

Vibrational Behavior of Guest Anions in the Li_3AsO_4 Structure

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We have investigated the vibrational behavior of the ν_3 mode of guest anions ($(\text{PO}_4)^{3-}$, $(\text{SO}_4)^{2-}$) forming a dilute solid solution with the two polymorphic species of Li_3AsO_4 . For the $(\text{PO}_4)^{3-}$ anion, the ν_3 mode is represented by a more or less resolved triplet, as expected from the low site symmetry and the small distortion of the host anion. But a much more complex vibrational behavior is exhibited by the $(\text{SO}_4)^{2-}$ anion, whose different charge must be chemically compensated for, either by a Li^+ vacancy, or by another suitable anion such as $(\text{SiO}_4)^{4-}$. Compensation by a vacancy leads to a large splitting of the triplet components, suggesting a close association between the $(\text{SO}_4)^{2-}$ anion and the vacancy; the multiplet observed for the HT polymorph is justified by the existence of two structurally different types of vacancies. Charge compensation by the $(\text{SiO}_4)^{4-}$ ion leads to a complex spectrum indicating the existence of two types of structurally different $(\text{SO}_4)^{2-}$ anions, in relation to two structurally different mechanisms of charge compensation. © 1995 Academic Press, Inc.

INTRODUCTION

The vibrational spectrum of dilute solid solutions is able to give information about the symmetry of complex anions in the host lattice; for the guest anion, the vibrational spectrum (which is free from factor group effects) is essentially determined by the site group, which is assumed to be the same as that of the host anion (1). Thus, for a tetrahedral anion, the triply degenerate mode ν_3 of the guest anion should be observed as either a single band, a doublet, or a triplet, depending, e.g., on the true T_d , C_3 , or C_2 (or lower) site symmetry of the host anion. Recent experiments carried out in this laboratory show that this is an oversimplified scheme, and that the vibrational behavior of the guest anion may be altered, particularly when the charges of the guest and of the host anion are different. This will be illustrated here by the case of guest anions in the Li_3AsO_4 structure.

EXPERIMENTAL

Synthesis of the Samples

Though the samples can be prepared by the conventional solid state reaction techniques, homogeneous dilute

solid solutions are more easily obtained by first reacting stoichiometric quantities of the necessary reagents ($\text{NH}_4\text{H}_2\text{PO}_4$, As_2O_3 , Li_2CO_3 , Li_2SO_4) with an excess of pure concentrated nitric acid. The resulting solution is evaporated to dryness, the dry residue is transferred into covered platinum crucibles, which are very progressively heated to a final temperature of 1000°C . The two polymorphic species of Li_3AsO_4 (or the dilute solid solutions) are easily isolated, either by rapid quenching from 1000°C (high temperature phase), or by slow cooling in the furnace (low temperature phase). Both polymorphs are easily identified by their X-ray powder diffractogram (2), and this technique has been used to check the purity of all samples using a Siemens D-5000 diffractometer.

IR Spectra

IR spectra were obtained with a Beckman 4250 spectrometer, using nonroutine recording conditions: spectral slit width of about 1.5 cm^{-1} ; scanning speed of $20\text{ cm}^{-1}\text{ min}^{-1}$; and 7 (instead of 2) mg of sample in the KBr pellet. Running the same experiments in Nujol mulls shows no modification with respect to the KBr discs method (2). We can conclude that no pressure effect influences structural phase transformation.

RESULTS

The investigated solid solutions have been classified into four types, depending on the valency of the guest anion, and on the possible occurrence of vacancies.

