Lithium disorder in the vicinity of the superionic phase transition in monoclinic and rhombohedral $Li_3In_2(PO_4)_3$

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Rhombohedral and monoclinic modifications of the $Li_3In_2(PO_4)_3$ compound have been studied by X-ray diffraction, infrared (i.r.) analysis, Raman light scattering, differential thermal analysis (DTA), differential scanning calorimetry (DSC) and impedance spectroscopy, in a wide temperature range of 290–600 K. Analysis of the data allows the suggestion that the superionic phase transition, observed in these materials in the temperature interval 370–385 K, belongs to Faraday type phase transformations. PO_4 tetrahedra, which are a partition of the $(In_2P_3O_{12})_{300}^{3-}$ rigid skeleton, have been found deformed. This seems to be due to an ordered lithium ion–vacancy distribution in the low temperature, non-superionic, polymorphs. With increasing temperature these deformations disappear. This disappearance can be caused by a decrease of the correlation length of the lithium ion–vacancy order.

1. Introduction

Lithium indium phosphate exists at room temperature in either rhombohedral [1], NASICON type, or monoclinic [2], $Fe_2(SO_4)$ type, modifications, depending on the synthesis conditions [3]. All these materials undergo a superionic phase transition within a rather narrow temperature range, 360–385 K [3]. Above the phase transition temperature, ionic conductivity, σ, reaches a value of 5×10^{-5} S cm^{-1} for the monoclinic modifications [prepared at temperatures, T of $\geqslant$ 1290 K and refered to in [3] as high temperature $Li_3In_2(PO_4)_3$], and for one of the rhombohedral [prepared at 1180 K $< T \leqslant$ 1230 K, low temperature (LT) $Li_3In_2(PO_4)_3$ [3]] modifications. In the case of the rhombohedral modification prepared at $T \leqslant$ 1100 K [LT' $Li_3In_2(PO_4)_3$ [3]], σ remains at about 7.5×10^{-7} S cm^{-1}, even at $T \simeq$ 450 K [3].

Thus, it is clear that the origin of the superionic state is not connected with the average symmetry of the crystals, and should be looked for in peculiarities of the ion–ion interactions in the materials.

This paper presents data on X-ray powder diffraction, i.r., Raman, DSC, DTA and impedance spectroscopy studies, for the whole set of lithium indium phosphate modifications, in a wide temperature range. The scope of these experiments was to investigate crystal behaviour in the vicinity of the superionic phase transition.

To make the lithium contribution to the experimental data more distinct a ^7Li by ^6Li substitution (up to 88 at %) has been carried out for the monoclinic modification of $Li_3In_2(PO_4)_3$.

2. Experimental procedure

All the samples under investigation were obtained by conventional solid state synthesis. This process is described in more detail in [3].

X-ray powder diffraction patterns were recorded in the 2θ range 10–60° with a Rigaku Geigerflex D3 automatic powder diffractometer ($\lambda = 0.15105$ nm). I.r. spectra of the samples were recorded in the frequency range 200–1400 cm^{-1} with Specord equipment, using the KBr matrix technique. Raman spectra have been obtained in the frequency range 10–1400 cm^{-1} ($\lambda = 514.4$ nm) at 293 K. During the experiments, temperature was maintained with $1 \pm$ K accuracy.

DSC studies were performed with a Perkin–Elmer DSC-7 unit, in the temperature range 290–600 K.

Ionic conductivity measurements were carried out using the impedance spectroscopy technique (for more details see [3]).

3. Results and discussion
3.1. Monoclinic modifications

Powder diffraction patterns of $^{6,7}Li_3In_2(PO_4)_3$ at 273 K were indexed using space group and lattice cell parameters found in [2]. The obtained results are presented in Table I. As can be seen from Table I, there are no significant differences in the lattice cell parameters of $^6Li_3In_2(PO_4)_3$ and $^7Li_3In_2(PO_4)_3$, although a slight decrease of the lattice cell volume in the latter case should be mentioned.

It should also be noted that the monoclinic angle of the lattice cell deviates less from 90° in both cases.

TABLE I Room temperature (298 K) powder diffraction data for ⁷Li₃In₂(PO₄)₃ and ⁶Li₃In₂(PO₄)₃

