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CRYSTAL STRUCTURE AND DYNAMICS OF
 $K_{2-x}(NH_4)_xSeO_4$ MIXED CRYSTALS STUDIED
BY X-RAY AND NEUTRON SCATTERING

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Исследование кристаллической структуры и динамики смешанных кристаллов $K_{2-x}(NH_4)_xSeO_4$ с помощью рассеяния нейтронов и рентгеновских лучей

Исследованы смешанные кристаллы $K_{2-x}(NH_4)_xSeO_4$ с помощью порошковой дифракции рентгеновских лучей и нейтронов, а также с помощью неупругого некогерентного рассеяния нейтронов в широком температурном интервале от 300 до 16 К. Фазовый переход в $(NH_4)_2SeO_4$ не наблюдался в интервале от комнатной температуры до 20 К. Потенциальные барьеры переориентации ионов аммония в смешанных кристаллах $K_{2-x}(NH_4)_xSeO_4$ возрастают с увеличением концентрации ионов аммония.

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Crystal Structure and Dynamics of $K_{2-x}(NH_4)_xSeO_4$ Mixed Crystals Studied by X-ray and Neutron Scattering

The $K_{2-x}(NH_4)_xSeO_4$ mixed crystals have been studied by powder X-ray and neutron diffraction and inelastic incoherent neutron scattering in a wide temperature range from 300 to 16 K. No phase transition is observed in $(NH_4)_2SeO_4$ in the range from room temperature to 20 K. The reorientation potential barriers of ammonium ions in the $K_{2-x}(NH_4)_xSeO_4$ mixed crystals increase with the increasing concentration of ammonium ions.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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1. INTRODUCTION

The compounds $(\text{NH}_4)_2\text{SeO}_4$ (or LAS) and K_2SeO_4 belong to the crystal family of the type $\text{AA}'\text{BX}_4$ ($\text{A}, \text{A}' = \text{Li}, \text{Na}, \text{Rb}, \text{NH}_4, \text{Cs}$, and others, and $\text{BX}_4 = \text{SO}_4, \text{SeO}_4, \text{ZnCl}_4, \text{ZnBr}_4, \text{BeF}_4, \text{MoO}_4, \text{WO}_4$, and others) which possess paraelectric–ferroelectric phase transitions [1]. It is known that some compounds undergo a series of phase transitions through incommensurate phase and due to the substitution of alkaline metal ions by a small amount of ammonium ions the incommensurate phase can disappear on the x - T phase diagram of such mixed crystals. This situation has been observed in the β - $\text{LiRb}_{1-x}(\text{NH}_4)_x\text{SO}_4$ mixed crystals [2] and in the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals [3].

Until recently, according to X-ray diffraction results [4], the ammonium selenate (hereafter abbreviated as $(\text{NH}_4)_2\text{SeO}_4$ or ASE), was known as a compound with a monoclinic crystal structure at room temperature. It was also indicated [5] that no phase transition was observed in the range from 5 to 300 K. However, a phase transition has been found above room temperature (possibly from 380 to 400 K). This phase transition goes *via* an intermediate phase but the high temperature crystal structure of ASE was not determined in that communication [5].

The $(\text{NH}_4)_2\text{SeO}_4$, as determined in [4], crystallizes in $C2/m$ space group ($Z = 4$) with the lattice parameters: $a = 12.152(6)$ Å, $b = 6.418(3)$ Å and $c = 7.711(4)$ Å, $\beta = 115.50(12)^\circ$. According to that study two crystallographically independent ammonium groups, $\text{NH}_4(1)$ and $\text{NH}_4(2)$, are deformed.

The purpose of our present X-ray and neutron scattering studies of $\text{K}_{1-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals in a broad temperature range is to understand the influence of the substitution of K^+ by NH_4^+ on the phase transitions in this system.

2. EXPERIMENTAL

The studies of crystal structures and dynamics of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals are carried out on powder samples. The $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ powder samples are produced by slow evaporation of aqueous solutions of $(\text{NH}_4)_2\text{SeO}_4$ and K_2SeO_4 mixtures at 313 K.

The degree of substitution of the obtained mixed crystals is determined by analyses of the N and H element contents with a Carlo Erba microanalyzer

EA1108, and K and Se concentrations by ICP (Induced Condensed Plasma) with a Jobin–Yvon analyzer. Crystal structures of the obtained powder samples with different concentrations are determined by X-ray diffraction.

X-ray powder diffraction studies are carried out on a Siemens D500 diffractometer with the Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation and a secondary monochromator. The indexation of powder diffraction patterns is performed using the TREOR computer program [6] and lattice parameters are refined with the CELREF program [7].

