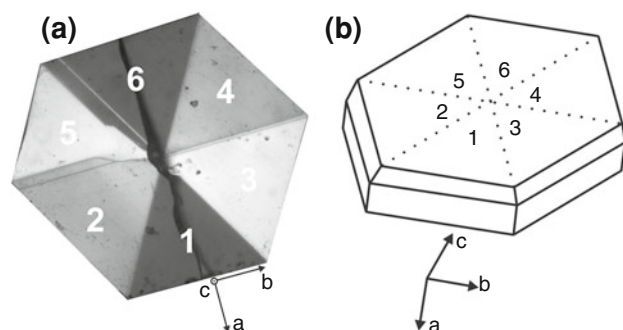## Technology of obtaining solid solutions of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ and $Cs_{0.85}(NH_4)_{0.15}LiSO_4$

The solid solutions of lithium cesium sulfate and lithium ammonium sulfate $Cs_x(NH_4)_{1-x}LiSO_4$, where: $x = 0.90$, 0.85, were obtained as a result of slow evaporation of aqueous solutions of Cs_2SO_4, $Li_2SO_4 \cdot H_2O$, and $(NH_4)_2SO_4$ compounds, taken in appropriate stechiometric proportions. The above-mentioned crystals were grown at a temperature of 305.5 ± 0.2 K. In order to provide test with the electron paramagnetic resonance method, samples were doped with vanadyl ions by adding hydrated vanadyl sulfate $VOSO_4 \cdot 5H_2O$ in the amount of 1 % mole to the initial compounds. Solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ crystallize in the form of a pseudohexagonal prism, which consists of growth twins. In polarized light, for a section perpendicular to a pseudohexagonal axis c, attenuation is observed every 60 degrees; hence, the crystal is built of 6 growth twins. Figure 2 shows the view of the growth twins in the polarized light (a) and the morphology of a solid solution of $Cs_x(NH_4)_{1-x}LiSO_4$, where: $x = 0.85$.

The ammonium ion content in the solid solutions ($x = 0.90$; 0.85) was determined using the Kjeldahl method [21] after making all non-destructive tests. For this purpose, a weighed sample was placed in a round-bottom flask being a part of the Parnas-Wagner apparatus. Next, a sodium hydroxide solution was added and ammonia was distilled off with steam into a receiver containing a standardized solution of sulfuric acid (VI). The excess of the acid was back-titrated with a standardized sodium hydroxide solution. It was found that the real ammonium ion concentration was twice lower than the one applied in the initial substances.

Research methodology

For the DSC tests, a Netzsch STA 409C analyzer was used with a controller which allows taking measurements within a wide temperature range: from the temperature of liquid nitrogen to 1,673 K, to an accuracy of ± 0.1 K. The rate of heating (cooling) may vary within the range from 0.1 K min^{-1} to 20 K min^{-1}. The measurements were performed in a controlled argon atmosphere.

For optical examinations, a polarizing microscope was used, Nikon Eclipse LV 100 POL, equipped with a heating and cooling system, THMS 600. Accuracy of temperature stabilization was ± 0.1 K.
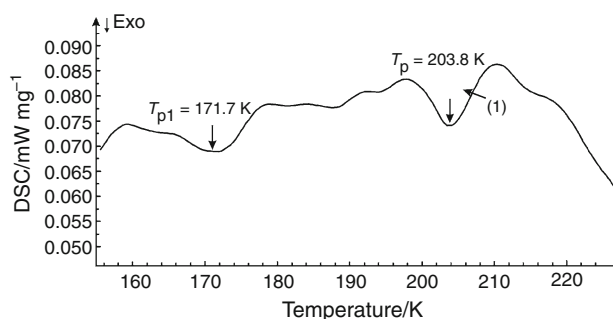
Results and discussion

Figure 3 presents a DSC curve which was recorded for the solid solution of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ during the cooling process conducted at a rate of 1 K min^{-1}.

Analysis of the DSC curve for the solid solution of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ reveal two thermal anomalies for the temperatures: $T_p = 203.8$ K and $T_{p1} = 171.7$ K, respectively. The anomaly that occurs at 203.8 K is connected with a structural ferroelastic phase transition (like in the case of crystal $CsLiSO_4$ where the transition proceeds from the orthorhombic system to the monoclinic system). The values of parameters T_o, T_p, and T_e for the thermal anomaly designated as (1) in Fig. 3 were calculated using the Proteus application [22]. They are presented in Table 1, where: T_o, T_p, and T_e designate the temperature at the initial, extreme, and final points of the anomaly.