\(^7\text{Li}_3\text{In}_2(\text{PO}_4)_3\)[a]				\(^6\text{Li}_3\text{In}_2(\text{PO}_4)_3\)[b]			
hkl	d_{calc}	d_{obs}	I/I_0	hkl	d_{calc}	d_{obs}	I/I_0
0 0 2	6.115	6.112	7	0 0 2	6.123	6.103	7
−1 1 1	5.501	5.500	11	1 1 1	5.493	5.480	9
0 2 0	4.431	4.431	18	0 2 0	4.428	4.418	15
−1 1 2	4.342	4.341	100	1 1 2	4.335	4.324	100
−2 0 0	4.272	4.275	27				
−2 1 0	3.848	3.854	12				
1 2 1	3.743	3.745	8	1 2 1	3.742	3.745	7
2 1 1	3.684	3.681	15	2 1 1	3.672	3.675	15
−1 1 3	3.402	3.401	10	−1 1 3	3.404	3.401	8
−1 2 2	3.311	3.312	11	1 2 2	3.305	3.300	7
−2 2 0	3.076	3.078	36				
0 0 4	3.058	3.060	26	0 0 4	3.059	3.066	31
−2 2 1	2.984	2.986	6	2 2 1	2.982	2.981	5
−2 2 2	2.750	2.749	14				
−1 1 4	2.741	2.739	24				
−1 3 1	2.723	2.723	21	−1 3 1	2.721	2.726	36
−1 3 2	2.541	2.542	26	−1 3 2	2.540	2.543	14
0 2 4	2.517	2.518	12	0 2 4	2.517	2.518	25
2 0 4	2.483	2.485	43	2 0 4	2.486	2.486	32
2 2 3	2.452	2.447	5				
−2 2 4	2.171	2.171	13	2 2 4	2.167	2.169	10
				−3 0 4	2.091	2.091	3
0 0 6	2.038	2.039	4				
				3 1 4	2.027	2.030	6
1 4 2	2.023	2.024	12	1 4 2	2.022	2.021	8
−4 1 2	1.968	1.968	8				
0 4 3	1.947	1.947	14				
				−1 1 6	1.938	1.938	27
				4 1 3	1.850	1.849	8
				4 2 2	1.836	1.836	15
				0 5 3	1.626	1.625	11
				5 1 2	1.619	1.619	13
				3 3 5	1.571	1.570	5

[a] $a = 0.8544$ nm, $b = 0.8863$ nm, $c = 1.2231$ nm, $\beta = 90.19(4)°$; space group $= P2_1/n$.
[b] $a = 0.8560$ nm, $b = 0.8853$ nm, $c = 1.2236$ nm, $\beta = 90.22(5)°$; space group $= P2_1/n$.

TABLE II Room temperature (298 K) powder diffraction data for ⁷Li₃In₂(PO₄)₃ and ⁶Li₃In₂(PO₄)₃

\(^7\text{Li}_3\text{In}_2(\text{PO}_4)_3\)[a]			\(^6\text{Li}_3\text{In}_2(\text{PO}_4)_3\)[b]		
hkl	d_{calc}	d_{obs}	hkl	d_{calc}	d_{obs}
0 0 2	6.119	6.112	0 0 2	6.117	6.103
1 1 1	5.501	5.500	1 1 1	5.496	5.480
0 2 0	4.432	4.431	0 2 0	4.431	4.418
1 1 2	4.341	4.341	1 1 2	4.337	4.324
2 0 0	4.282	4.275			
1 2 1	3.747	3.745	1 2 1	3.745	3.745
2 1 1	3.677	3.681	2 1 1	3.671	3.675
1 1 3	3.401	3.401	1 1 3	3.399	3.401
1 2 2	3.310	3.312	1 2 2	3.308	3.300
2 2 0	3.079	3.078			
0 0 4	3.060	3.060	0 0 4	3.059	3.066
2 2 1	2.986	2.986	2 2 1	2.983	2.981
1 3 1	2.723	2.723	1 3 1	2.722	2.726
2 2 2	2.751	2.749			
1 1 4	2.740	2.739			
1 3 2	2.541	2.542	1 3 2	2.540	2.543
0 2 4	2.518	2.518	0 2 4	2.517	2.518
2 0 4	2.483	2.485	2 0 4	2.487	2.486
2 2 3	2.458	2.447			
2 2 4	2.170	2.171	2 2 4	2.169	2.169
			2 3 3	2.087	2.091
0 0 6	2.040	2.039	0 0 6	2.043	2.042
1 4 2	2.024	2.024	1 4 2	2.022	2.021
2 4 0	1.968	1.968			
3 3 2	1.946	1.947	1 1 6	1.935	1.938

[a] $a = 0.8563$ nm, $b = 0.8863$ nm, $c = 1.2238$ nm; space group $= Pbcn$.
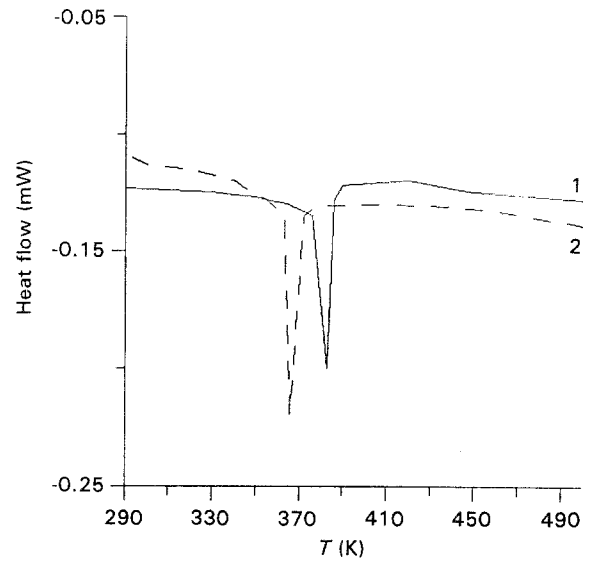[b] $a = 0.8544$ nm, $b = 0.8861$ nm, $c = 1.2234$ nm; space group $= Pbcn$.

Figure 1 DSC curves of monoclinic (1) ⁷Li₃In₂(PO₄)₃, and (2) ⁶Li₃In₂(PO₄)₃.

Perhaps this feature allows the use of orthorhombic symmetry (space group *Pcan*) for indexation of the same diffraction data (see Table II).

