

Crystallographic and dielectric properties of the $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ solid solution

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Crystallographic and dielectric studies of the system LiZnAsO_4 – LiZnPO_4 have been investigated. Solubility limits of phosphorous into LiZnAsO_4 was found. A new solid solution $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ with $0 \leq x \leq 0.5$ is then evidenced. IR spectra show the presence of XO_4 groups in the network of these materials. Correlations between structure and dielectric properties are established.

I. INTRODUCTION

Our work relates to the compounds of the type $\text{A}^{\text{I}}\text{B}^{\text{II}}\text{XO}_4$ (A^{I} = monovalent cation, B^{II} = bivalent cation and $\text{X} = \text{As, P or V}$). We granted an interest particular to the compounds formed by cations A^{I} and B^{II} of small sizes. The latter are likely to be put in the tetrahedral sites of phenacite (Be_2SiO_4 [1]). The only compounds, currently known, which crystallize in this structure are; LiZnXO_4 with: $\text{X} = \text{As, P, V}$ [2-7]. The orthovanadate LiZnVO_4 presents two allotropic varieties [6,8]. The first of the spinel type is obtained with high pressure and the second of the phenacite type is prepared in the normal conditions. In the same way for orthophosphate LiZnPO_4 , it presents also two allotropic forms. The phase α - LiZnPO_4 [5,9] which has a monoclinical symmetry with the group of space Cc. The other allotropic form obtained at high pressure is the hexagonal phase of phenacite type [4]. On the other hand, the arsenate LiZnAsO_4 crystallizes in a hexagonal system and adopts the standard phenacite structure with the parameters, $a = 14.052 \text{ \AA}$, $c = 9.378 \text{ \AA}$ $Z = 18$ and its space group is non-centrosymmetric R3. Its structure is described by the three-dimensional sequence of the regular tetrahedrons LiO_4 ZnO_4 and AsO_4 which share all the corners.

This arrangement lets appear two types of tunnels entirely vacuums according to the direction [001]. The large tunnels have a hexagonal section whereas the small ones have a base rhombus (Figure1).

of x-rays. Measurements of densities and IR spectroscopy characterization of the samples was carried out to bring additional information of these crystalline phases.

II. EXPERIMENTAL PROCEDURE

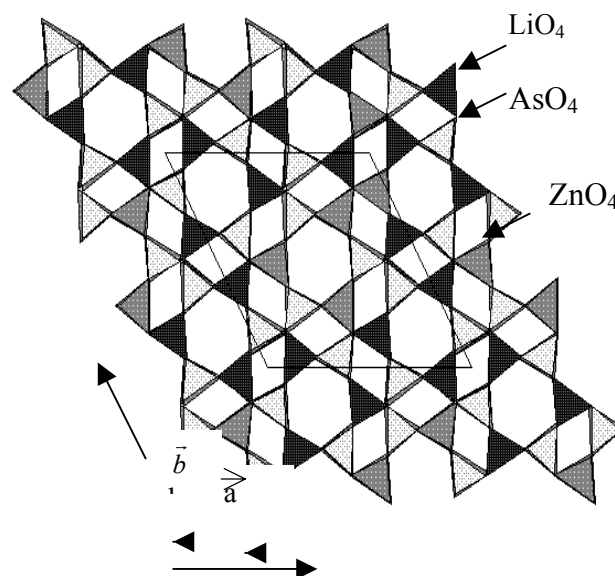
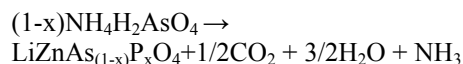


FIGURE 1: Projection parallel to the c direction of the structure of LiZnAsO_4 .

In this work, we are interested in the phosphoarsenates compounds. For that, we made a cristallochimic study of the phases resulting from the LiZnAsO_4 - LiZnPO_4 system. The known data relatives to the structures LiZnAsO_4 and LiZnPO_4 were used to understand the structure and the physical properties of the solid solution compositions. The limits of this solid solution were determined by the diffraction

The samples in the form of polycrystalline powders are prepared by solid state reaction under atmospheric air, starting from the reagents of high purity (99%), according to the following reaction process:

$$\text{ZnO} + 1/2\text{Li}_2\text{CO}_3 + x\text{NH}_4\text{H}_2\text{PO}_4 +$$



The starting products are mixed in stoichiometric proportions then crushed in an agate mortar. Then, they are transferred in a furnace where they are subjected to heat treatments. The latter are intersected with intimate crushing to ensure the homogeneity of the mixture and to support the diffusion in a solid state within the sample. The heat treatments are made in a progressive way. The temperature of the final treatment depends on the chemical composition and can reach 850°C. The last heat treatment is followed of an air cooling.