Figure 4 presents a DSC curve which was recorded for the solid solution of $Cs_{0.85}(NH_4)_{0.15}LiSO_4$ also during the cooling process conducted at a rate of 1 K/min.

The dependence presented in Fig. 4 has two characteristic thermal anomalies at $T_p = 230.1$ K and $T_{p1} = 197.1$ K. This seems to have some similarity with DSC curve for the sample of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$.

The thermal anomaly at the temperature of 230.1 K testifies to an expected increase in the temperature of the structural ferroelastic phase transition in the process of substituting Cs^+ cations with NH_4^+ cations. In addition, the values of parameters T_o, T_p, and T_e were calculated for the

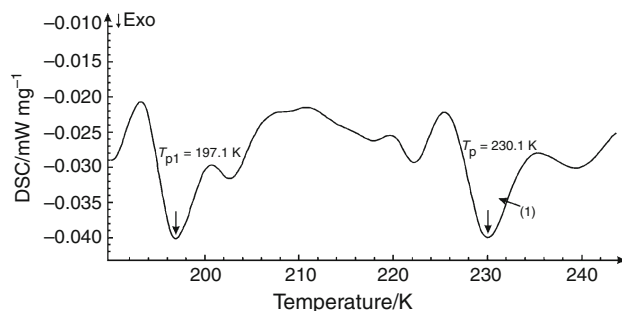**Fig. 2** Crystal of the solid solution of $Cs_{0.85}(NH_4)_{0.15}LiSO_4$: **a** the view of growth twins in polarized light; **b** morphology of the crystal

Fig. 3 DSC curve for the solid solution of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$

Table 1 Values of parameters T_o, T_p, and T_e of the solid solution of $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ for thermal anomaly (1)

Temperature at the initial point of the anomaly T_o/K	Temperature at the extreme point of the anomaly T_p/K	Temperature at the final point of the anomaly T_e/K
199.5	203.8	209.2

The anomaly that appears at the temperature of 171.7 K will be the object of further detailed research

Fig. 4 DSC curve for the solid solution of $Cs_{0.85}(NH_4)_{0.15}LiSO_4$

Table 2 Values of parameters T_o, T_p, and T_e of the solid solution of $Cs_{0.85}(NH_4)_{0.15}LiSO_4$ for thermal anomaly (1)

Temperature at the initial point of the anomaly T_o/K	Temperature at the extreme point of the anomaly T_p/K	Temperature at the final point of the anomaly T_e/K
225.6	230.1	235.3

thermal anomaly designated as (1) in Fig. 4, and presented in Table 2.

Due to the ferroelastic nature of the structural phase transition, expected in solid solutions, it can be presumed that a domain structure will become visible below the phase transition temperature. For this purpose, both crystals were examined using polarization microscopy. Figure 5 shows the forming of and temperature related changes in the ferroelastic domain structure of the solid solution crystal $Cs_{0.85}(NH_4)_{0.15}LiSO_4$ at selected temperatures.

In the high-temperature phase, growth twins are observed which are distinguished by different colors. (Fig. 2a). Equations of the planes constituting boundaries of the twinned areas are given by: $x = 0$, $y = 0$, $y = \pm\sqrt{3}\,x$, $y = \pm 1/\sqrt{3}\,x$ (determined in the system of hexagonal axes of the prototype phase $P6_3/mmc$). They satisfy the equations derived by Sapriel for domain walls [23] as well as the relationships imposed by the symmetry elements lost during the transformation which lead to a reduction of symmetry according to the scheme $6/mmm \rightarrow mmm$.

During the lowering of temperature of the solution $Cs_{0.85}(NH_4)_{0.15}LiSO_4$, the color of the twins observed in polarized light changes. The formation of a domain structure begins at temperature $T_c = 223 \pm 2$ K from the appearance of optically inhomogeneous regions. Since crystals from the $ALiSO_4$ family belong, according to Aizu's notation, to mmmF2/m [24]; in accordance with the change of the crystal symmetry during a structural phase transition, the ferroelastic domain structure is built of ferroelastic domains of two types, S_1 and S_2. The domains are separated by mutually perpendicular domain walls of two types, $W_{a, b}$, parallel to axis a or b of the crystal, respectively; this is in accord with the theoretical equations [23] for ferroelastic domain walls: $x = 0$, $y = 0$ (in the rhombic system).