So, the diffraction experiments give no answer on the true symmetry of the non-rhombohedral samples. The same phenomenon was observed earlier during diffraction studies of the monoclinic modification of the Li₃Fe₂(PO₄)₃ compound. The symmetry of its crystal structure was originally found to be ortho-rhombic (space group $P22_12_1$) at room temperature [4], due to pseudo-orthorhombic lattice cell parameters (small deviation of the monoclinic angle from 90°) and pseudomerohedrical twinning of the crystals [5].

Taking into account that monoclinic Li₃In₂(PO₄)₃ is isostructural to monoclinic Li₃Fe₂(PO₄)₃ and Li₃Sc₂(PO₄)₃, in accordance with [2, 6], one can suppose that the observed orthorhombic symmetry of the diffraction pattern is pseudosymmetric, indeed, and that the samples have monoclinic symmetry.

Both DSC and impedance spectroscopy data can be considered as confirmations of the suggestion. Fig. 1 shows DSC curves of the materials under considera-tion. As can be seen from Fig. 1, there are peaks on these curves at ≃ 381 and ≃ 369 K for ⁷Li₃In₂(PO₄)₃ and ⁶Li₃In₂(PO₄)₃, respectively. Besides, anomalies of the temperature dependencies of the ionic conductiv-ity are also observed at these temperatures, see Fig. 2. Thus, the investigated samples undergo a phase trans-ition. As was shown in [7, 8], monoclinic modifica-tions of Li₃M₂(PO₄)₃-type crystals undergo phase transitions; while, according to [9], orthorhombic

modifications of these compounds undergo no phase transformation in the temperature interval 290–570 K.

At the superionic phase transition point ($\simeq$ 369 K) the X-ray diffraction pattern of $^6Li_3In_2(PO_4)_3$ is changed (see Fig. 3). As can be seen from Fig. 3, degeneration is observed of both the (0 2 0)–(1 1 2) doublet and ($\bar{1}$3 2)–(0 2 4)–(2 0 4) triplet above 370 K. It may be
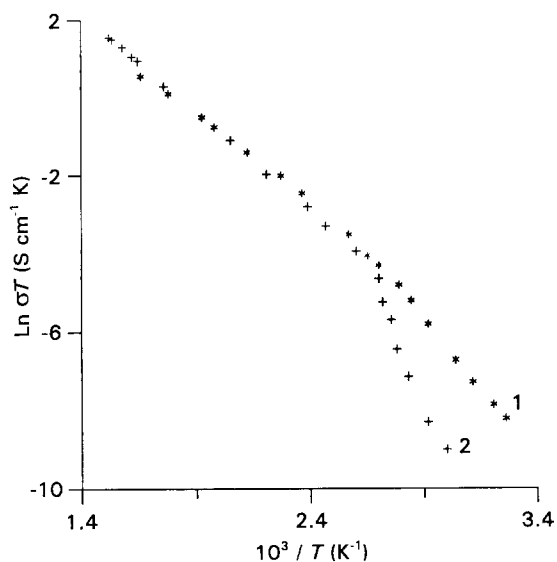

Figure 2 Temperature dependencies of the ionic conductivity of the monoclinic modifications of (1) $^7Li_3In_2(PO_4)_3$, and (2) $^6Li_3In_2(PO_4)_3$.

considered as a consequence an increase in crystal structure symmetry, but the ($\bar{1}$3 1) singlet is split simultaneously at the phase transition point into the (2 2 2)–(3 1 0) doublet (see Fig. 3b).

Thus, monoclinic symmetry of the $^6Li_3In_2(PO_4)_3$ crystal structure seems to be preserved at this phase transformation. As can be seen from Table III, the diffraction pattern of the lithium indium phosphate can be indexed using the same monoclinic space group ($P2_1/n$) for 373 K as for 293 K.

It should be pointed out that this is a rather usual situation for $Li_3M_2(PO_4)_3$ type compounds. As was shown elsewhere [10], using precise single crystal diffraction studies, the $\alpha \rightarrow \beta$ phase transformations in $Li_3Sc_2(PO_4)_3$ and $Li_3Fe_2(PO_4)_3$ are also accompanied by no symmetry changes. Above and below the phase transition point these crystals have the same monoclinic symmetry (space group $P2_1/n$). Such a type of phase transition is sometimes called a Faraday transition [11].

On the other hand, from the point of view of the Landau theory, this phenomenon can be classified as a first-order phase transition, occuring above a critical point on the corresponding phase diagram.