Type A Solid Solutions: $(\text{PO}_4)^{3-}$ as Guest Anion

The simplest case is the replacement of some Li_3AsO_4 (1 mole%) by the equivalent amount of Li_3PO_4 , leading to the $\text{Li}_3[(\text{AsO}_4)^{3-}]_{0.99}[(\text{PO}_4)^{3-}]_{0.01}$ solid solution. This gives, for the ν_3 mode of the $(\text{PO}_4)^{3-}$ anion, the spectra represented in Fig. 1, curve Ia (low temperature polymorph) and curve Ib (high temperature polymorph). This latter exhibits the triplet expected for the C_s site symmetry of the anion (3), whereas the bands coalesce into a single band and a shoulder in the LT polymorph, probably as a

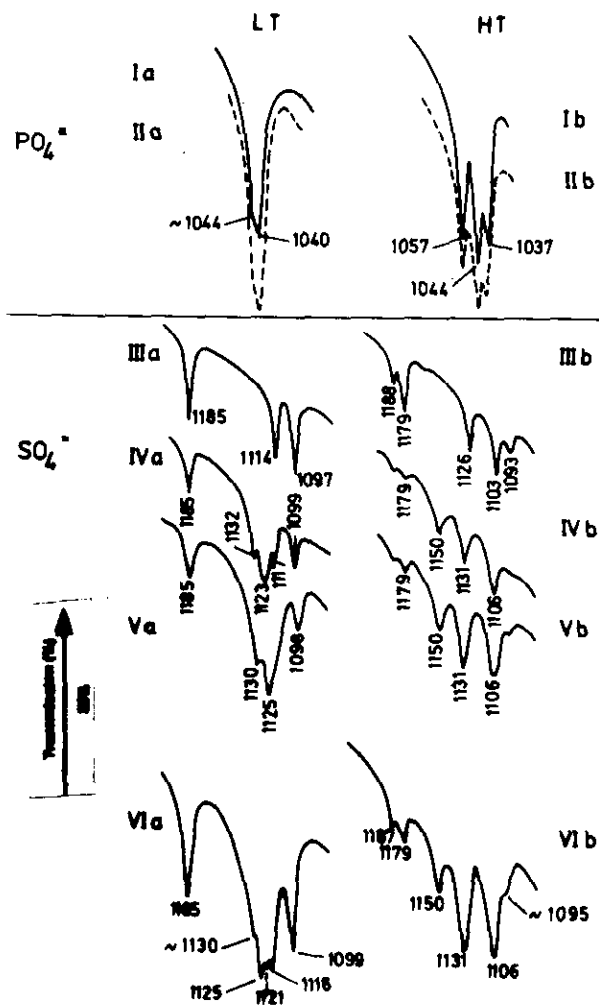


FIG. 1. Vibrational spectrum of the ν_3 mode of the guest anion in the Li_3AsO_4 structure: (a) series LT polymorphs; (b) series HT polymorphs. I. $(\text{PO}_4)^{3-}$ as Li_3PO_4 ; II. $(\text{PO}_4)^{3-}$ as $\text{LiZn}\square\text{PO}_4$; III. $(\text{SO}_4)^{2-}$ with vacancies; IV. $(\text{SO}_4)^{2-}$ with $(\text{SiO}_4)^{4-}$ for charge compensation; V. $(\text{SO}_4)^{2-}$ with $(\text{GeO}_4)^{4-}$ for charge compensation; and VI. Complex solid solution.

consequence of a very small distortion of the tetrahedral anion (see Discussion).

Another possibility is replacing Li_3AsO_4 by LiZnPO_4 , thus introducing an equivalent amount of vacancies in the structure, i.e., $[\text{Li}_3^{II}(\text{AsO}_4)^{3-}]_{0.99}[\text{Li}^I\text{Zn}^{II}\square(\text{PO}_4)^{3-}]_{0.01}$, which could also be written $\text{Li}_{2.98}^{II}\text{Zn}_{0.01}^{II}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.99}[(\text{PO}_4)^{3-}]_{0.01}$. The result is practically the same (Figs. 1-IIa and 1-IIb), with however a very small (possibly non-significant) decrease in the sharpness of the bands.

Type B Solid Solutions: $(\text{SO}_4)^{2-}$ as Guest Anion

The formation of a $(\text{Li}_3\text{AsO}_4)_{0.99}(\text{Li}_2\text{SO}_4)_{0.01}$ solid solution implies the formation of vacancies: $\text{Li}_{2.99}^{II}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.99}[(\text{SO}_4)^{2-}]_{0.01}$. The spectra (Fig. 1, curves IIIa

and IIIb) are drastically different from the spectrum of Li_2SO_4 itself, and there is no doubt that we are dealing with true solid solutions. The main features here are the very large splitting of the $(\text{SO}_4)^{2-}$ triplet in the LT polymorph (88 cm^{-1} against about 4 cm^{-1} for the $(\text{PO}_4)^{3-}$ anion) and additional multiplicity appearing in the $(\text{SO}_4)^{2-}$ spectrum for the HT polymorph. This rather peculiar behavior should be related to the simultaneous occurrence of vacancies and of a heterovalent guest anion (see Discussion).