The measurements of powder neutron diffraction (NPD) and inelastic incoherent neutron scattering (IINS) for the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals are carried out on a NERA-PR neutron spectrometer set on the IBR-2 neutron pulsed source (FLNP JINR, Dubna, Russia) [8].

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Neutron Diffraction of $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ Mixed Crystals. The K_2SeO_4 undergoes two successive phase transitions [9, 10]:

$$\text{Phase I} \leftrightarrow 129.5 \text{ K} \leftrightarrow \text{Phase II} \leftrightarrow 93 \text{ K} \leftrightarrow \text{Phase III.}$$

Some details of crystal structures of different phases are described in Table 1.

Table 1. Crystal structures of different K_2SeO_4 phases

	Phase I [11], paraelectric	Phase II [12, 13]	Phase III [14, 15], ferroelectric
T , K	293		80
Sp.gr.	$Pnam$	$Pna2_1$, Incommensurate,	$Pna2_1$
a , Å	7.661	$Q = 1/3(1-\delta)a^*$, where a^* is a	22.716
b , Å	10.466	reciprocal-lattice vector along	10.339
c , Å	6.003	the [100] direction, δ decreases	5.967
		and vanishes at 93 K	

Crystal structures of $(\text{NH}_4)_2\text{SeO}_4$ and K_2SeO_4 are different at 313 K as they have two different space groups $C2/m$ and $Pnam$, respectively, and this fact can explain why $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ solid solutions are formed only in the limited region of concentrations: $0.0 < x \leq 0.55$. The $Pnam$ orthorhombic symmetry of powder samples of $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals, obtained from aqueous solutions, with $x \leq 0.55$ at 293 K is confirmed by X-ray powder diffraction. Mixed crystals with ammonium concentration $x > 0.55$, obtained from aqueous solutions as well, crystallize in two phase systems $[(\text{NH}_4)_x\text{K}_{2-x}]\text{SeO}_4 + (\text{NH}_4)_2\text{SeO}_4$.

The investigations of crystal structures of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals are carried out for $x = 0.0, 0.09, 0.15, 0.19, 0.24, 0.32$, and 0.55 in a wide

temperature range from 293 to 20 K. X-ray powder diffraction studies show that the paraelectric-incommensurate transition temperature increases from 127 K for $x = 0.0$ to 154 K for $x = 0.19$ and starting from $x = 0.24$ (this phase transition is not observed) [3].

The powder neutron diffraction spectrum of K_2SeO_4 measured on the NERA-PR spectrometer at $T = 16$ K is shown in Fig. 1. The first part of this spectrum

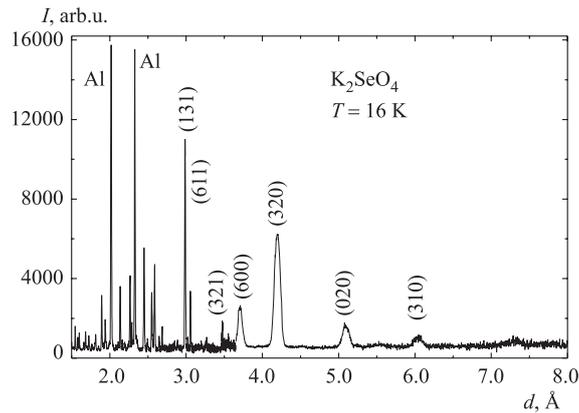


Fig. 1. Neutron powder diffraction of K_2SeO_4 at 16 K in phase III (spectrum from 1.5 to 3.7 Å is measured at $2\Theta = 143.2^\circ$ and from 3.7 to 8 Å at $2\Theta = 45^\circ$)

is measured at the scattering angle $2\Theta = 143.2^\circ$ for the interplane distances from 1.5 to 3.7 Å and the second part at $2\Theta = 45^\circ$ with the interplane distances from 3.7 to 8 Å. The indexing of the diffraction spectra is fulfilled in accordance with the lattice parameters determined in [14, 15].

The neutron powder diffraction spectra of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals with $x = 0.15$ at temperatures 16, 85, and 160 K are shown in Fig. 2. The temperature interval is selected in order to have an opportunity to observe possible transitions from phase III to phase II or phase I. However, such phase transitions were not observed. The neutron powder diffraction spectra of a mixed crystal with $x = 0.32$ at similar temperatures are shown in Fig. 3. These spectra do not confirm the presence of these phase transitions as well.

The NPD spectra for the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystal at 20 K for ammonium concentrations $x = 0.0, 0.15$ and 0.32 are shown in Fig. 4.