It is worthy to note that there is, in principle, another possibility to describe the above-considered σ and C_p (heat capacity) anomalies, suggesting that a Shottky type process [12] takes place instead of phase transitions. In such a way one should consider the lithium indium phosphate as, at least, a two-level
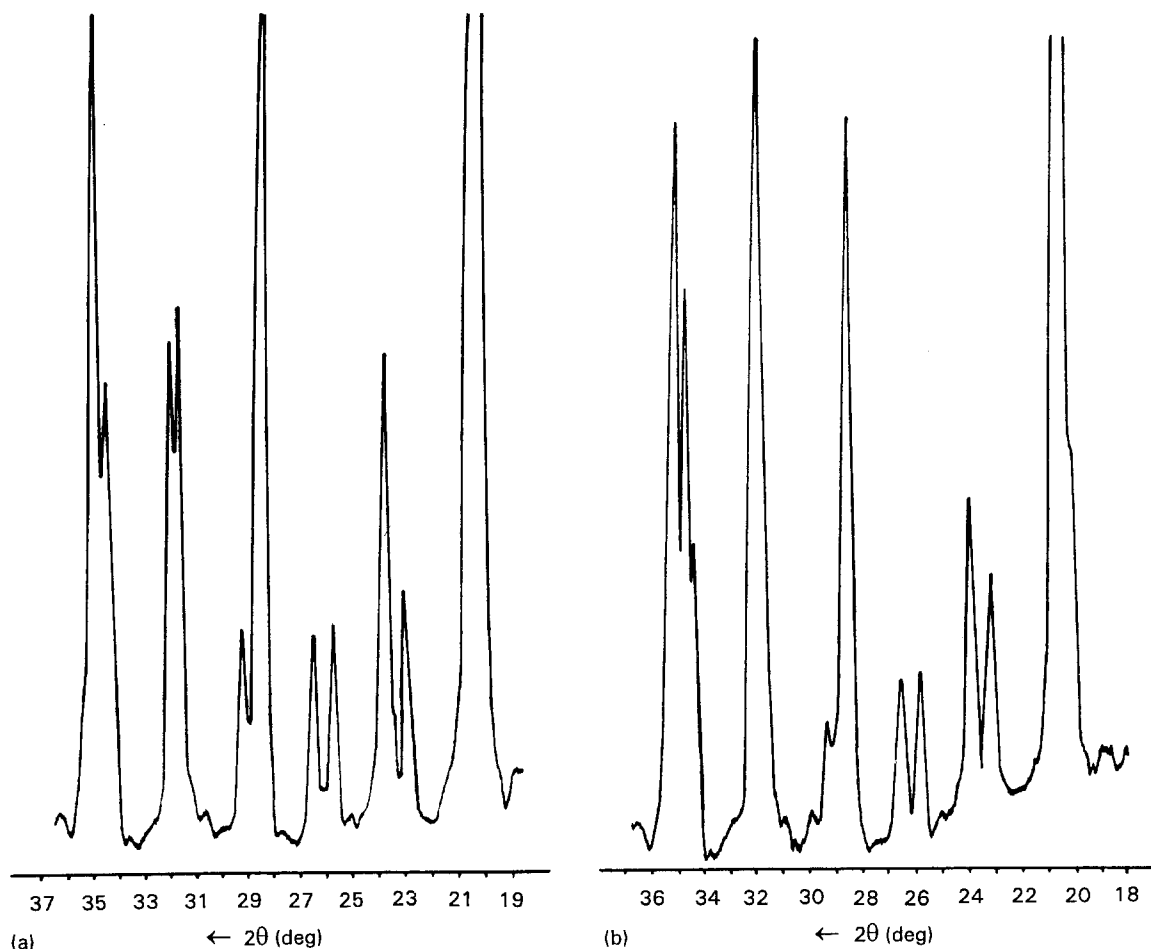

Figure 3 Powder diffraction patterns of $^6Li_3In_2(PO_4)_3$ at (a) 293 K, and (b) 373 K.

TABLE III Powder diffraction data for $^6Li_3In_2(PO_4)_3$ at 373 K for space group $P2_1/n$ and space group $Pbcn$

Space group $P2_1/n$[a]				Space group $Pbcn$[b]		
hkl	d_{calc}	d_{obs}	I/I_0	hkl	d_{calc}	d_{obs}
1 1 0	6.163	6.146	6	1 1 0	6.161	6.146
1 1 1	5.497	5.504	8	1 1 1	5.503	5.504
1 1 2	4.336	4.322	100	1 1 2	4.342	4.322
− 1 2 1	3.746	3.746	5	1 2 1	3.742	3.746
2 1 1	3.693	3.696	21	2 1 1	3.685	3.696
− 1 1 3	3.408	3.405	9	1 1 3	3.402	3.405
1 2 2	3.305	3.306	9	1 2 2	3.307	3.306
2 2 0	3.081	3.076	48	2 2 0	3.080	3.076
− 2 2 1	2.991	2.992	9	2 2 1	2.987	2.992
2 2 2	2.749	2.748	24	2 2 2	2.752	2.748
3 1 0	2.725	2.724	22	3 1 0	2.725	2.724
0 2 4	2.517	2.515	20	0 2 4	2.516	2.515
2 0 4	2.494	2.493	41	2 0 4	2.493	2.493
0 4 1	2.175	2.177	14	0 4 1	2.174	2.177
− 4 0 0	2.148	2.149	5	4 0 0	2.148	2.149
4 0 2	2.027	2.028	5	4 0 2	2.027	2.028
− 2 4 0	1.966	1.966	7	2 4 0	1.965	1.966
3 3 2	1.945	1.945	35	3 3 2	1.947	1.945
4 2 1	1.907	1.908	7	4 2 1	1.909	1.908
3 0 5	1.857	1.857	7	4 1 3	1.859	1.857
− 4 2 2	1.845	1.845	11	2 0 6	1.843	1.845
2 4 3	1.769	1.768	9	2 4 3	1.770	1.768
3 2 5	1.715	1.715	10	3 2 5	1.715	1.715
5 1 2	1.627	1.627	18	5 1 2	1.627	1.627

[a] $a = 0.8593$ nm, $b = 0.8842$ nm, $c = 1.2243$ nm, $\beta = 90.27$ (3) °
[b] $a = 0.8594$ nm, $b = 0.8837$ nm, $c = 1.2242$ nm.

system. These levels could arise, for example, from an energy difference, ΔE, between crystallographically independent lithium ion sites [as was shown in [2], there are three crystallographically independent lithium ion sites in $Li_3In_2(PO_4)_3$].