The x-ray diffractograms of each composition of the solid solution $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ were recorded using a diffractometer D5000 SIEMENS, equipped with a copper anticathode ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$). The experimental densities are measured at the ambient temperature by pycnometry in the diethyl orthophthalate as a fluid.

The study of the dielectric properties is carried out in a broad range of temperature 100-650°C at various frequencies by means of a LCR-meter (standard A701203). Measurements of the permittivity ϵ_r are carried out on cylindrical pellet with a diameter 13 mm and thickness approximately 1 mm. Pellet ceramics have been sintered at 900°C in order to increase their compactness and reduce at some extent the effect of grain boundaries. A fine layer of conducting silver lacquer is deposited on the two faces of the ceramic pellet. The electrical contact is ensured by a very thin platinum wire.

III. RESULTS AND DISCUSSION

III.1 Crystallographic study

Analysis of the diffractograms of each composition of the system $\text{LiZnAsO}_4\text{-LiZnPO}_4$ showed the existence of a solid solution going from $x=0$ to $x=0.5$. Figure 2 presents the diffractograms of the various compositions of this solid solution. A displacement of the lines towards the great values of theta (θ) is observed. The examination of these spectra shows that all the peaks could be indexed as being due to a phenacite phase (LiZnAsO_4 structure type). Figures 3a and 3b represent the variations of the crystallographic parameters (a, c and V) according to the composition (x), respectively.

One notes that when the rate of phosphorus increases the lattice parameters decrease. The displacement of the lines, the reduction in the parameters and volume (Figures 2 and 3b) are in agreement with the substitution of a large anion $(\text{AsO}_4)^{3-}$ by smaller $(\text{PO}_4)^{3-}$ ones. Indeed the ionic radii of arsenic in a tetrahedral site is worth 0.335 Å whereas, that of phosphorus has as a value 0.17 Å [10].

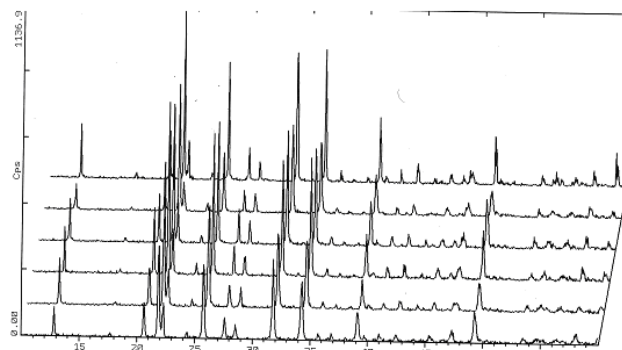


FIGURE 2: Room temperature X-ray diffraction patterns of the solid solution $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ (up to bottom $x=0.5$; 0.4; 0.3; 0.2; 0.1; 0).

III.2. Density measurements

The results of measurements of density are gathered in table 1. The density theoretical values of the compositions are given in the same Table 1.

Table 1: Experimental and theoretical specific masses of the $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ solid solution

x	0,0	0,1	0,2	0,3	0,4	0,5
$\rho_{\text{the}}(\text{g/cm}^3)$	1,98	1,95	1,92	1,88	1,86	1,82
$\rho_{\text{exp}}(\pm 0,01 \text{ g/cm}^3)$	1,95	1,93	1,89	1,86	1,83	1,80

One notes that there is a very good agreement between the experimental values and the theoretical values calculated on the basis of the standard phenacite LiZnVO_4 phase. This confirms well that the compositions under study adopt the phenacite structure. The variation of the density (ρ_{exp}) as a function of the composition is represented in the figure 3-b. It shows that the closeness packing of the composition decreases with increasing phosphorus content in the solid solution. This result is associated with the atomic properties which differ from P to As elements. Based on these atomic considerations, we correlate the decrease of the density to the reduction of the molar mass when we substitute arsenic by phosphorus. Indeed, according to the formula $\rho = ZM_x/NV_x$ where M_x = molar mass, V_x = volume molar, when x value increases the reverse of volume ($1/V$) increases slowly and at the same time the molar mass M_x decreases quickly. For instance, when phosphorus replaces arsenic element in the solid solution the molar mass M_x decreases by a value of 43.948 g.mol⁻¹ ($M_{\text{As}} = 74.922 \text{ g/mol}$, $M_{\text{P}} = 30.974 \text{ g/mol}$).