The measured neutron powder diffraction spectra (NPD) from $(\text{NH}_4)_2\text{SeO}_4$ at 294 and 20 K with the interplane distances from 2.4 to 3.7 Å are displayed in Fig. 5. The profile fitting for the refinement of atomic positions is very difficult owing to a significant background and low intensities of Bragg reflections of these NPD spectra. However, these NPD spectra from ASE can confirm the results of [4] about the absence of a phase transition in ASE from room to low temperatures.

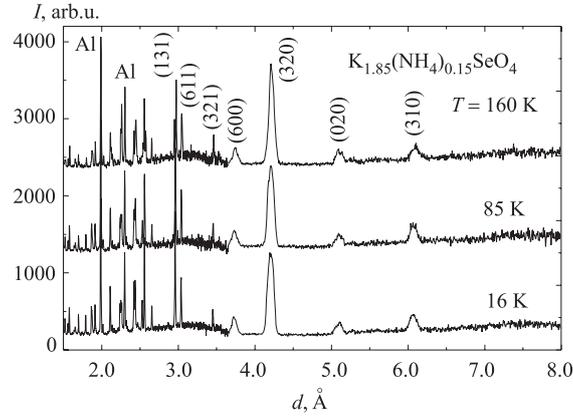


Fig. 2. The diffraction spectra for the $K_{1.85}(NH_4)_{0.15}SeO_4$ mixed crystals showing the absence of phase transition in the temperature range from 16 to 160 K

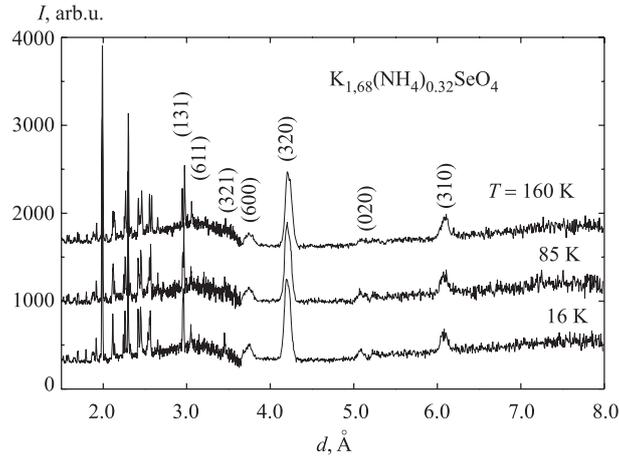


Fig. 3. The diffraction spectra for the $K_{1.68}(NH_4)_{0.32}SeO_4$ mixed crystals showing the absence of a phase transition in the temperature range from 16 to 160 K

The refinement of atomic positions in $(NH_4)_2SeO_4$ was based on recent X-ray and neutron single-crystal diffraction data [16]. The experimental conditions, the refined atomic positions and determined N–H bond lengths are given in [16]. Single-crystal neutron diffraction of ASE confirmed the $C2/m$ space group ($Z = 4$) and determined the lattice parameters: $a = 12.432(4) \text{ \AA}$, $b = 6.574(4) \text{ \AA}$, $c = 7.885(3) \text{ \AA}$, and $\beta = 115.51(2)^\circ$. A comparison of an average N–H bond length determined by X-ray diffraction [4] with that determined by

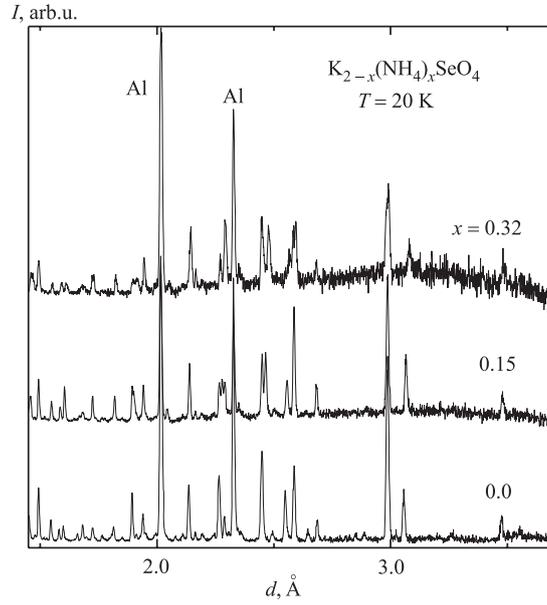


Fig. 4. Neutron powder diffraction spectra for the $K_{2-x}(NH_4)_xSeO_4$ mixed crystals with $x = 0.0, 0.15$ and 0.32 at 20 K

