



X-ray diffraction investigations of structural modifications in In-doped tin pyrophosphates



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HIGHLIGHTS

- $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ samples are isomorphous under all conditions used in this study.
- lattice parameter (a) exhibits a robust peak at $x = 0.1$ at all temperatures (T).
- a vs. $x|_T$ peak vanishes when samples are measured under vacuum or inert gas.

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ABSTRACT

Laboratory and synchrotron x-ray powder diffraction were used to investigate the structural modifications that occur upon indium doping of tin pyrophosphate. The data collected under air, vacuum, and inert gas sample environments at temperatures (T) from 50 °C to 300 °C show that regardless of the In-doping level ($0 \leq x \leq 0.18$) all $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ samples are isomorphous (have the same P a -3 cubic crystal structure) at all temperatures and under all the conditions investigated. The cubic lattice parameter (a) increases linearly with T at all doping levels, but the “ a vs. $x|_T$ ” isotherms exhibit a robust peak at $x = 0.1$ when data are collected on samples measured in air. On the other hand, Rietveld refinements against data collected on $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ samples yield values of O–O bond lengths and P–O–P bond angles that show no major changes at $x = 0.1$ at any temperature. This is significant, as the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ ($x = 0.1$) compound is known to exhibit the highest proton conductivity within the series, but the microscopic details responsible for the increased proton conductivity are not understood. Finally, the peak observed in the “ a vs. $x|_T$ ” curves vanishes if the measurements are taken on samples kept either under vacuum or in an inert gas environment. This is a remarkable behavior as it lends further support to our hypothesis that a key microscopic feature responsible for the large proton conductivity of the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ compound is the enlargement of the lattice constant at $x = 0.1$.

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1. Introduction

Over the past two decades, materials that function as fuel cell electrolytes at intermediate temperatures (within the 150 °C and 400 °C range) have attracted significant interest [1–7]. Such compounds are important as they have the potential to address many of the critical issues related to both low- and high-temperature fuel cell functionality, such as the need for pure H_2 fuel, expensive Pt electrodes, CO poisoning, and less than ideal durability [8].

One example is represented by SO_4^- and PO_4^- -based solid acids (such as CsHSO_4 , CsH_2PO_4 , and RbH_2PO_4), materials that are not

good proton conductors at room temperature, but, upon heating above a temperature threshold, undergo a so-called superprotonic transition where their proton conductivity increases by up to four orders of magnitude [9]. CsHSO_4 was the first superprotonic solid acid to be successfully used as a fuel cell electrolyte [10], but it was soon realized that the inherent chemical instability of sulfates in the presence of molecular hydrogen severely limits the applicability of these compounds as intermediate-temperature fuel cell electrolytes. Similarly, superprotonic phosphate based membranes have been observed to dehydrate and decompose in the absence of special saturated water vapor or high pressure conditions [6–9].

Pyrophosphates, such as MP_2O_7 ($M = \text{Si}, \text{Zr}, \text{Ti}, \text{Sn}$), represent a viable alternative as these compounds do not have any chemical stability issues at intermediate temperatures and a high proton conductivity ($> 10^{-2} \text{ S cm}^{-1}$) has recently been observed in SnP_2O_7

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[11–13]. Moreover, it was found that doping with trivalent cations such as In^{+3} , Sc^{+3} , Sb^{+3} and Al^{+3} can be used to control the proton conductivity of these pyrophosphates, which was observed to depend on the dopant type, dopant concentration x , and temperature T for the mixed systems $\text{M}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ ($\text{M} = \text{In}, \text{Sc}, \text{Sb}, \text{Al}$) [14–17]. Particularly interesting is the case of indium doping, i.e. the $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ series, for which previous investigations [13] have shown that the proton conductivity of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ is four times greater than that of the undoped compound, SnP_2O_7 . Yet, the crystal structure and micro-dynamics features responsible for the proton conductivity enhancement at a specific cation-doping value remain largely unknown. Understanding (and eventually controlling) such microscopic details is of significant importance, as it might eventually enable the rational design of highly efficient proton conductors for intermediate temperature fuel cell applications.

Here, in-house and synchrotron x-ray diffraction (XRD) were used to study the structural modifications that occur in $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ as a function of indium doping ($0 \leq x \leq 0.18$) and temperature ($25^\circ\text{C} \leq T \leq 300^\circ\text{C}$). It was found that the cubic (P a -3) crystal structure of the parent compound persisted at all doping values (x) and all temperatures (T). Also, the O–O bond lengths and the P–O–P bond angle values determined from Rietveld refinements [18] exhibited slight variations upon doping, but no major tetrahedral distortion was present at $x = 0.1$ at any temperature. On the other hand, full profile refinements carried out using the LeBail method [19] against temperature-resolved synchrotron XRD data collected in air on samples of different indium doping values showed that the cubic lattice parameter, a , measured as a function of x , exhibits a robust peak at $x = 0.1$ at all temperatures within the investigated range. Interestingly, the peak observed in these a vs. $x|_T$ curves vanish if the XRD measurements are performed on samples kept under vacuum. These are the first findings hinting to a possible microscopic origin for the enhanced proton conductivity in the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ compound, namely the doping-induced enlargement of the unit cell constant at $x = 0.1$.

2. Experimental details

$\text{Sn}_{1-x}\text{In}_x\text{P}_2\text{O}_7$ samples were prepared by an oxide-acid method, using SnO_2 , In_2O_3 (Aldrich, 99.99%) and H_3PO_4 as precursors. The metal oxides were mixed with an H_3PO_4 solution of 85% wt. in H_2O ; a metal to phosphorous ratio in excess of 1:10 Sn/In:P was used. The mixture was then heated in an alumina crucible, kept for 5 h at 650°C , and then left to cool overnight.