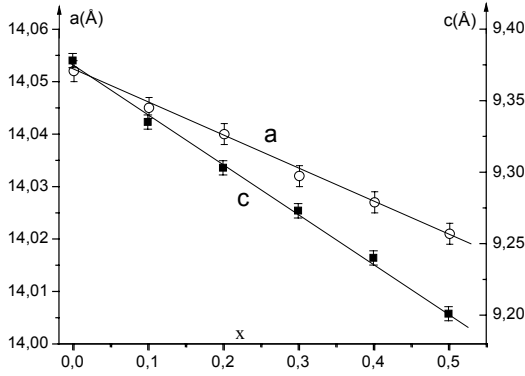


FIGURE 3a: Composition dependences of lattice parameters at 300 K.

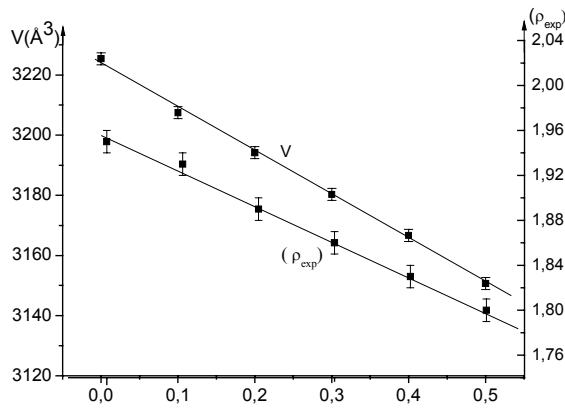


Figure 3b: Composition dependences of unit cell volume and specific mass at 300 K.

III.3 IR Vibrational study

Figure 3 represents the infra-red spectra of the compositions $\text{LiZnAs}_{1-x}\text{P}_x\text{O}_4$ (with $x = 0; 0.2; 0.3; 0.4$ and 0.5). For $x=0$, the bands located between 800 and 900 cm^{-1} are attributed to the vibrations of valence of the As-O bonds in AsO_4 groups. The bands raised around 400 and 520 cm^{-1} are associated with the angular deformation of O-As-O [11-12]. As of the introduction of the groupings PO_4 into the unit cell ($x \neq 0$) one observes the appearance

of two new bands. The first at around 1050 cm^{-1} is relatively broad and dissymmetrical. It is attributed to the antisymmetric valence vibrations of the groupings PO_4 . The second band is located near 600 cm^{-1} . It is dissymmetrical and is attached to the antisymmetric deformation of O-P-O angles. In parallel, it is noted that the bands relating to the arsenates groupings are decreasing in intensity as the rate of substitution x increases. These observations authorize us to confirm that phosphorus replaces arsenic in the crystal lattice of the solid solution under study. This incorporation of phosphorous induces, however, the disappearance of the

shoulders around $800 - 900 \text{ cm}^{-1}$ and the widening of the band centred on 850 cm^{-1} . Therefore, the replacement arsenic by phosphorus in the network is accompanied by introducing some structural disorder in the framework of the materials under study.

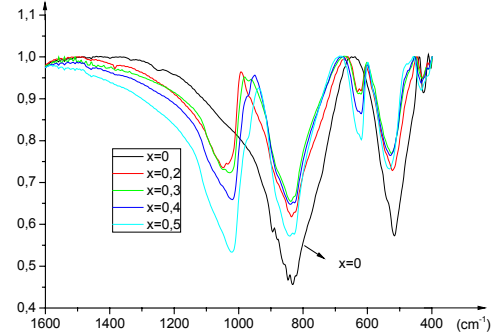


FIGURE 3: IR spectra of the compositions issued from the solid solution.

III.4 Dielectric properties

The permittivity of the solution solid $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ ($0 \leq x \leq 0.5$) compositions is studied upon the temperature at various frequencies ($200, 500, 1 \text{ KHz}$).