Type C Solid Solutions: Coupled Anionic Substitutions

In order to check the validity of the preceding hypothesis, it is necessary either to create vacancies without introducing heterovalent anions (this is illustrated by the $\text{Li}_3\text{AsO}_4\text{-Li}^I\text{Zn}^{II}\square\text{PO}_4$ solid solution considered above), or to introduce the $(\text{SO}_4)^{2-}$ heterovalent anion without creating vacancies. This can be achieved by a coupled anionic substitution leading to the same overall charge, such as $2(\text{AsO}_4)^{3-} \rightarrow (\text{SO}_4)^{2-} + (\text{SiO}_4)^{4-}$.

This type of substitution is well known in the fluorophosphate $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (apatite structure) where the replacement $2(\text{PO}_4)^{3-} \rightarrow (\text{SO}_4)^{2-} + (\text{SiO}_4)^{4-}$ leads to a complete series of solid solutions terminating at the end member $\text{Ca}_{10}(\text{SO}_4)_3(\text{SiO}_4)_3\text{F}_2$ (4).

Experiments actually carried out in this laboratory show that this type of replacement is possible (at least to a limited extent) in other families of phosphates and arseniates (5). In the actual case of $\text{Li}_3^{II}\{[(\text{AsO}_4)^{3-}]_{0.98}[(\text{SO}_4)^{2-}]_{0.01}[(\text{SiO}_4)^{4-} \text{ or } (\text{GeO}_4)^{4-}]_{0.01}\}$ solid solutions, the spectrum exhibits a complex pattern of bands (Fig. 1, curves IVa, IVb, Va, and Vb).

—Some of the bands correspond clearly (though with a more or less reduced intensity) to bands already observed in the spectrum of the $[\text{Li}_3^{II}(\text{AsO}_4)^{3-}]_{0.99}[\text{Li}_2^{II}(\text{SO}_4)^{2-}]_{0.01}$ solid solutions (Figure 1, curve III): the bands at 1185 and 1097 cm^{-1} for the LT polymorph; and the doublet at $1188\text{--}1179\text{ cm}^{-1}$ and the band at 1093 cm^{-1} for the HT polymorph.

—New bands appear at 1132 and 1123 cm^{-1} (LT polymorph) or $1150\text{--}1131\text{--}1106\text{ cm}^{-1}$ (HT polymorph). The 1106 cm^{-1} band is considered a new one (and not simply a "remainder" of the 1103 cm^{-1} band) for intensity reasons.

A similar behavior is not observed for the ν_3 mode of the $(\text{SiO}_4)^{4-}$ or $(\text{GeO}_4)^{4-}$ anions. No $(\text{SiO}_4)^{4-}$ band can be observed in the spectrum; weak bands in the $750\text{--}700\text{ cm}^{-1}$ region are present in the spectrum of the $(\text{GeO}_4)^{4-}$ -bearing solid solution, but they do not exhibit the characteristic pattern observed for the $(\text{SO}_4)^{2-}$ bands. This peculiar behavior should be ascribed to the proximity of the $(\text{SiO}_4)^{4-}\text{--}(\text{AsO}_4)^{3-}$, and $(\text{AsO}_4)^{3-}\text{--}(\text{GeO}_4)^{4-}$ vibrational frequencies. This leads to important vibrational interactions, and thus to a noncharacteristic vibrational behavior of the guest anion.