As can be seen in Fig. 5, close to a temperature of 213 K, the domain structure consists of a large number of domains in the form of narrow strips; the domains are separated with W_b type walls of one family only (parallel to plane (010)). As the temperature further decreases, close to 198 K, the existence of domains in the form of narrow strips is still observed; however, these strips are separated with mutually perpendicular walls of $W_a \parallel (100)$ and $W_b \parallel$

Fig. 5 Evolution of the domain structure in the crystal of solid solution $Cs_{0.85}(NH_4)_{0.15}$ during the lowering of temperature: **a** 218 K, **b** 213 K, **c** 198 K along with a system of ferroelastic domains, S_1 and S_2, separated by two allowed, mutually perpendicular domain walls $W_a \parallel (100)$ and $W_b \parallel (010)$
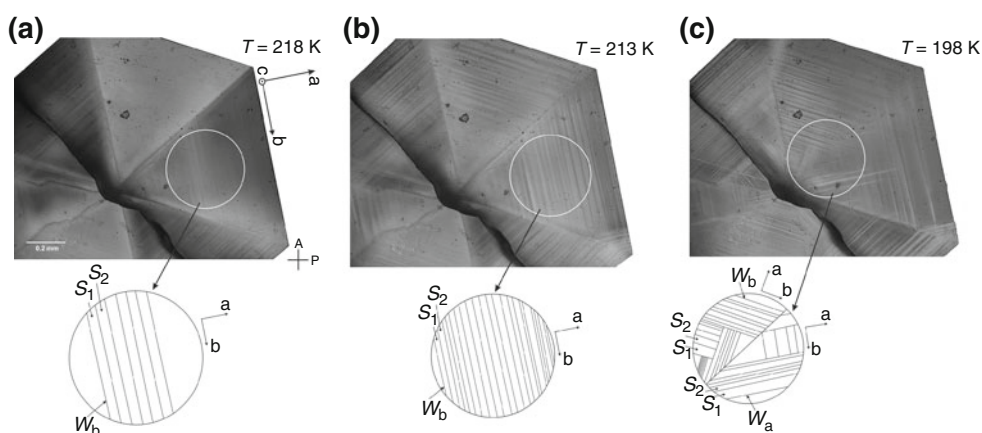
(010) type. Also in the $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ solution, the structural phase transition is observed through a similar system of ferroelastic domains which appear near the temperature of 205 K.

In the base crystal, $CsLiSO_4$, the refinement of the domain structure is maintained within a very narrow range of temperatures (2 K below T_c). Beyond these temperatures big domains are formed and are stable in terms of temperature [6, 25]. In both of the investigated crystals of the solid solution $Cs_x(NH_4)_{1-x}LiSO_4$, a fine domain structure is maintained within a wide temperature range below the temperatures of their phase transitions.

Conclusions

Through slow evaporation of water solutions of the compounds: Cs_2SO_4, $Li_2SO_4 \cdot H_2O$, and $(NH_4)_2SO_4$ at temperature $T = 305.5$ K, two types of solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ were grown, where $x = 0.90$; 0.85. Using Kjeldahl method it was found that the real ammonium ion concentration is twice lower than the one applied in the initial substances, which testifies to the loss of ammonium ions during the crystallization process. The DSC examinations of the solid solutions of $Cs_x(NH_4)_{1-x}LiSO_4$ with the content of $x = 0.90$ and 0.85 show that the temperature of the ferroelastic phase transition increases as the Cs^+ ions get replaced with NH_4^+ ions. This temperature increases from 202 K for pure $CsLiSO_4$ to the temperature of 203.8 K for $Cs_{0.90}(NH_4)_{0.10}LiSO_4$, and 230.1 K for $Cs_{0.85}(NH_4)_{0.15}LiSO$. The formation of the ferroelastic domain structure in the solid solutions $Cs_{0.85}(NH_4)_{0.15}LiSO_4$, and $Cs_{0.90}(NH_4)_{0.10}LiSO_4$ is connected with the structural phase transition from the paraelastic to ferroelastic phase.