This approach was previously used to describe the $C_p(T)$ behaviour in PbF_2 near the superionic phase transition [13].

In such a case one could observe an anomaly in the heat capacity temperature dependence at $T \simeq T^*$, where T^* satisfies the following equation

$$kT^* = \Delta E$$

(where k is the Boltzmann constant). Taking into account the T^* value found from DSC data, one can calculate the ΔE value, i.e. $\simeq 0.04$ eV.

It should be stressed that in the case of the Shottky type process, disordering has to take place in the absence of interactions between lithium ions, because in the opposite case a phase transition would occur.

However, DTA data show heat absorption or emanation by $Li_3In_2(PO_4)_3$ (under increasing or decreasing temperature, respectively), at the same temperature points at which the C_p anomalies are observed. It indicates that there are entropy changes at these temperatures, so the anomalies found are caused by first-order phase transitions.

Thus, monoclinic modifications of $Li_3In_2(PO_4)_3$ undergo Faraday type phase transitions within the temperature range 369–381 K.

It should be especially mentioned that in such a case a superionic state in the lithium indium phosphate

appears in the monoclinic phase. According to the literature [5, 7] the monoclinic phases, both in $Li_3Sc_2(PO_4)_3$ and in $Li_3Fe_2(PO_4)_3$, are characterized by full occupation of the lithium ion sites. If one supposes that the same holds for $Li_3In_2(PO_4)_3$, this will contradict the well known (see, for example, [11]) point of view on the structural features of a superionic state (statistic occupation of the mobile ion sites).

So, one believes that lithium ions occupy more than three sets of sites in the crystal structure of the high temperature monoclinic modification of $Li_3In_2(PO_4)_3$. Below the superionic phase transition point the lithium sublattice should undergo some ordering. However, there are two possible ways for realization of the ordering process. On the one hand this could be due to a decrease in the number of available sites and full occupation of the three sets of four-fold positions. On the other hand it could be ion–vacancy ordering within the high temperature four sets of the four-fold positions. To study these possibilities i.r. spectroscopy data have to be used.

As can be seen from Fig. 4 (curve 1) the i.r. spectra of the $^6Li_3In_2(PO_4)_3$ and $^7Li_3In_2(PO_4)_3$ are similar at room temperature, with the exception of the frequency range 350–500 cm^{-1}. The difference in the latter frequency range is observed more distinctly in the Raman spectra of the materials (see Fig. 5). The origin of the difference is not clear yet.

Changes have been found in the i.r. spectrum of both compounds with increasing temperature (see Fig. 4, curves 2, 3). Heating the samples causes the disappearance of the 550 and 635 cm^{-1} modes in the temperature range 345–355 K. It should be mentioned that these modes disappear in $^7Li_3In_2(PO_4)_3$ at a slightly ($\simeq 5$ K) higher temperature than in $^6Li_3In_2(PO_4)_3$. With decreasing temperature these modes appear again at the same frequencies, indicating the reversibility of this phenomenon.

From our point of view these changes are not directly connected with changes in lithium ion vibrations, because the pointed modes do not undergo an isotope shift under $^6Li \rightarrow {}^7Li$ substitution. On the other hand these modes lie within the frequency range corresponding to deformational vibrations of the PO_4 tetrahedra [14, 15]. So, one attributes these modes to deformational vibrations of the PO_4 tetrahedra.

As mentioned above, there are no structural phase transitions below the superionic phase transition point in $Li_3In_2(PO_4)_3$. So, the observed changes in the deformation state of the PO_4 tetrahedra should be caused by the behaviour of the lithium subsystem.

It was earlier observed [16] that deformation of the PO_4 tetrahedra in $[M_2P_3O_{12}]_{300}$ skeletons can be caused by asymmetrical alkali ion–vacancy distribution around the tetrahedra. The long range order in the alkali ion subsystem multiplies the effect, resulting in the appearance of an additional deformation band in the vibrational spectrum of the compound. Correspondingly, the lack of long range order will result in the disappearance of the deformation mode.

Thus, the observed disappearance of the 550 and 635 cm^{-1} modes can be attributed to disappearance of long range order in the lithium subsystems of the