Type D: Additional Complex Substitutions

We have completed the previous data by the study of an additional, more complex solid solution whose overall composition can be written $\text{Li}_{2.99}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.97}[(\text{SO}_4)^{2-}]_{0.02}[(\text{SiO}_4)^{4-}]_{0.01}$. This is in fact the sum of the two previous types of solid solutions, namely $\text{Li}_{2.99}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.99}[(\text{SO}_4)^{2-}]_{0.01}$ and $\text{Li}_3[(\text{AsO}_4)^{3-}]_{0.98}[(\text{SO}_4)^{2-}]_{0.01}[(\text{SiO}_4)^{4-}]_{0.01}$. The spectra (Fig. 1, curves VIa and VIb) are very similar to those of curves IVa and IVb, the main difference being a very significant increase in the relative intensities of the bands 1185, 1116, and 1099 cm^{-1} (LT polymorph) or 1187, 1179, and 1095 cm^{-1} (HT polymorph), namely those bands which were previously assigned to remainders of the $\text{Li}_{2.99}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.99}[(\text{SO}_4)^{2-}]_{0.01}$ solid solution. This assignment is thus definitely supported by the actual results. We may also notice that the 1123 cm^{-1} band (Fig. 1, curve IVa) is now split into two very sharp components at 1125 and 1121 cm^{-1} (Fig. 1, curve VIa).

Thus, if we subtract from the spectrum the bands originating from the $(\text{SO}_4)^{2-}$ anion associated with a vacancy (as in the $\text{Li}_{2.99}\square_{0.01}[(\text{AsO}_4)^{3-}]_{0.99}[(\text{SO}_4)^{2-}]_{0.01}$ solid solutions), there remains, for the $(\text{SO}_4)^{2-}$ ion associated with the $(\text{SiO}_4)^{4-}$ ion, either the triplet 1130–1125–1121 cm^{-1} (LT polymorph), or the triplet 1150–1131–1106 cm^{-1} (HT polymorph).

INTERPRETATION

Some Essential Features of the Li_3AsO_4 Structure

Single crystal data are not available for Li_3AsO_4 itself, but X-ray powder diffraction data (2) show the existence of two polymorphic species structurally similar to either Li_3PO_4 (LT and HT polymorphs) or Li_3VO_4 (LT polymorph only). The isomorphism of these compounds is also supported by the existence of continuous series of solid solutions (2).

The following structure features are deduced from single crystal diffraction studies on Li_3PO_4 (LT^[6] and HT^[7] polymorphs) and Li_3VO_4 (LT polymorph only (8)):

- (i) All cations are tetrahedrally coordinated.
- (ii) The site symmetry of the tetrahedral anion (PO_4^{3-} , AsO_4^{3-} , VO_4^{3-}) is low (e.g., C_s in both polymorphs of $\text{Li}_3\text{PO}_4^{(3)}$), but the effective distortion (i.e., the departure from an ideal T_d symmetry) is very small. The variations of the P–O distances and of the O–P–O angles are practically within the experimental errors.
- (iii) The three Li^+ cations are distributed over two different sites, namely two $\text{Li}_{(1)}$ on C_1 , and one $\text{Li}_{(2)}$ on C_s . Both types of LiO_4 tetrahedra are significantly distorted, but the error on the Li positions does not allow more than a semiquantitative estimation of this distortion.
- (iv) Every oxygen atom is surrounded by one pentava-

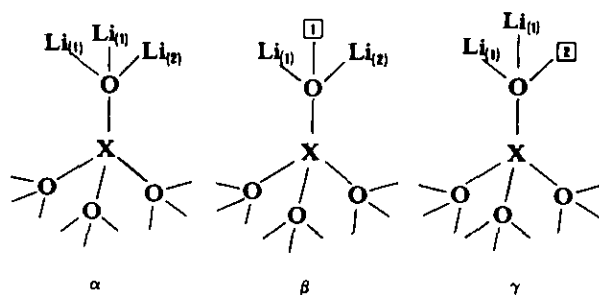


FIG. 2. Three possible configurations around an XO_4 tetrahedron in the Li_3AsO_4 structure: α , no vacancy; β , vacancy on the $\text{Li}_{(1)}$ site; and γ , vacancy on the $\text{Li}_{(2)}$ site.

lent atom (P, As, V) and three Li cations ($2\text{Li}_{(1)} + 1\text{Li}_{(2)}$) which give a Pauling electrostatic valency of +2.

