Far-infrared spectroscopy of the $K_{1-x}(NH_4)_xI$ orientational glass

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1. Introduction

In ideally ordered quasi-harmonic crystals, infrared (IR) and Raman spectroscopies yield basically the first-order active phonons from the Brillouin zone (BZ) centre and the number of active modes can be predicted from the knowledge of the site symmetry of all atoms in the unit cell by a standard factor-group analysis (see, e.g. Ref. [1]). In the case of orientational and dipolar glasses, the local symmetry is broken and a relaxation of the selection rules is usually observed and more peaks appear in the spectra than predicted from factor-group analysis because the phonons from the whole BZ can be activated in the spectra reflecting a weighted phonon density of state (PDOS). Apparent higher-mode damping and also stronger temperature dependence of mode parameters (eigenfrequency, damping, spectral strength) can be expected. Until now we have studied these effects on the well-known dipolar glass system $Rb_{1-x}(NH_4)_xH_2PO_4$ and on its deuterated analog [2, 3]. In this paper, we report on new far-IR (FIR) results obtained on $K_{1-x}(NH_4)_xI$ orientational glass.

FIR properties of pure and doped potassium iodide (KI) were studied many times already long ago, in connection with the investigation of one- or two-mode behaviour in mixed crystals (e.g.,

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Ref. [4]) and in the context of local impurities or resonant modes [5].

Pure ammonium iodide (NH_4I) was also intensively studied, because it undergoes two order-disorder phase transitions (PTs) (see, e.g. Ref. [6]) at ambient pressure. The high-temperature α-phase has a NaCl-type structure ($O_h^5 - Fm\bar{3}m$), where the NH_4 molecules are reorienting among eight symmetry-equivalent positions. Around 250 K a martensitic-type transformation occurs into an intermediate CsCl structure (β-phase, with ($O_h^1 - Pm3m$) space group, $Z = 1$) in which the NH_4 molecules reorient between two energetically equivalent orientations [6]. Finally, below ~230 K octupolar order is established in a slightly distorted CsCl structure of tetragonal symmetry. This γ phase belongs to the $D_{4h}^7 - P4/nmm$ space group ($Z = 2$) and reveals antiparallel ordering of the NH_4 ions [6]. Both PT temperatures are given only approximately because, owing to a martensitic character of the 250 K PT, large hysteresis effects were observed and supercooling of the α-phase has been detected [7].

It is well known for a long time that NH_4I and KI are completely miscible [8], however $K_{1-x}(NH_4)_xI$ has been studied intensively again during the last 10 years when neutron-scattering experiment [9, 10] and dielectric measurement [11] discovered an orientational-glass behaviour at low temperatures in compositions with x below some critical concentration x_c . First attempts to construct a schematic x, T-phase diagram of $K_{1-x}(NH_4)_xI$ were made in 1992 [10, 12]; however, the complete phase diagram has been determined only recently using detailed neutron-diffraction experiments and dielectric spectroscopy [13]. It was found that the low-temperature γ modification, observed in pure NH_4I, is already suppressed in mixed crystals with $x = 0.94$ and the β modification is stable down to the lowest temperatures for $0.78 < x < 0.94$. A strong decrease of the first PT temperature with decreasing x was also observed [10, 13].

A new ε-phase with trigonal symmetry ($C_{3v}^5 - R3m$) has been recently found by neutron diffraction study at low temperatures for $0.58 < x < 0.78$ [14]. This phase is characterized by two inequivalent sites of the four ammonium molecules per unit cell. The NH_4^+ group at the trigonal axis is almost perfectly tetrahedral. The other three ammonium molecules are 0.18 Å off centre and exhibit C_{3v} symmetry with the polar axis along the remaining three body diagonals. Hence, this ε-phase reveals a complex dipolar order with a residual dipole moment along the trigonal axis and is therefore polar.