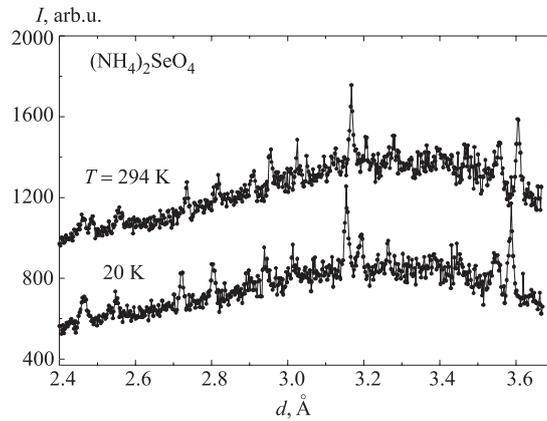


Fig. 5. Neutron powder diffraction spectra of $(NH_4)_2SeO_4$ at 20 and 294 K

neutron diffraction has shown that the latter is longer by 0.128 \AA . Contrary to the X-ray results [4] the N–H bond lengths determined by neutron diffraction suggest that ammonium ions are regular tetrahedra.

It is interesting to note that average experimental S–O and N–H bond lengths determined by neutron diffraction are longer (0.018 and 0.032Å, respectively) than equivalent parameters calculated for free SeO_4^{2-} and NH_4^+ ions. The bond lengths for free SeO_4^{2-} and NH_4^+ ions are calculated using the GAUSSIAN98 program [17] at the HF/6-31G* level. A projection of the $(\text{NH}_4)_2\text{SeO}_4$ unit cell along the Y axis is shown in Fig. 6.

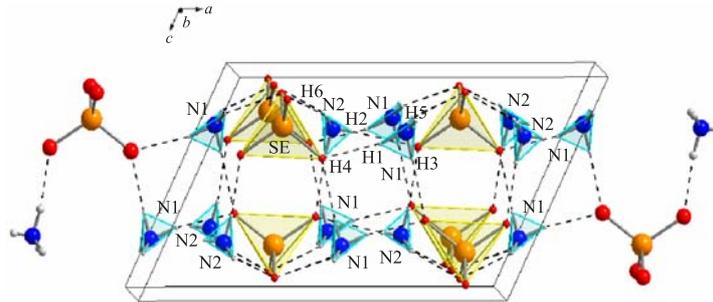


Fig. 6. A projection of the unit cell contents of $(\text{NH}_4)_2\text{SeO}_4$ along the Y axis

3.2. Inelastic Incoherent Neutron Scattering of $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ Mixed Crystals. The IINS spectra for the $\text{K}_{1.85}(\text{NH}_4)_{0.15}\text{SeO}_4$ mixed crystal are measured at 20, 85, and 160 K in order to find some possible changes in the dynamics of crystal lattice at phase transitions. The IINS spectra are changed significantly above 85 K. The increase in quasielastic incoherent neutron scattering (QINS) is observed on the wings of the elastic Bragg peak from monochromator crystals with the centre of this peak at $\lambda = 4.15$ Å. Peak broadening is observed in the IINS spectra for different phonon modes (see Fig. 7, *a*). The calculated generalized phonon density of state ($G(E)$) spectra in one-phonon approximation without multiphonon neutron scattering contribution for this mixed crystal at different temperatures demonstrate different peak broadening with different excitation energies. The broadening increases significantly at 160 K (see Fig. 7, *b*). Similar changes are observed in the IINS and $G(E)$ spectra obtained for the $\text{K}_{1.68}(\text{NH}_4)_{0.32}\text{SeO}_4$ mixed crystal at 20, 85, and 160 K (see Fig. 8, *a* and *b*).

The IINS spectra from $(\text{NH}_4)_2\text{SeO}_4$ are measured at 30, 60, 110, 160, 210, and 257 K. These IINS spectra are presented in Fig 9, *a*. The $G(E)$ spectra calculated from the IINS spectra are shown in Fig. 9, *b*.

The $G(E)$ spectra of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystal with ammonium concentrations of: $x = 0.15, 0.32$ and 2.0 at 16 K are shown in Fig. 10.