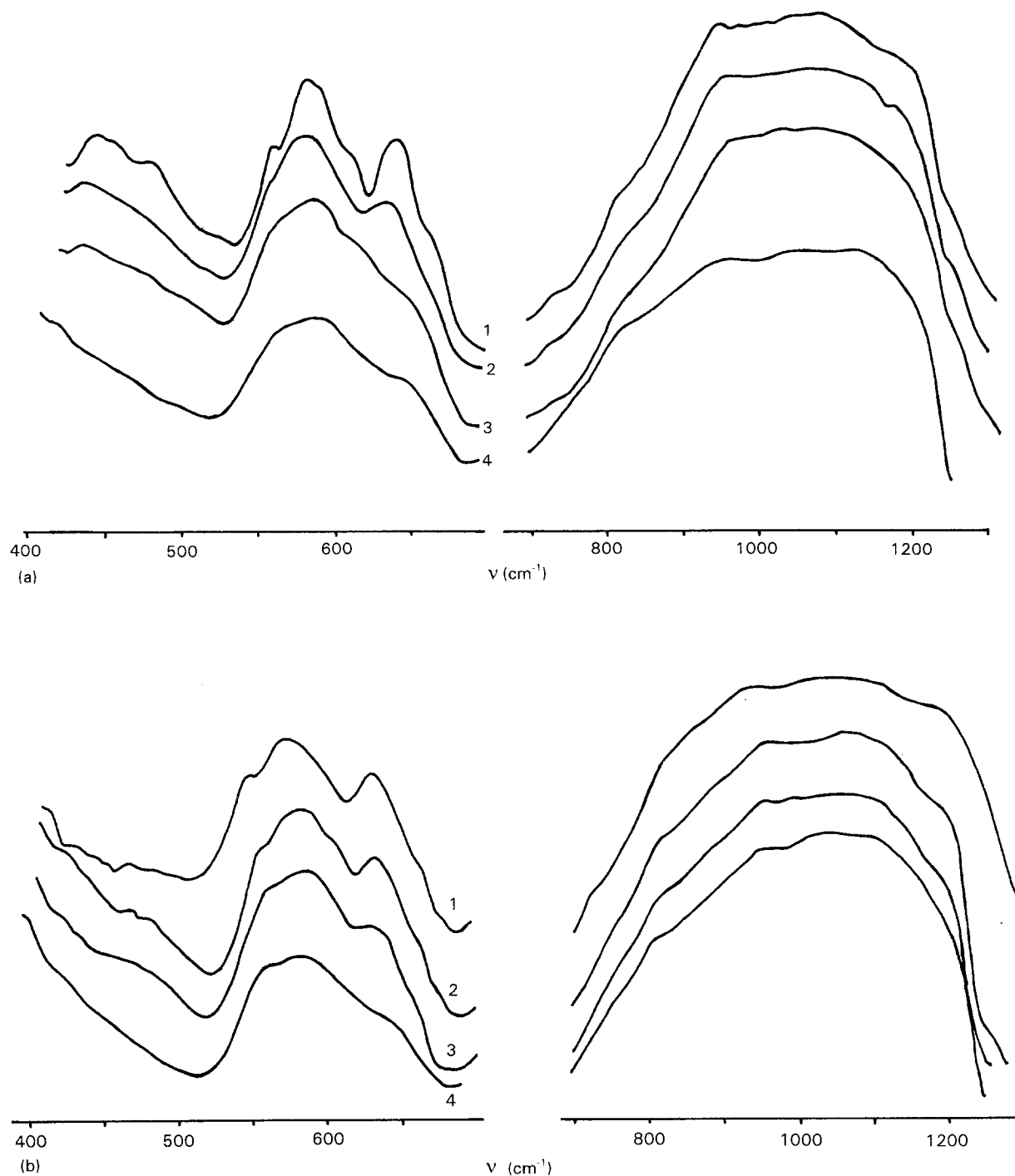*Figure 4* I.r. spectrum of monoclinic (a) $^7Li_3In_2(PO_4)_3$: (1) 293, (2) 344, (3) 351, (4) 497 K; and (b) $^6Li_3In_2(PO_4)_3$: (1) 293, (2) 344, (3) 353, (4) 497 K.

$Li_3In_2(PO_4)_3$ modifications, within the temperature range 345–355 K.

This temperature range lies at least 10 K below the superionic phase transition temperature found from DSC and impedance spectroscopy data (see Figs 1 and 2). Thus, it should not be a pre-critical phenomena, e.g. continuous decrease of the long range order. For example, in the case of domain microstructure in the crystal, the situation will correspond to decreasing domain size.

Similar changes of the i.r. spectra were observed earlier [17] for $Na_3Fe_2(PO_4)_3$, where an ordered state of the sodium sublattice, below the superionic phase transition point, has been found by X-ray diffraction [8].

3.2. Rhombohedral modifications

Powder diffraction patterns obtained from the samples prepared at $T \leqslant 1230$ K clearly indicate the rhombohedral symmetry of the crystal structure of these materials [3]. However, there are two different rhombohedral modifications of $Li_3In_2(PO_4)_3$: LT and LT', as mentioned above.

A phase transition from LT' to LT is observed at $T \simeq 1207$ K [3]. The crystal structure of a single crystal of a rhombohedral modification of the lithium indium phosphate has been studied in [1]. However, the type of rhombohedral phase, LT or LT', studied in [1] remains unknown.