Below the critical concentration $x_c \approx 0.58$ the NaCl structure is stable down to at least 1 K [13] and the reorienting dipoles undergo a cooperative freezing transition without long-range orientational order [10, 11]. Two anomalies in the dielectric loss $\varepsilon''(T)$ [13, 15] and a NMR study [16] even revealed two different glassy states for $0.45 < x < 0.58$. Paasch et al. [13] suggested that the glass state g_1 might be characterized by a short-range-ordered ε-phase, while the glass state g_2 might be due to a random freezing of some residual orientational degrees of freedom. First, NMR measurement of deuteron spin–lattice relaxation [16] showed that the PT into the glass states is driven by the freezing of random bonds. Recent ^{14}N and ^{127}I NMR experiments [17, 18] revealed that the glass transition is of the random-bond–random-field type. The random-bond contribution is about three times stronger than the random-field one [17].

For the mixed compounds with $0.42 < x < 0.62$ an incomplete softening of the transverse acoustic (TA) modes, propagating along the fourfold axis and the growth of a quasi-elastic central peak, were observed on decreasing temperature at the BZ boundary (X-point) [19, 20]. This effect manifests coupling between the dipolar orientational fluctuations and TA phonon branch. From Brillouin scattering [21] and ultrasonic [22] measurements it follows that this so-called rotation–translation coupling is weak at the BZ centre, efficient for wave vectors $q^* \geqslant 0.5$ and the largest at the X-point of BZ [20].

An activation of transverse and longitudinal acoustic phonons at the BZ boundary was observed in Raman spectra of the ε and glass phases, owing to a breaking of the local symmetry in the mixed crystal [11, 23, 24]. Observation and evaluation of a similar effect in the FIR spectra of $K_{1-x}(NH_4)_xI$ will be reported in this paper.

2. Experimental details

The three single crystals of $K_{1-x}(NH_4)_xI$ studied in FIR region were grown from aqueous solution with nominal concentration $x = 0.1$, 0.55 and 0.7. The actual ammonium concentrations in the mixed crystals ($x = 0.08$, 0.43 and 0.59) were determined from the concentration dependence of the lattice parameter published in Ref. [13].

FIR reflectivity and transmission spectra in the range 12–650 cm^{-1} were obtained using a Bruker IFS 113v Fourier spectrometer equipped with a helium-cooled Ge bolometer. No polarizer was used because of the cubic symmetry (optical isotropy) of the crystals. Reflectivity measurements were performed using a continuous-flow Oxford CF104 cryostat, where the sample is mounted on a cold finger in vacuum. The transmission spectra were obtained down to 5 K using the UTRECS cryostat, where the sample is placed in the helium-transfer gas.

Plane-parallel plates of 0.1–0.36 mm thickness for transmission and ~2 mm for reflection measurement were cut and polished from single crystals (volumes 0.5–1 cm^3) of good optical quality. We have focused mainly on the investigation of external lattice vibrations of $K_{1-x}(NH_4)_xI$ mixed crystals, therefore all the spectra were taken in the range 12–650 cm^{-1} (transmission) or 25–650 cm^{-1} (reflectivity).

3. Results and evaluation

The room-temperature reflectivity spectra of all three samples with different NH_4 concentrations are shown in Fig. 1a. Spectra are plotted in the region below 250 cm^{-1} because the reflectivity is almost constant at higher frequencies. At room temperature the number of reflection bands corresponds to the result of the factor-group analysis which predicts only one IR active external mode (of F_{1u} symmetry) in the pure crystal of the NaCl structure [6, 25]. In our case, we see a two-mode behaviour in the mixed crystals. The first reflectivity band near 100 cm^{-1} corresponds predominantly to $K^+ \leftrightarrow I^-$ and the second one at ~150 cm^{-1} to $NH_4^+ \leftrightarrow I^-$ translation mode. Therefore, the