The IINS spectra of $(\text{NH}_4)_2\text{SeO}_4$ have the following peculiarities. The contributions of QINS in the IINS spectra of $(\text{NH}_4)_2\text{SeO}_4$ are not observed at entire temperature range from 20 K to room temperature on the wings of the neutron

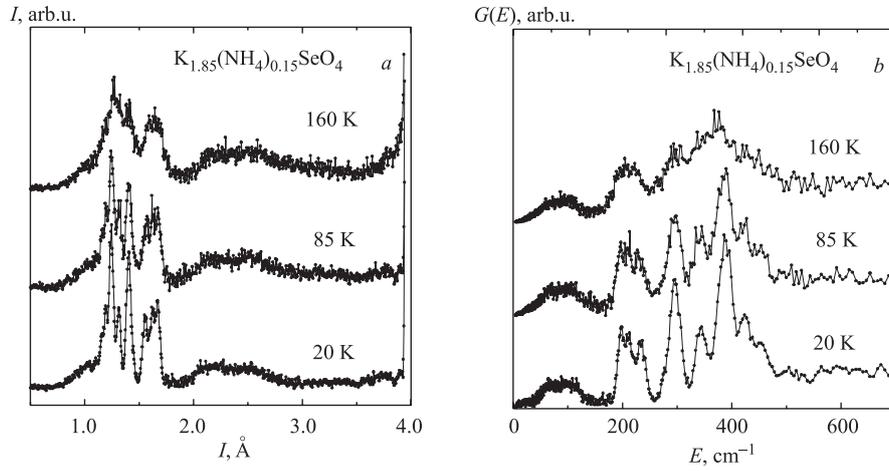


Fig. 7. The IINS (a) and $G(E)$ (b) spectra of the $\text{K}_{1.85}(\text{NH}_4)_{0.15}\text{SeO}_4$ mixed crystal at different temperatures

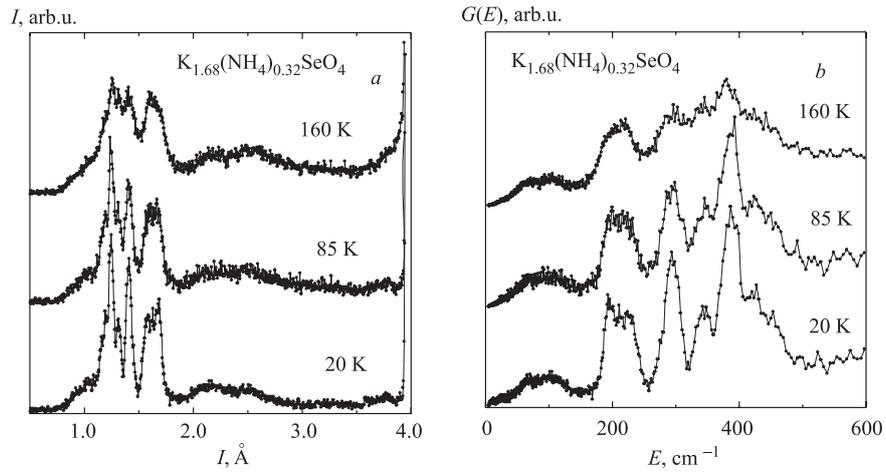


Fig. 8. The IINS (a) and $G(E)$ (b) spectra of the $\text{K}_{1.68}(\text{NH}_4)_{0.32}\text{SeO}_4$ mixed crystal at different temperatures

elastic scattering profile from the monochromators or beyond the pale of the resolution function of the NERA-PR spectrometer determined as a full width at half maximum (FWHM) of the elastic peak $\Delta E = 0.6$ meV.

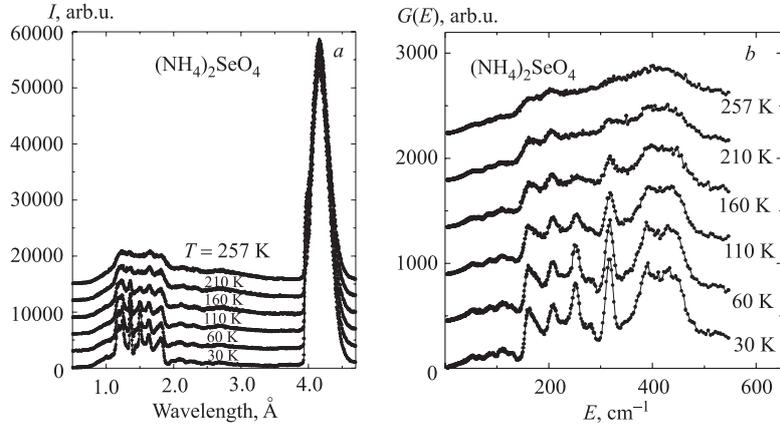


Fig. 9. *a*) The IINS spectra of $(\text{NH}_4)_2\text{SeO}_4$ and *b*) the $G(E)$ spectra of $(\text{NH}_4)_2\text{SeO}_4$ at different temperatures