The $R\bar{3}$ space group was established for the symmetry description of the atomic structure of
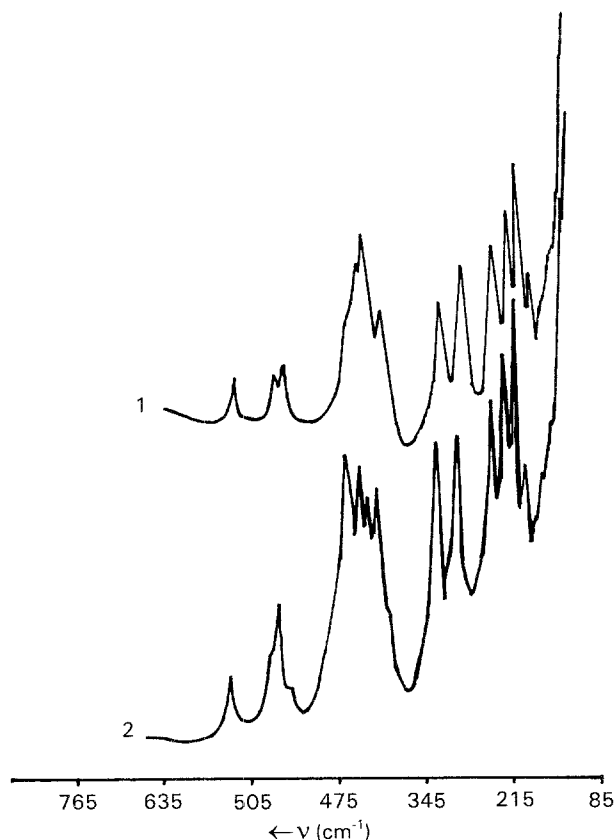
Figure 5 Raman spectra of (1) $^7Li_3In_2(PO_4)_3$, and (2) $^6Li_3In_2(PO_4)_3$ at 293 K.

ature. It also makes clear the i.r. data on the rhombohedral modifications (see Fig. 6).

As can be seen from Fig. 6, the obtained spectra are similar to the i.r. spectra of the monoclinic modifications (see Fig. 4). This is a rather surprising result, indicating that the packing array of $2InO_6$–$2PO_4$ complexes (rhombohedral or monoclinic) does not effect the vibrational states (both deformation and valency) of these polyhedra.

The only difference is observed for the 635 cm^{-1} mode, which is practically absent in the i.r. spectrum of the LT′ modification and weak in the i.r. spectrum of the LT modification. This suppression of the 635 cm^{-1} band may mean, as for the monoclinic compounds, that lithium ions are already disordered in these compounds. However, from our point of view it only reflects another type of spatial distribution of lithium ions within the rhombohedral-packed framework with respect to the monoclinic-packed framework. So, the PO_4 tetrahedra undergo further deformation in the rhombohedral than in the monoclinic modifications.

Besides, there is also a difference between the i.r. spectra of LT and LT′ modifications. Compared with the spectrum of the LT modification there is no $\simeq 565$ cm^{-1} band in the spectrum of the LT′ modification. Unfortunately, due to the low resolution of the i.r. technique, the existence of this band is reflected only in the general shape of the line (see Fig. 6).

Taking into account the abovementioned suggestions that possible additional lithium sites occur in the crystal structure of the rhombohedral modifications, one can, by analogy with monoclinic phases, say that the 565 cm^{-1} band arises from the long range ordered distribution of the lithium ions and vacancy (in the LT′ modification the additional site is practically unoccupied, so no long range order will appear). Thus, the behaviour of the different properties of the crystals can be explained assuming only an existing vacancy and long range order in the lithium subsystem.

Then with the increasing temperature approach, the 565 cm^{-1} band in the i.r. spectrum of the LT modification should disappear below the superionic phase transition point, due to long range order decrease.

Indeed, this band disappears at $\simeq 322$ K making the neighbouring mode ($\simeq 555$cm^{-1}) distinctly observable. The temperature is lower than the superionic phase transition point in the LT modification (339 K [3]). So, the behaviour of the rhombohedral modifications is quite similar to the behaviour of the monoclinic polymorphs of $Li_3In_2(PO_4)_3$.

the sample under investigation in [1]. This result would enable a structural phase transition to true NASICON type symmetry, described by $R\bar{3}c$ space group. However, no change in the diffraction pattern symmetry (i.e. additional forbidden reflections due to the appearance of the symmetry centre) was found under the temperature increase, in spite of the data in [3] indicating a phase transition within the temperature range 339–385 K, both in LT and LT′ modifications. This result indicates that a Faraday type phase transition seems to be appropriate for the description of the phase transitions.

In accordance with the literature [1], all the lithium ions in the crystal structure of rhombohedral modification of $Li_3In_2(PO_4)_3$ are situated on 18(e) positions (Wyckoff notation for the $R\bar{3}$ space group) at 293 K. It means that the lithium subsystem consists of isolated six-fold rings separated each from the other. If the lithium ion distribution does not change under the phase transition it is hardly possible to understand the high σ values of LT $Li_3In_2(PO_4)_3$ found in [3] in the temperature range above 385 K. Thus, the appearance of additional lithium sites between the rings should be supposed in order to explain the high ionic conductivity of the compound. Then, the number of available lithium sites will be more than the number of lithium ions. In other words, one once again obtained the situation considered previously for monoclinic modifications of $Li_3In_2(PO_4)_3$: lithium ions and vacancies should exist in the crystal structure of the material.