Thermal variations of the permittivity ϵ'_r for the various compositions have a similar shape. The typical curves obtained for $x = 0.2$ and $x = 0.4$ compositions are shown in Figures 4a and 4b. Table 2 gives the temperatures corresponding to maximum of ϵ'_r for the different samples. The value of the transition temperature increases with increasing the amount of phosphorous. One can note that this transition temperature increases rapidly for the first substitution of As by P ($x = 0.1$). The permittivity temperature dependence of each composition in the solid solution is mimetic to that of compounds exhibiting a transition phase. Hence, we can suggest that the samples inside the $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ perform phase transition at temperature depending on the composition. Although the nature of the suggested phase transition is not yet known, it is possible that this transition corresponds to the structural rearrangement allowing the conversion of space group $R3$ to $R\bar{3}$. Moreover, this later could be explained by the following facts: (i) the space group of the various compositions at the ambient temperature is $R3$; (ii) at the high temperatures, symmetry is often higher than that corresponding to the low temperatures (R in our case). Since $R3$ and $R\bar{3}$ are non-centrosymmetric and centrosymmetric groups, respectively, one can state that the observed transitions are ferroelectric-paraelectric type [13].

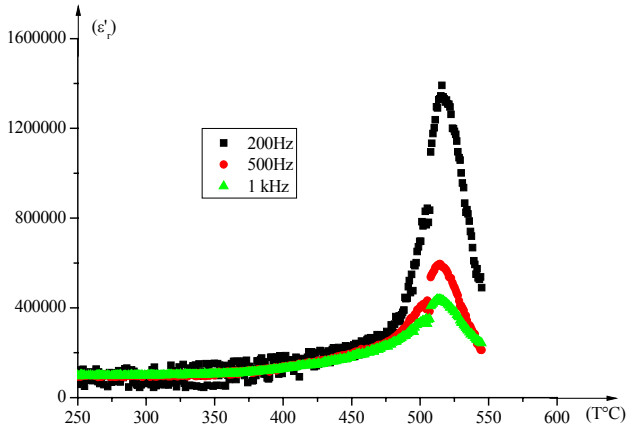


FIGURE 4a: Temperature dependences of ϵ'_r for a material corresponding to $x = 0.2$ sintered at 900°C for 2 hours.

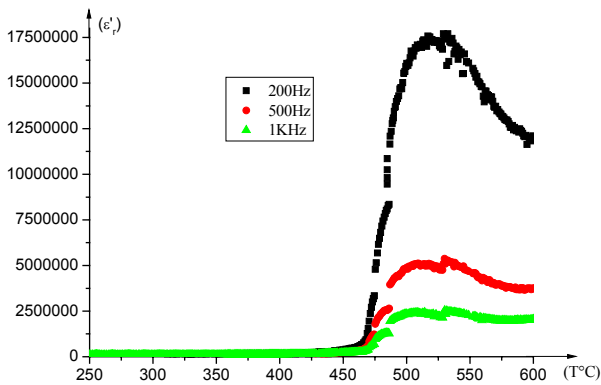


FIGURE 4b: Temperature dependences of ϵ'_r for a material corresponding to $x = 0.4$ sintered at 900°C for 2 hours..

Table 2: Influence of the composition(x) on transition temperature (T).

X	0	0,1	0,2	0,3	0,4	0,5
T ($\pm 5^\circ\text{C}$)	384	507	516	517	520	577

Let us now to explain why the transition temperature is increasing function of phosphorous content in the composition? As a fresh approach to the problem we shall consider the properties of the end members of this solid solution. The M-O ($M = \text{P}, \text{As}$) bond strength decreases from $M = \text{P}$ to $M = \text{As}$. Hence, the introduction of phosphorous in the network structure results in an increase of the mean bond strength. On the other hand, the transition temperatures of LiZnPO_4 and LiZnAsO_4 end members of the solid solution. are 384°C and $T_c > 650^\circ\text{C}$, respectively. Therefore, a displacement of the transition temperature towards a high value, with increasing P content, is due to a concomitant effects: (i) increasing bond strength when P replaces As, and (ii) a high transition temperature of LiZnPO_4 phase.

It is also interesting to answer the following question: why there is a dispersion in the permittivity ϵ'_r dependence temperature shown in Figures 4a and 4b? The sample exhibits a strong maximum of dielectric permittivity at each frequency. The frequency dependence is nevertheless high. This behaviour is in agreement with a ferroelectric phase transition with dielectric relaxation in the frequency range investigated (200 Hz-1KHz) [14].

IV. CONCLUSION

X-Ray diffraction study of materials belonging to the $\text{LiZnAsO}_4\text{-LiZnPO}_4$ system showed the existence of a new solid solution $\text{LiZnAs}_{(1-x)}\text{P}_x\text{O}_4$ ($0 \leq x \leq 0.5$). Between ambient temperature and 600°C , it is concluded that each material undergoes a phase transition. This transition is confirmed by the dielectric study. The transition temperature from ferroelectric phase to paraelectric ones is composition dependence and it varies from 384 to 577°C .

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