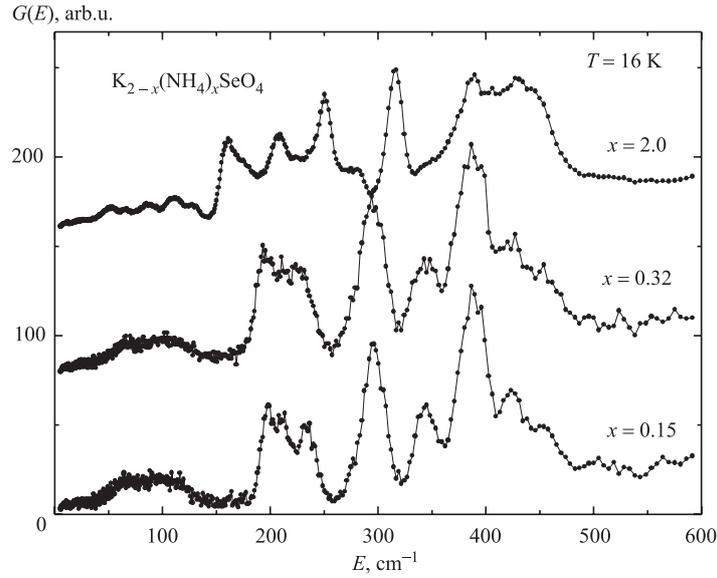


Fig. 10. The $G(E)$ spectra of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals with $x = 0.0, 0.15$ and 0.32 at 16 K

The explanation of the behavior of ammonium ions in the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals can be given on the basis of the theory describing rotational movements of a regular tetrahedral molecular ion as a rigid body in a potential well in a crystal lattice [18].

The generalized phonon density of states $G(E)$ calculated from inelastic incoherent neutron scattering can be presented as the sum of partial phonon density of states $G_i(E)$ of each atom i

$$G(E) = \sum_i f_i b_i^{\text{inc}} G_i(E),$$

where f_i is the atomic fraction and b_i^{inc} is the cross section of incoherent scattering for each atom type. The values of the incoherent scattering cross sections for different atoms in the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals have strong difference ($b_{\text{H}}^{\text{inc}} = 79.9$, $b_{\text{N}}^{\text{inc}} = 0.49$, $b_{\text{K}}^{\text{inc}} = 0.25$, $b_{\text{Se}}^{\text{inc}} = 0.33$, $b_{\text{O}}^{\text{inc}} = 0.0$ b [18]). The huge value of the incoherent scattering cross section of hydrogen atoms helps one to select partial phonon density of states for ammonium ions from general $G(E)$.

The study of lattice dynamics of potassium selenate is known within a semi-empirical rigid-ion model, with the help of which phonon density of states for K_2SeO_4 at 293 K was calculated [19]. The obtained $G(E)$ for K_2SeO_4 has the Debye cut-off energy at 165 cm^{-1} describing acoustic and optic phonons of potassium and SeO_4^{2-} and librational vibrations of rigid selenate groups. The comparison of the $G(E)$ spectra of K_2SeO_4 [19] and the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals shows that, indeed, the $G(E)$ spectra of mixed crystals with $x = 0.15$ and 0.32 , respectively, at 16 K are presented in the energy region up to 165 cm^{-1} by a spectrum of phonon density of states, which is approximately similar to that calculated for K_2SeO_4 . The $G(E)$ spectra of mixed crystals with $x = 0.15$ and 0.32 in the energy region from 165 to 500 cm^{-1} are presented by the complex patterns of peaks with significant intensities which can be described by local modes of ammonium ions. These local modes present optic translational (ν_5) and librational (ν_6) modes of ammonium ions. The selection and interpretation of these modes are difficult without model calculations. These model calculations of phonon density of states for a molecular-ion mixed crystal are very complex.

However, there is a possibility to use the crystal structure peculiarity of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals. One can notice that the $G(E)$ spectra of ASE and mixed crystals are closely spaced in the energy region from 320 to 500 cm^{-1} and it is possible to select the following modes with energies 296 , 344 , 389 , 424 , and 452 cm^{-1} for $x = 0.15$; 295 , 343 , 388 , 424 , and 451 cm^{-1} for $x = 0.32$; and 316 , 357 , 387 , 428 , and 455 cm^{-1} for ASE for the analysis. Among these modes, one can accept that modes with the energies 389 ($x = 0.15$), 388 ($x = 0.32$), and 387 ($x = 2.0$) correspond to ν_6 librational mode and modes with the energies 424 ($x = 0.15$), 424 ($x = 0.32$), and 428 ($x = 2.0$) correspond to another ν_6 librational mode. The energies of the selected modes for different mixed crystals are closely spaced but their partial contributions $G_i(E)$ in $G(E)$ are different (the contribution of each mode is considered as the area under the profile presented by the Gaussian).