This approach can explain the lower σ values for the LT′ modification [3], supposing lower occupation of the additional sites due to lower synthesis temper-

4. Conclusions

The behaviour of the lithium ion subsystem in $Li_3In_2(PO_4)_3$ does not depend on the symmetry of the crystal structure, but seems to be determined by features of ion–ion interactions within the system. At low temperatures there is a tendency for creation of long range order in the lithium sublattice. With a following temperature increase the size of the ordered domains seems to diminish, and within the temperature range 339–385 K all modifications of
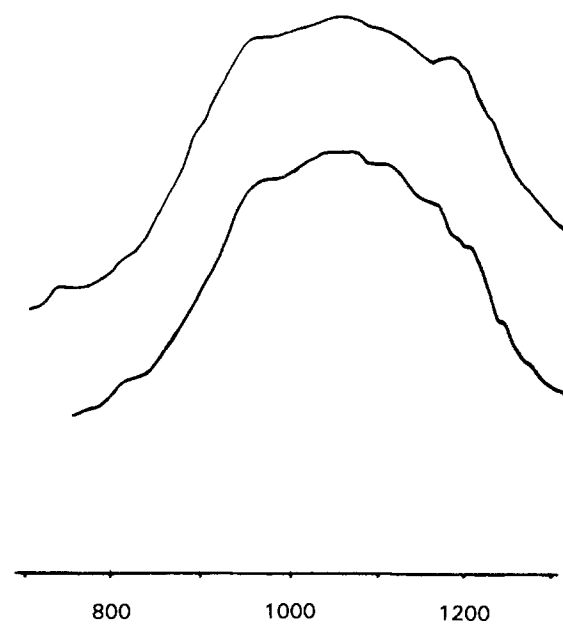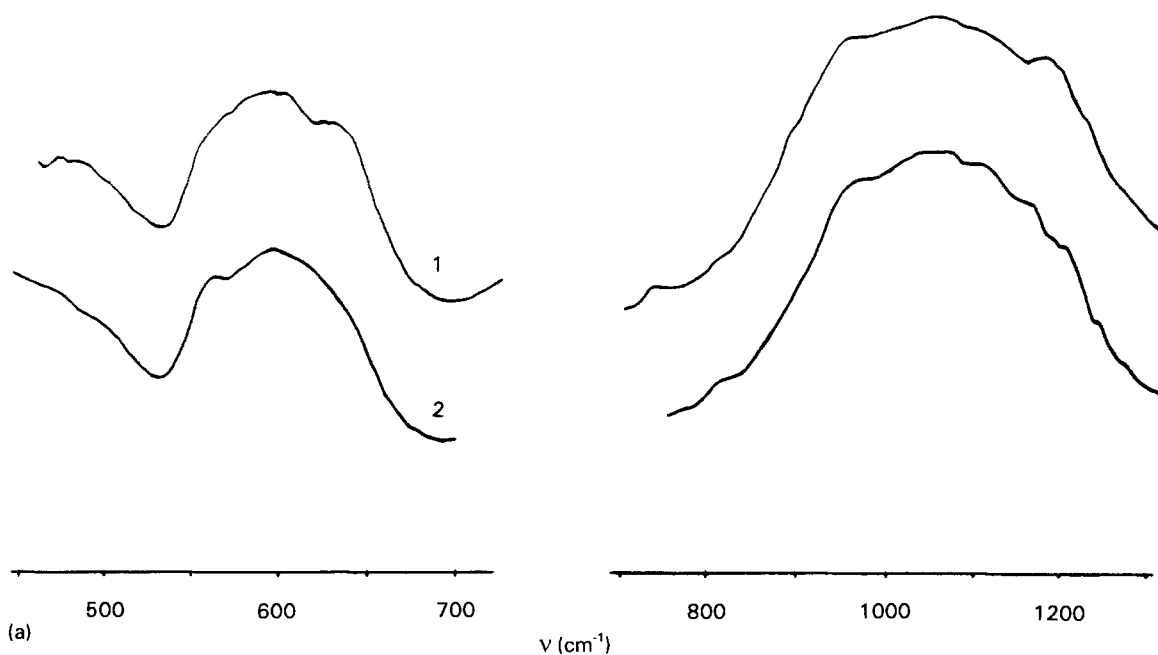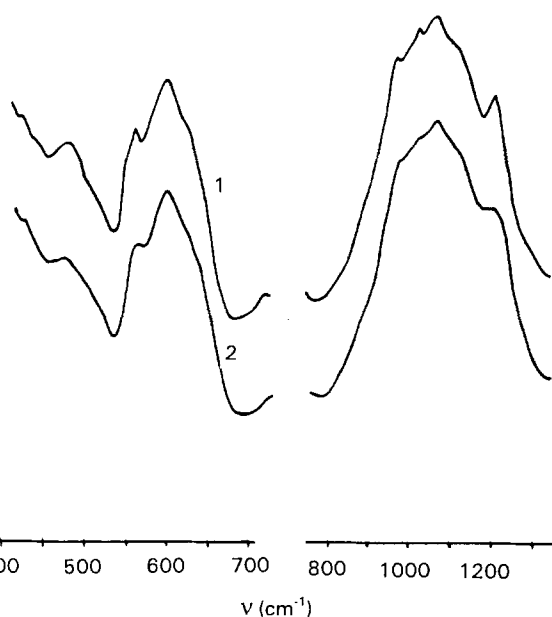
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$Li_3In_2(PO_4)_3$ undergo a Faraday type phase transition.

It should be pointed out that this picture has only a qualitative character, as based mainly on the i.r. data. Diffraction experiments have to be carried out to confirm the proposed model, as well as to study temperature changes in lithium ion distribution. Neutron diffraction seems to be preferable due to weak scattering of X-rays by Li^+ ions. This is the aim of our further work.

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