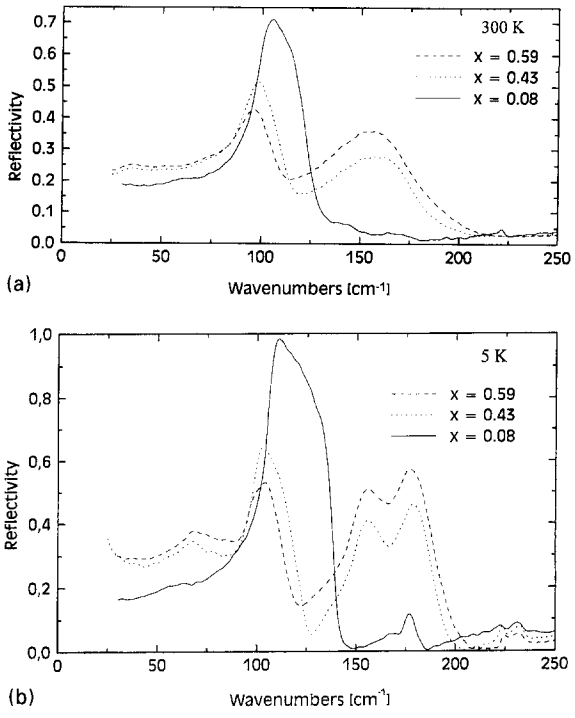

Fig. 1. FIR reflectivity spectra of three $K_{1-x}(NH_4)_xI$ mixed crystals ($x = 0.08$, 0.43, 0.59) at (a) room temperature and (b) 5 K.

intensity of the first band decreases and the intensity of the second one increases with the NH_4 concentration.

In Fig. 1b we show the FIR reflectivity spectra of the same samples at 5 K. The height of all reflection bands increases on cooling due to decreasing mode damping, while the frequency of the reststrahl mode at ~100 cm^{-1} decreases with increasing NH_4 concentration and hardens on cooling. The reststrahl mode in the region 150–180 cm^{-1} also hardens on cooling in all the samples, nevertheless, the mode in the $x = 0.08$ sample has the highest frequency at room temperature and two new modes appear in the reflectivity spectra below 100 K at ~150 and ~170 cm^{-1}. In the other two samples the mode at ~150 cm^{-1} is active already at room temperature and only one new mode appears at ~170 cm^{-1} below 200 K (see Fig. 7). A new band appears also at ~70 cm^{-1} and its intensity increases with NH_4 concentration. Weak bands near 230 cm^{-1} belong to ice which

crystallizes in small amounts on the sample at low temperatures (due to the imperfect vacuum), and are not taken into account for the data evaluation.

Infrared transmission spectra of all three investigated samples are shown in Fig. 2a–Fig. 2c at 300 and 5 K. The samples are opaque in the region of the reflection bands; however, weak absorption bands are seen especially at low temperatures in the remaining spectral regions. The transmission spectrum of the $x = 0.08$ sample has a qualitatively different shape compared to the other two samples – three absorption bands appear below 70 cm^{-1} (see Fig. 3). Low- temperature transmission spectra of the samples with $x = 0.43$ and 0.59 are similar in the region above 200 cm^{-1}, multiphonon absorption features at ~350, 460 and 610 cm^{-1} are seen in Fig. 2b and Fig. 2c. These multiphonon peaks are seen in the $x = 0.08$ sample at different frequencies (~450 and ~515 cm^{-1}). The libration of NH_4^+ groups was revealed near 230 cm^{-1} in transmission spectra of all samples.