If the contributions of the librational modes with the energies 387 and 428 cm^{-1} in ASE have the approximate ratio of 1:1 then the contributions of the librational modes with similar energies in mixed crystals ($x = 0.15$ and 0.32) have the approximate ratio of 3:1. It can be explained in the following way. It is known from X-ray study of $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ [3] that only the substitution of $\text{K}^+(1)$ is produced by NH_4^+ in contradiction to the substitution of $\text{K}^+(2)$ by NH_4^+ . If $\text{K}^+(1)/\text{NH}_4^+(1)$ occupies an 11-coordinated site then $\text{K}^+(2)/\text{NH}_4^+(2)$ occupies a 9-coordinated site. This property of the substitution of K^+ ions by NH_4^+ ions helps one to explain the difference in the $G(E)$ spectra of $(\text{NH}_4)_2\text{SeO}_4$ and the mixed crystals ($x = 0.15$ and 0.32) in the energy region of librational modes. Thus, it is possible to consider that ν_6 librational mode with the energy of 428 cm^{-1} belongs to $\text{NH}_4^+(2)$ in $(\text{NH}_4)_2\text{SeO}_4$ and ν_6 librational modes with the energy of 424 cm^{-1} belong to $\text{NH}_4^+(2)$ in the above-mentioned mixed crystals. The inelastic incoherent neutron scattering is more sensitive to the detection of hydrogen content in comparison with the X-ray diffraction method and the present result assumes that a small quantity of K(2) ions can be substituted by ammonium ions in K_2SeO_4 and actually the substitution of K(1) and K(2) by ammonium ions is produced in the ratio of 3:1, respectively.

The analysis of the $G(E)$ spectra of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals from the point of view of ammonium ion librations as regular tetrahedra leads to the decomposition of the $G(E)$ spectra on different modes with energies presented in Table 2. Different selected peaks in $G(E)$ can be assigned to lattice phonons and ammonium ion modes. It is interesting to compare all modes of the ammonium ions presented in Table 2 for the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals.

The mode with the energies 451 cm^{-1} appears in the $G(E)$ spectra of the mixed crystals ($x = 0.15$ and 0.32) and the mode with the energy of 455 cm^{-1} appears in $G(E)$ spectrum of $(\text{NH}_4)_2\text{SeO}_4$. This mode can be assigned to the ν_2 inner mode of the SeO_4^{2-} ion. The results of optic experiments [20], calculations of inner modes for the SeO_4^{2-} ion with the help of the GAUSSIAN98 program [17] and inelastic incoherent neutron scattering data are presented in Table 3. The comparison of values for ν_2 inner mode of the SeO_4^{2-} ion, observed by optic and neutron scattering experiments and calculated shows their closeness, which confirm the presence of ν_2 inner mode of SeO_4^{2-} ion in the $G(E)$ spectra of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals. The ν_4 inner mode of SeO_4^{2-} with calculated energy of 324 cm^{-1} is very close to the ammonium ion modes of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals: 296 ($x = 0.15$), 295 ($x = 0.32$), and 316 ($x = 2.0$) cm^{-1} . It is possible to consider these selected modes with close energies to be the ridden mode of ammonium ions related with ν_4 inner mode of SeO_4^{2-} through N-H...O hydrogen bond between NH_4^+ and SeO_4^{2-} ions.

The QINS contribution usually gives an evidence for the reorientation of the ammonium ions during the process of neutron inelastic scattering. The absence of visible QINS contributions in the IINS spectra of ASE in a wide temperature

Table 2. The energies of modes determined in $K_{2-x}(NH_4)_xSeO_4$ (energy in cm^{-1})

$K_{2-x}(NH_4)_xSeO_4, T = 20 K$			Assignment
$x = 0.15$	$x = 0.32$	$x = 2.0$	
		52	Lattice phonons
		67	
		86	
		111	
		129	
		159	
		173	Translational modes (ν_5) of NH_4^+
197	195	207	
212	211	233	
234	227		
		251	
		273	$\nu_4-SeO_4^{2-}$ ridden mode
296	295	316	
344	343	357	ν_5 or ν_6
389	388	387	ν_6
424	424	428	ν_6
451	451	455	$\nu_2-SeO_4^{2-}$

Table 3. Energies of ν_2 and ν_4 inner modes of SeO_4^{2-} , determined by optic experiment [20], calculated with the help of program [17] and determined by recent IINS data for the $K_{2-x}(NH_4)_xSeO_4$ mixed crystals (energy in cm^{-1})

Modes of SeO_4^{2-}	Optic exp. [20]	Calculated	$x = 0.15$	$x = 0.32$	$x = 2.0$
ν_1		898			
ν_2	428	421	451	451	455
ν_3		812			
ν_4		324	296	295	316

range asserts that a significant potential barriers prevent ammonium ions from the reorientations.