References

1. Van den Berg AJ, Tuinstra F. The space group and structure of α-K_2SO_4. Acta Crystallogr B. 1978;34:3177–81.
2. Aleksandrov KS, Beznosikov BV. Strukturnyje fazovye perekhody v kristalakh. Novosibirsk: Nauka; 1993.
3. Dollase A. NH_4LiSO_4: A variant of the general tridymite structure. Acta Crystallogr B. 1969;25:2298–302.
4. Flerov IN, Kartashev AV, Grankina VA. Phase transitions and thermal capacity in $Cs_x(NH_4)_{1-x}LiSO_4$, NH_4LiSO_4 and $RbLiSO_4$. FTT. 2005;47:696–704.
5. Kruglik AI, Simonow MA, Żelezin EP, Bielow NW. Crystalline structures of phases I and III in double lithium and caesium sulfates. Doklady Akademii Nauk SSSR. 1979;247:1384–7.
6. Pietraszko A, Tomaszewski PE, Łukaszewicz K. X-ray and optical study of the phase transition in $CsLiSO_4$. Phase Transitions. 1981;2:141–50.
7. Pakulski G, Mróz B, Krajewski T. Ferroelastic properties of $CsLiSO_4$ crystals. Ferroelectrics. 1983;48:259–66.
8. Asahi T, Hasebe K. X-Ray study of $CsLiSO_4$ in connection with its ferroelastic phase transition. J Phys Soc Jpn. 1988;57:4184–90.
9. YCh Cho, Sim HY, Jeong HT, Huang JY, ChR Cho, Jeong SY. The mechanical study on the low temperature phase of $CsLiSO_4$ crystal. J Phys Soc Jpn. 2002;71:1072–5.
10. Zapart W, Zapart MB, Czaja P. Electron paramagnetic resonance of Cr^{3+} ions in ferroelastic $CsLiSO_4$. Phase Transition. 2008;11–12:1141–50.
11. Mitsui T, Oka T, Shiroishi Y, Takashige M, Ito K, Sawada S. Ferroelectricity in NH_4LiSO_4. J Phys Soc Jpn. 1975;39:845–6.
12. Loiacono GM, Delfino M, Smith WA, Bell MI, Shaulov A, Tsuo YH. Dielectric, pyroelectric and thermal properties of NH_4LiSO_4 and ND_4LiSO_4. Ferroelectrics. 1980;23:89.
13. Tomaszewski PE, Pietraszko A. Thermal expansion of lithium ammonium sulphate. Phys Stat Sol (a). 1979;56:467–72.
14. Gaffar MA, Abu El Fadl A, Mohamed GA. Specific heat and electrical resitivity of pure and doped lithium-ammonium sulphate single crystals. Physics B. 1996;217:274–84.
15. Mel'nikova SV, Grankina VA, Kartashev AV. A study of the effect of gradual substitution $NH_4 \rightarrow Cs$ on phase transitions in NH_4LiSO_4 crystals. FTT. 2002;44:365–70.
16. Mel'nikova SV, Grankina VA. Optical investigations of the effect of gradual substitution $NH_4 \rightarrow Cs$ on the ferroelastic phase transition in a $CsLiSO_4$ crystal. FTT. 2004;46:500–4.
17. Zamkowa NG, Zinenko VI. Monte Carlo investigation of the phase transitions in the $CsLiSO_4$ and $CsLiCrO_4$ crystals. J Phys Condens Matter. 1994;6:9043–52.
18. Mel'nikova SV, Vasiliev AD, Grankina VA, Voronov VN, Aleksandrov KS. Optical and X-ray studies of mixed crystals $Cs_xRb_{1-x}LiSO_4$. Ferroelectrics. 1995;170:139–43.
19. Lima RJC, Sasaki JM, Freire PTC, Ayala AP, Guedes I, Melo FEA, Filho JM. A new phase in the $LiRbSO_4$ - $LiCsSO_4$ system. J Phys Condens Matter. 2000;12:7559–68.
20. Katkanant V. Theoretical studies of phase transitions in the mixed crystals $Cs_xRb_{1-x}LiSO_4$. Phys Rev B. 1995;51:146–52.
21. Collective work: Nitrogen determination by Kjeldahl method. Issue VI. Farmakopea Polska. 2002; pp. 46–47.
22. Czaja P. Obtaining ferroic solid solutions $Cs_x(NH_4)_{1-x}LiSO_4$ and their phase transitions. Ph.D. Dissertation, Częstochowa. 2007; pp. 148–150.
23. Sapriel J. Domain-wall orientations in ferroelastics. Phys Rev B. 1975;12:5128–40.
24. Aizu K. Determination of the state parametrs and formulation of spontaneous strain for ferroelastic. J Phys Soc Jpn. 1970;28:706–16.
25. Leong HT, Kim SK, Ahn HY, Leong SY. The twin-domain structures of lithium cesium sulfate crystal. J Korean Phys Soc. 1998;32:768–70.