Synchrotron XRD measurements were performed on the X16 C beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. X-rays of wavelength 0.705 \AA selected by a channel-cut Si (111) monochromator were used. Samples were placed in a glass capillary mounted in the transmission geometry on a two circle diffractometer. A Ge (111) analyzer crystal was used in the secondary beam. Heating was achieved using a custom made furnace that surrounds the capillary containing the sample. Laboratory XRD data collection was performed on a Panalytical Empyrean system equipped with a Paar HTK high-temperature chamber that allows experiments on samples kept under vacuum or inert gas flow in the reflection geometry. In both setups, powder XRD patterns corresponding to a $1.2 \text{ \AA} - 4.4 \text{ \AA}$ d-spacing range were collected at different temperatures from 50°C and 300°C increasing the temperatures in 50°C steps. Data were analyzed via full profile (Le Bail) fits using the FULLPROF software [20] to determine the dependence of the lattice parameter (a) on the temperature (T) and In-doping level (x). Rietveld refinements were also carried out using the General Structure Analysis System (GSAS) [21] in order to uncover temperature- and In-doping-induced crystal structure modifications in the title compounds.

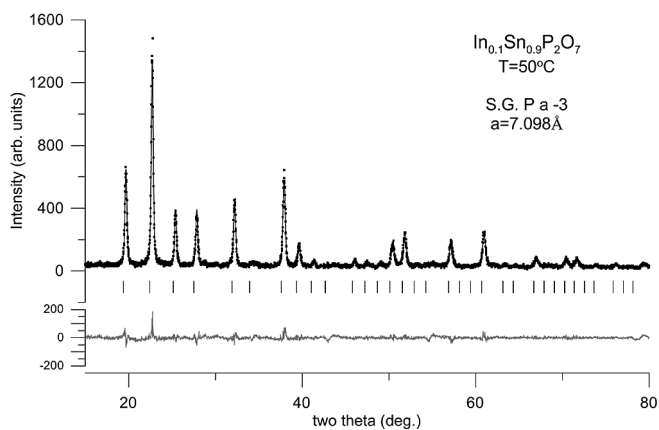


Fig. 1. Full profile (Le Bail) refinement against XRD data collected on the $\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$ ($x = 0.1$) sample at $T = 50^\circ\text{C}$. The solid symbols are the observed intensities I_{obs} measured at detector angles (2θ) between 10 and 80 deg. The solid line represents the calculated intensities I_{calc} and the vertical bars mark the angular positions of the Bragg reflections. The lower trace is the difference curve between the observed and calculated intensities $I_{\text{obs}} - I_{\text{calc}}$. The fit yields a lattice parameter for the cubic (P a -3) unit cell $a = 7.098 \text{ \AA}$.

3. Results and discussion

Fig. 1 shows the powder diffraction pattern (observed intensities I_{obs}) collected at $T = 50^\circ\text{C}$ on the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ ($x = 0.1$) compound (solid symbols). The solid line is a full profile (Le Bail) refinement of the lattice parameters of the cubic P a -3 unit cell (calculated intensities I_{calc}), the vertical bars mark the angular positions of the Bragg reflections, and the lower trace in the difference curve between the calculated and the observed intensities $I_{\text{calc}} - I_{\text{obs}}$. In a LeBail fit the unit cell parameters, integrated intensities, and

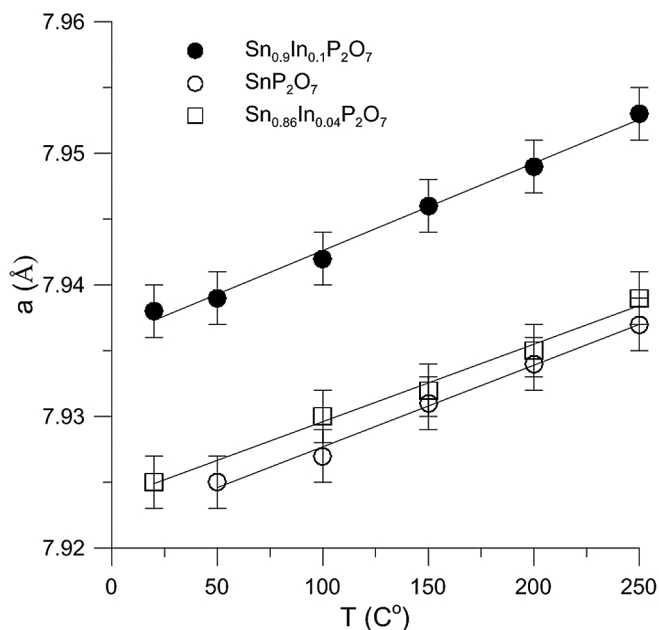


Fig. 2. Temperature dependence of the lattice parameter a (obtained from LeBail fits to XRD data) of three samples from the $\text{In}_x\text{Sn}_{1-x}\text{P}_2\text{O}_7$ series: $x = 0.1$ (solid circles), $x = 0$ (empty circles) and $x = 0.04$ (empty squares). The lattice parameter varies smoothly with temperature for all values of x indicating that neither structural phase transitions nor chemical modifications occur within this temperature range. Yet, the lattice parameter of the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ ($x = 0.1$) compound is larger than that of its $x = 0$ and $x = 0.04$ counterparts.

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