Structural Information Deduced from the IR Spectra

Type A solid solutions: $(\text{PO}_4)^{3-}$ as a guest anion. The triplet observed for the HT polymorph of the $\text{Li}_3[(\text{AsO}_4)^{3-}]_{0.99}[(\text{PO}_4)^{3-}]_{0.01}$ solid solution (Fig. 1, curve Ib) is in agreement with the pattern expected for the ν_3 mode of a tetrahedral anion located on a site of low symmetry. The relatively small splitting is in qualitative agreement with the very small distortion derived from X-ray diffraction studies. On this basis, we can explain the pattern given by the LT polymorph (Fig. 1, curve Ia) by assuming that, owing to a still smaller distortion, the components of the triplet coalesce into an ill-separated doublet. As stated previously, the precision of the existing X-ray data is not sufficient to prove or disprove this interpretation.

We have seen that the $[\text{Li}_3(\text{AsO}_4)^{3-}]_{0.99}[\text{Li}^{\text{I}}\text{Zn}^{\text{II}}\square(\text{PO}_4)^{3-}]_{0.01}$ solid solution gives the same results: in this case, the existence of vacancies has no significant influence on the vibrational behavior of the $(\text{PO}_4)^{3-}$ anion. This can be explained by considering the following points:

- (i) We have only 1% vacancies and 1% $(\text{PO}_4)^{3-}$ anions in the structure.
- (ii) If the distribution of these vacancies and anions is statistical (and there is no major reason to have another type of distribution because the vacancies are associated with the cationic charge distribution), the probability of finding a $(\text{PO}_4)^{3-}$ anion associated with a vacancy (such as the configurations β and γ of Fig. 2, where X would be phosphorus) is very low. Most of the $(\text{PO}_4)^{3-}$ anions will be in configuration α , as in $\text{Li}_3[(\text{AsO}_4)^{3-}]_{0.99}[(\text{PO}_4)^{3-}]_{0.01}$ solid solutions, and its spectrum will accordingly be the same.

Type B solid solutions: $(\text{SO}_4)^{2-}$ as a guest anion with vacancies. It does not seem possible to explain the observed, very large splitting of the ν_3 components of the $(\text{SO}_4)^{2-}$ ion by a statistical distribution of the $(\text{SO}_4)^{2-}$

anions and of the vacancies. On the contrary, these results suggest the preferential formation of pairs, as in configuration β or γ of Fig. 2, where X is sulfur. In this case, one of the four oxygen atoms of the $(\text{SO}_4)^{2-}$ tetrahedron is bound to $\text{Li}_2\Box$, whereas each of the three remaining ones is bound to Li_3 ; this implies a strengthening of the peculiar S–O ($\text{Li}_2\Box$) bond, and a correlative weakening of the others. The observed splitting is the result of this unequal distribution of the bonding forces. This behavior is very different from that previously noticed for the $[\text{Li}_3(\text{AsO}_4)^{3-}]_{0.99}[\text{Li}^1\text{Zn}^{11}\Box(\text{PO}_4)^{3-}]_{0.01}$ solid solutions, and is a consequence of the charge difference between the host $(\text{AsO}_4)^{3-}$ and the guest $(\text{SO}_4)^{2-}$ anion.

In the hypothesis of a statistical distribution of the $(\text{SO}_4)^{2-}$ anions and vacancies, the most probable configurations would be:

- (i) for the $(\text{SO}_4)^{2-}$ anions, configuration α (which implies a local excess of positive charges).
- (ii) for the vacancies, configuration β or γ , where X is no longer the guest, but is the host atom (arsenic), and consequently there is a local defect of positive charges.

Thus this type of distribution would lead to a double local electrical imbalance, and thus a structure which is certainly less stable than that resulting from the formation of pairs between a vacancy and a $(\text{SO}_4)^{2-}$ anion.