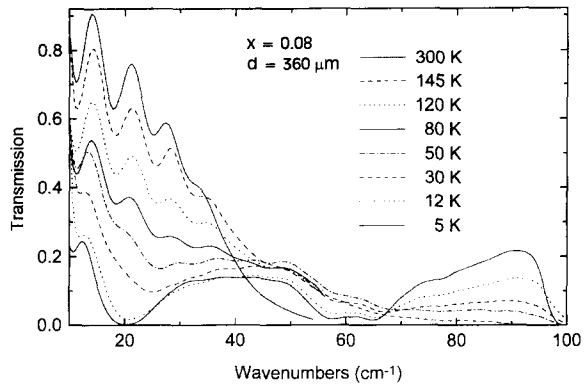

Fig. 3. Temperature dependence of submillimetre transmission spectra of the $x = 0.08$ sample.

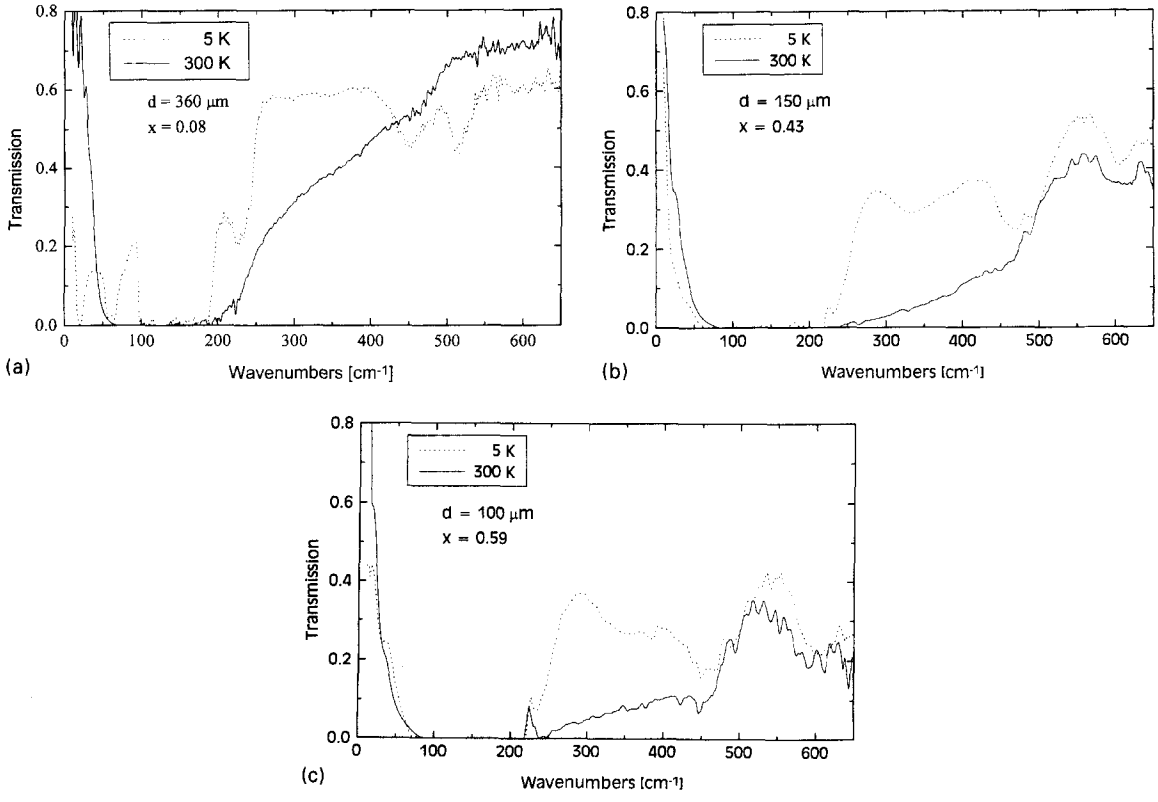

Fig. 2. FIR transmission spectra of (a) $x = 0.08$, (b) $x = 0.43$ and (c) $x = 0.59$ samples at 300 and 5 K.