The $G(E)$ spectra of ASE at different temperatures show that the increase in temperature is accompanied by peak broadening for different modes. It is worth to note that peaks of librational modes broaden with the increase of temperature more significantly than peaks of the phonon modes. The librational peaks (ν_6) inside of the energy transfer region from 350 to 450 cm^{-1} are already entirely overlapped at 257 K, whereas the broadening of translational peaks (ν_5) is not finished.

Temperature increase leads to appearance of anharmonicity in crystal lattice. This is accompanied by the broadening of the peaks. The anharmonicity in crystal lattice with molecules or with molecular ions may be of the two types: phonon modes and librational modes. However, the reorientation of molecular ions can influence also on peak broadening. Thus, the ammonium reorientations seem not to be the reason of peak broadening in $(\text{NH}_4)_2\text{SeO}_4$.

The crystal structure refinement results for $(\text{NH}_4)_2\text{SeO}_4$ showed that the ammonium ions in this compound can be considered as regular tetrahedra. This conclusion lightens significantly the identification of observed IINS spectra from the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals. The comparison of the IINS spectra from ASE at different temperatures from 30 to 257 K (see Fig. 10, *a*) with that from the mixed crystals ($x = 0.15$ and 0.32) at different temperatures (from 20 to 160 K) points out that the QINS contributions in the IINS spectra of ASE and mixed crystals are different. Therefore, the observed QINS contributions in the IINS spectra from the mixed crystals (Figs. 7, *a* and 8, *a*) at high temperature (160 K) suggest the occurrence of the ammonium ion reorientations. According to the theory, if the ammonium ions do not perform the reorientation over the potential barriers, then the QINS contributions are absent, and vice versa. However, the appearance of the QINS contributions in the IINS spectra of the mixed crystals can suggest a decrease in the potential barrier reorientations of the cations with the decrease in ammonium concentrations.

Then the broadening of the peaks of the $G(E)$ spectra for $(\text{NH}_4)_2\text{SeO}_4$ is due to the anharmonicity of translational and librational vibrations of the crystal lattice and the broadening of mixed crystal peaks is due to the anharmonicity of translational and librational vibrations as well as of the ammonium ion reorientations.

4. CONCLUSIONS

The obtained results allow us to draw the following conclusions.

The neutron powder diffraction studies of the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals ($x = 0.15$ and 0.32) have not detected any phase transition from phase III to phases II or I within a temperature range from 20 to 160 K and phase transition in $(\text{NH}_4)_2\text{SeO}_4$ below room temperature up to low temperature in accordance with the results of [5].

The dynamics studies of $(\text{NH}_4)_2\text{SeO}_4$ by inelastic incoherent neutron scattering show the absence of the QINS contribution in the IINS spectra. The study of the IINS spectra from the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals at different temperatures shows the observation of the QINS contribution at 160 K, decreasing at cooling down to 80 K. Thus, the absence of QINS contribution to the IINS spectra of $(\text{NH}_4)_2\text{SeO}_4$ in comparison with that in the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed

crystals suggests that the reorientation potential barriers of the ammonium ions in $(\text{NH}_4)_2\text{SeO}_4$ are more significant than those in mixed crystals. On the other hand, the peaks of $G(E)$ ascribed to different modes for the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals and $(\text{NH}_4)_2\text{SeO}_4$ are broadened with temperature increase. Anharmonicity and reorientation of ammonium ions are responsible for peak broadening in $G(E)$ for mixed crystals. However, only the anharmonicity seems to be responsible for peak broadening in $(\text{NH}_4)_2\text{SeO}_4$.

It has been shown that the ν_6 librational mode with the energy of 386 cm^{-1} in $(\text{NH}_4)_2\text{SeO}_4$ can be ascribed to $\text{NH}_4(1)$ ion and the ν_6 libration mode with the energy of 428 cm^{-1} is due to the $\text{NH}_4(2)$ ion. The energy of ν_2 inner mode of the SeO_4^{2-} ion in the $\text{K}_{2-x}(\text{NH}_4)_x\text{SeO}_4$ mixed crystals and in $(\text{NH}_4)_2\text{SeO}_4$ is determined as 451 and 455 cm^{-1} , respectively.

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