The peculiar pattern given by the HT solid solution (Fig. 1, curve IIIb) can be explained as follows. It must be first recalled that there are two nonequivalent crystallographic sites for the Li^+ ions, $\text{Li}_{(1)}$ and $\text{Li}_{(2)}$, with a 2:1 ratio (6–8), and accordingly two types of nonequivalent vacancies in the same ratio. These two possibilities are illustrated by configurations β and γ of Fig. 2 and should give, for the ν_3 mode of the $(\text{SO}_4)^{2-}$ anion, two triplets. Now, Fig. 1, curve IIIb shows that four of the five observed bands may be considered as pairs (1188–1179 and 1103–1093 cm^{-1}) with an approximately 2:1 intensity ratio; moreover, if we assume that the remaining band at 1126 cm^{-1} is due to the overlapping of two bands, the observed pattern is immediately interpreted by the existence of the two expected triplets, namely 1179–1126–1103 cm^{-1} (vacancy on the $\text{Li}_{(1)}$ site) and 1188–1126–1093 cm^{-1} (vacancy on the $\text{Li}_{(2)}$ site).

From this point of view, the single triplet given by the LT solid solution (Fig. 1, curve IIIa) is unexpected. It may be tentatively explained as follows:

- (i) either the two configurations β and γ (Fig. 2) are so similar that they lead to nearly identical frequencies (overlap of two triplets);
- (ii) or, on the contrary, one of these configurations is significantly more stable than the other and is thus largely predominant in the LT phase (one triplet only).

In view of the lack of precise structural data, a definite

choice between these hypotheses is difficult. However, we may notice that the sharpness of the bands suggests the existence of one triplet only. Moreover, the existing crystallographic data on the LT polymorph of Li_3PO_4 (6) and Li_3VO_4 (8) show that the average $\text{Li}_{(1)}\text{--O}$ distance is significantly shorter than the average $\text{Li}_{(2)}\text{--O}$ distance. This is probably true also for the LT Li_3AsO_4 , and this structural difference between $\text{Li}_{(1)}\text{O}_4$ and $\text{Li}_{(2)}\text{O}_4$ tetrahedra supports the second hypothesis.

Type C solid solutions: Coupled, charge-compensated substitutions: $2\text{PO}_4^{3-} \rightarrow \text{SiO}_4^{4-} + \text{SO}_4^{2-}$. We have previously noticed that the spectra of such solid solutions exhibit, with a nonnegligible intensity, the bands already observed in the spectra of the $[\text{Li}_3^1(\text{AsO}_4)^{3-}]_{0.99}[\text{Li}_2^1\Box(\text{SO}_4)^{2-}]_{0.01}$ solid solutions.

According to the above-discussed assignments, this indicates that some vacancies (or, more precisely, $(\text{SO}_4)^{2-}$ -vacancy pairs) are present in the structure, despite the fact that such vacancies are not required by the overall composition. The concentration of these pairs seems to be much lower in the HT polymorph, as suggested by the relative intensities of the IR bands.

The complex spectrum given by the $(\text{SO}_4)^{2-}$ anion in these solid solutions can thus be explained by the existence of two types of structurally different $(\text{SO}_4)^{2-}$ ions:

- (i) Many of them are in the "normal" configuration α (Fig. 2), without vacancies in which the charge compensation is ensured by the proximity of an $(\text{SiO}_4)^{4-}$ ion; they are responsible for the 1132–1123 cm^{-1} doublet in the LT polymorph (Fig. 1, curve IVa) and the 1150–1131–1106 cm^{-1} triplet in the HT polymorph (Fig. 1, curve IVb).
- (ii) The remaining ions are associated with vacancies (configurations β and/or γ). However, since the overall molecular formula contains three Li^+ cations (as in pure Li_3AsO_4 itself), the existence of these vacancies implies the existence of an equal number of interstitial Li^+ cations, which are expected to lie in the vicinity of the $(\text{SiO}_4)^{4-}$ anions. This is a bit surprising, but not unreasonable. Since all atoms are tetrahedrally coordinated, and since LiO_4 and AsO_4 tetrahedra are held together by corner sharing, (6) Li_3AsO_4 is an example of an "open" structure, which can easily accommodate a small number of interstitial cations.