Both transmission and reflectivity spectra were simultaneously fitted with the sum of classical oscillators. Two oscillators (needed for reflection bands fit) are not sufficient for fitting the transmission spectra and additional oscillators are needed even at room temperature. The resulting calculated permittivity ε' and dielectric loss ε'' spectra are plotted in Figs. 4–6.

In our case, the absorption can be fitted only approximately with the model of harmonic oscillators. Three oscillators were used for describing the transmission minima below 100 cm^{-1} and the absorption background was fitted with one overdamped oscillator near 70 cm^{-1}. The temperature dependence of all mode frequencies observed below 180 cm^{-1} (except for overdamped background oscillators) is shown in Fig. 7 together with the modes from other samples.

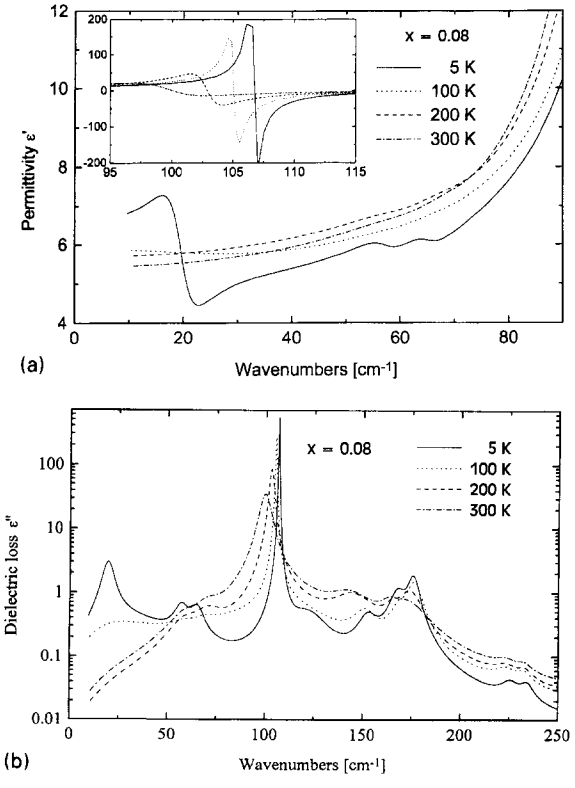

Fig. 4. Temperature dependence of (a) dielectric permittivity ε' and (b) dielectric loss ε'' of the $x = 0.08$ sample calculated the from classical harmonic oscillator model fits of the reflectivity and transmission spectra. Note the logarithmic scale in (b).

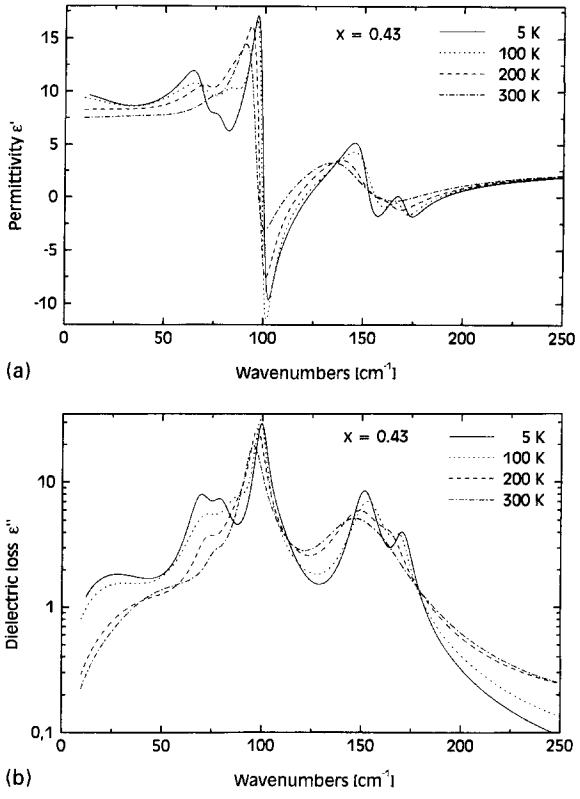

Fig. 5. Temperature dependence of (a) dielectric permittivity ε' and (b) dielectric loss ε'' of the $x = 0.43$ sample.

4. Discussion

4.1. x = 0.08 sample

According to the phase diagram [13], the NaCl structure of the KI sample with 8% of NH_4 should be stable down to the lowest measured temperatures. Nevertheless, on cooling, the spectra change quite significantly. Additional absorption appears below 100 cm^{-1}, besides lowering of the main modes damping and resulting in higher intensities of the reflection bands. This is seen mainly in the transmission spectra. In contrast to the spectra of usual pure crystals, the transmission below 75 cm^{-1} decreases on cooling and three transmission bands appear at low temperatures (see Fig. 3). The strengths of these modes are too small to be detected in the reflectivity spectra.

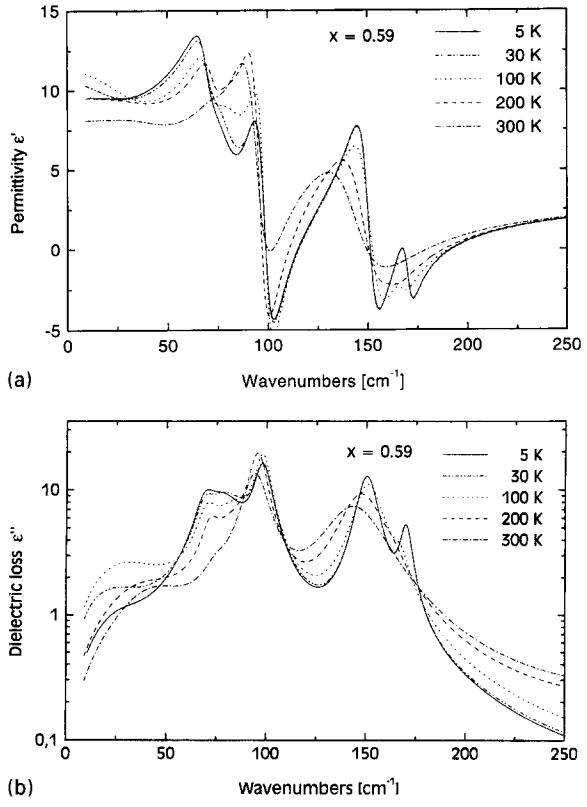

Fig. 6. Temperature dependence of (a) dielectric permittivity ε' and (b) dielectric loss ε'' of the $x = 0.59$ sample. Note the decreasing dielectric loss below 100 K at frequencies below 50 cm^{-1}.

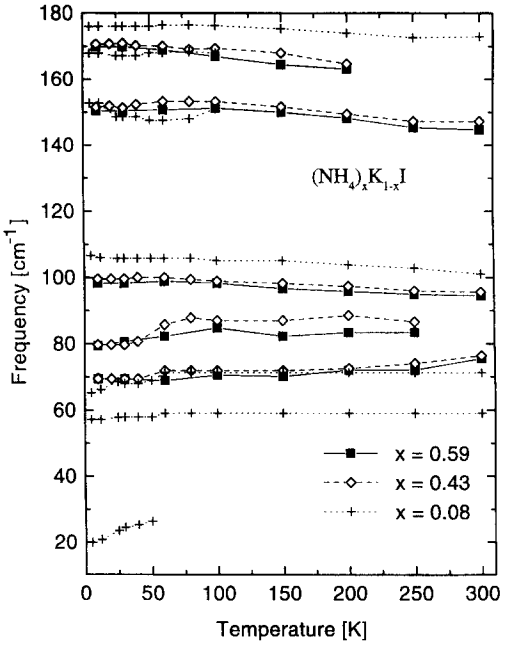

Fig. 7. Temperature dependence of the mode frequencies below 180 cm^{-1} observed for all samples investigated.