To summarize, the vibrational behavior of these dilute solid solutions with coupled substitutions suggests that the charge compensation occurs through two distinct structural mechanisms:

- (i) A direct mechanism, essentially characterized by the proximity, in the crystal structure, of one $(\text{SO}_4)^{2-}$ and one $(\text{SiO}_4)^{4-}$ anion.
- (ii) A two-step mechanism, implying the formation of two different structural associations, namely, a pair va-

TABLE 1
Vibrational Frequencies and Maximum Splitting of the Split ν_3 Mode of Guest Anions
in the Li_3AsO_4 Structure

Guest anion	LT Polymorph		HT Polymorph	
	ν (cm^{-1})	$\Delta\nu$	ν (cm^{-1})	$\Delta\nu$
$(\text{PO}_4)^{3-}$ as Li_3PO_4	1044–1040	4	1057–1044–1037	20
$(\text{PO}_4)^{3-}$ as $\text{LiZn}\square\text{PO}_4$	1044–1040	4	1057–1044–1037	20
$(\text{SO}_4)^{2-}$ with $(\text{SiO}_4)^{4-}$ charge compensation	1030–1125–1121	9	1150–1131–1106	44
$(\text{SO}_4)^{2-}$ and Vacancy	1185–1114–1097	88	1179–1126–1103 1188–1126–1093	76 95

cancy– $(\text{SO}_4)^{2-}$ (deduced from the vibrational spectrum), and a pair interstitial Li^+ – $(\text{SiO}_4)^{4-}$ (assumed).

The real structure is the result of a competition between these two mechanisms, the first one being dominant in the actual case of Li_3AsO_4 .

Frequency splitting of the ν_3 mode: correlation with the crystal structure and the charge of the guest anion. Table 1 summarizes the different spectroscopic data discussed in this paper and the frequency difference $\Delta\nu_{\text{max}}$ between the extreme components of the split ν_3 mode. In the case of the LT polymorph, the splitting is very small for the $(\text{PO}_4)^{3-}$ anion, as a consequence of the very small distortion of the host anion. This point has been briefly discussed previously. This splitting increases slightly but significantly (from 4 to 9 cm^{-1}) for the $(\text{SO}_4)^{2-}$ anion in the case of a charge compensation by $(\text{SiO}_4)^{4-}$ anion. This is probably resulting from the different charge of the $(\text{SO}_4)^{2-}$ anion, which may be responsible for some inequality in the distribution of the bonding forces. This inequality becomes very great for the $(\text{SO}_4)^{2-}$ anion associated with a vacancy and, as discussed above, is responsible for the very large splitting (88 cm^{-1}) observed in this case.

The same trend is observed for the HT polymorph, but with (in most cases) larger values of splitting. This can be tentatively explained by a somewhat larger distortion of the $(\text{AsO}_4)^{3-}$ anion in the HT polymorph, but we have no crystallographic support for this hypothesis. Single crystal data on Li_3AsO_4 (either LT or HT polymorph) are not available; moreover, the crystal structure of HT Li_3PO_4 (7) is not known with sufficient precision to allow a significant comparison of the PO_4 distortion in LT and HT polymorphs; thus, an extrapolation to the Li_3AsO_4 structure is ruled out.

To the contrary, the splitting is nearly the same for the LT and HT polymorphs in the particular case of the $(\text{SO}_4)^{2-}$ ion associated with a vacancy. In this case, the importance of the splitting is essentially determined by the unequal distribution of the bonding forces, and not by the main distortion of the host anion.

RAMAN SPECTRA

These effects cannot be evidenced in the Raman spectra for the following reasons: (i) the intensity of the ν_3 components are too weak to be observed, (ii) the intensity of the ν_1 mode is relatively weak in the spectra of solid solutions, and (iii) the ν_1 mode of $(\text{SO}_4)^{2-}$ ions is nondegenerate; so it is not possible to put into evidence splitting due to a low symmetry effect. In principle, it could reveal different type of $(\text{SO}_4)^{2-}$ ion environments. We always observed only one relatively broad peak.

CONCLUDING REMARKS

Most of the structural aspects discussed in this paper correspond to rather local features and cannot affect significantly the reticular planes of the crystal structure. They cannot be approached by X-ray diffraction. We intend to carry out thermoluminescence experiments, which should give additional information about some of the structural features discussed in this paper.

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