In spite of the absence of macroscopic change of symmetry, the NH_4^+ ions break the translational periodicity of the KI lattice, change the local symmetry and, in consequence, the IR selection rules are relaxed. All phonons from the BZ may be active and, to a first approximation, we assume that the spectra are proportional to the one-phonon density of state (PDOS). In pure KI and NH_4I, the PDOS was calculated on the basis of inelastic neutron scattering measurements of phonon dispersion curves [26, 27]. Let us compare this PDOS with our FIR data.

The lowest frequency mode appears below ~50 K at 27 cm^{-1} and softens on cooling down to 20 cm^{-1} at 5 K. This frequency is very close to the frequency of the first maximum in PDOS observed in pure KI at 90 K near 30 cm^{-1} [26], whereas in the case of pure NH_4I its frequency is even lower at 21.2 cm^{-1} [27]. This maximum in the PDOS exactly corresponds to the frequency of TA phonon from the BZ boundary in the direction (1, 0, 0) (X-point) [26]. The same TA phonon from the X-point was observed in Raman spectra [23, 24] in samples with higher NH_4 concentration (16–62%) and it revealed also slight softening on cooling [24]. In the Raman spectra of the $x = 0.07$ sample this mode was not observed [23], presumably due to its low intensity. Softening of the TA phonon near the BZ centre below 100 K (by 8%) was observed also in Brillouin scattering experiments [21]. The anomalous behaviour of TA phonons was interpreted as a function of temperature via the rotation–translation coupling [19, 20].

The other two modes at 57 and 65 cm^{-1}, which are clearly seen in the transmission spectra (Fig. 4), were also observed in Raman scattering [23] at 55 and 63 cm^{-1} and they correspond to TA (55 cm^{-1}) and LA (68 cm^{-1}) phonons with the wave vector (0.5, 0.5, 0.5) (L-point) in pure KI [26]. Another possible explanation of the mode at 57 cm^{-1} is

the LA phonon from the X-point of BZ (in pure KI this frequency is 52 cm^{-1}), as it was assigned in Ref. [24]. The PDOS in pure KI crystal exhibits maxima at similar frequencies (53 and 63 cm^{-1}) [26].

4.2. $x = 0.43$ sample

The $x = 0.43$ sample should transform into an orientational-glass state below ~ 10 K [13]. Nevertheless, the influence of disorder can be seen in the spectra at all temperatures. The damping of the reststrahl phonon near 100 cm^{-1} at 5 K is 15 times higher (see Fig. 5) than in the former sample, providing evidence of higher disorder in the latter case. Activation of the modes below 90 cm^{-1} and near 170 cm^{-1} again is possible only due to local symmetry breaking. The oscillator strengths of these modes are more than one order of magnitude higher than that of the $x = 0.08$ sample, therefore the modes can be easily detected in the reflectivity spectra (Fig. 1) and even a thin (150 μm) sample is opaque in the region 70–220 cm^{-1} at all temperatures (Fig. 2b). Like in the former sample, the transmission below 80 cm^{-1} decreases (i.e. the absorption increases – see Fig. 5b) on cooling in the whole temperature range. The modes at $\sim$ 70 and 80 cm^{-1} correspond again to the PDOS maxima in the acoustic phonon range like in the former sample, but the frequencies are indicating that the PDOS maxima in mixed $K_{1-x}(NH_4)_xI$ crystals are shifted to higher frequencies [26, 27]. However, the modes do not correspond to the peaks observed in Raman scattering on the $x = 0.46$ sample at 53 and 61 cm^{-1} for $T = 15$ K [23, 24]. Apparently, the weighting of PDOS cannot always be neglected in calculating the Raman and/or IR response in the low-frequency range.

The transmission minimum due to TA phonons at ~ 20 cm^{-1} (observed in the case of $x = 0.08$ sample) is not seen in this case. Instead, an overdamped oscillator at about 30 cm^{-1} is necessary for the fit of transmission spectra, which indicates a different PDOS in the low-frequency range in mixed crystals with an increased number of NH_4 groups.

4.3. $x = 0.59$ sample

The crystal structure of this sample should transform to antiferroelectrically ordered ε-phase with the polar trigonal C_{3v}^5 –R3m symmetry at $\sim$ 40 K [14]. Its primitive unit cell is four times larger than in the parent phase (O_h^5), therefore many new modes should be activated. Let us assume that within the spirit of two-mode behaviour in mixed crystals, we can simply add the phonon modes of pure KI and NH_4I. Then the factor group analysis in the cubic α-phase yields $2F_{1u}$ IR-active translational mode. A similar procedure performed for the ε- phase yields $9A_1$ (IR, R) + $6A_2(-)$ + 15E (IR, R) external optic modes, where the IR and Raman (R) activity is denoted in parantheses. So we could expect the appearence of 22 new modes in our FIR spectra, mainly due to the BZ folding.

However, even at low temperatures we can see the same number of modes like in the $x = 0.43$ sample, which means five modes below 180 cm^{-1} (see Figs. 6 and 7) plus one overdamped oscillator near 35 cm^{-1} which describes the continuous absorption below 90 cm^{-1}. New modes at $\sim$170 and 70–80 cm^{-1} appear in the reflectivity spectra below 200–250 K like in the $x = 0.43$ sample. The intensity of these modes is higher which is a consequence of the higher NH_4 concentration and long-range order in the sample.

The temperature dependence of the dielectric-loss spectra below 100 cm^{-1} is qualitatively different from that in both previous samples (see Fig. 6b). The intensity of the bands at 70–80 cm^{-1} increases on cooling (like in the other samples), but the loss ε'' exhibits a non-monotonous temperature dependence at lower frequencies. The strength of the overdamped absorption band near $\sim$ 35 cm^{-1} increases on cooling down to 100 K, but decreases below 100 K and its value at 5 K is comparable with that at 300 K (see Fig. 6b). This phenomenon is apparently connected with the structural phase transition into the ordered phase ε. At high temperatures the long-range order is disturbed by NH_4 dopants and the local symmetry is broken like in the former samples. However, at lower temperatures the structure starts to order prior to the appearence of the ε-phase below $\sim$40 K. Nevertheless, the residual value of dielectric loss at 5 K near

$30\,cm^{-1}$ gives evidence for a partial presence of disorder in this sample.

5. Conclusions

The breaking of IR selection rules, valid for pure crystals, was observed at all temperatures below 300 K in all three mixed crystals of $K_{1-x}(NH_4)_xI$ which were investigated. Similar effects were observed in Raman experiments [23, 24]. Due to the local symmetry breaking not only the mode at $\sim 170\,cm^{-1}$ splits, but also the acoustic modes from the BZ boundary are activated in the spectra. The strengths of the activated acoustic modes in the FIR spectra increase with NH_4 concentration due to an increasing influence of symmetry breaking. The soft TA phonon at $\sim 25\,cm^{-1}$, which corresponds very well to the result of inelastic neutron scattering measurements from the X-point of the BZ [20], is most clearly seen in the transmission spectra of the sample with the lowest NH_4 concentration, whereas in the spectra of samples with higher NH_4 concentration only a broad absorption was observed. LA and TA phonons from the L-point of the BZ, which are also seen in our FIR spectra, also slightly soften on cooling and their frequencies are approximately by $10\,cm^{-1}$ lower in the $x = 0.08$ sample than in other two samples (see Fig. 7).

No clear effect connected with the glass transition was observed in our FIR spectra. Disorder manifests itself in the spectra already at room temperature but is more apparent at low temperatures. The transition to the ordered ε phase (in $x = 0.59$ sample) is demonstrated by a decrease in dielectric loss below 100 K in the low-frequency part.

Acknowledgements

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