Na$_3$Bi(PO$_4$)$_2$ type solid solutions; investigation of structural and electrical properties

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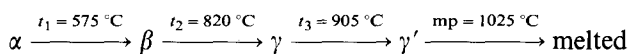*59652 Villeneuve d'Ascq Cedex (France)*

Abstract

The Na$_3$PO$_4$–BiPO$_4$ phase diagram displays a definite compound Na$_3$Bi(PO$_4$)$_2$ and a solid solution of related structure Na$_{3-3x}$Bi$_x$Bi(PO$_4$)$_2$. Both exhibit three phase transitions and a decrease in the transition temperatures is observed when Bi^{3+} substitutes for Na$^+$. Density measurements and evolution of cell parameters *vs.* the substitution ratios are in agreement with model's constant numbers of anions. Other ionic substitutions were carried out in order to modulate the physical properties of Na$_3$Bi(PO$_4$)$_2$: replacement of Na$^+$ by Li$^+$, K$^+$, Pb^{2+}, Er^{3+}; replacement of Bi^{3+} by Pb^{2+}, Er^{3+}; substitution of PO$_4^{3-}$ by VO$_4^{3-}$. Investigations of some structural and electrical properties of solid solutions are presented.

1. Introduction

Numerous investigations of compounds of general formula M$^I_3$M^{III}(XO$_4$)$_2$ (M^I ≡ Na, K, Rb, Cs, Tl; M^{III} ≡ rare earth, X ≡ P, V, As) have already been realized [1–6], owing to various potential applications such as luminescence, ferroelectricity or ionic conductivity. These compounds adopt different crystal structures at room temperature and exhibit one or several phase transitions before melting.

Na$_3$Bi(PO$_4$)$_2$ was found during study of the Na$_3$PO$_4$–BiPO$_4$ system [7]. Astonishingly enough it is the first double phosphate of bismuth and alkali metal discovered. This compound exhibits three phase transitions before melting:

$$\alpha \xrightarrow{\ t_1 = 575\,^\circ C\ } \beta \xrightarrow{\ t_2 = 820\,^\circ C\ } \gamma \xrightarrow{\ t_3 = 905\,^\circ C\ } \gamma' \xrightarrow{\ mp = 1025\,^\circ C\ } \text{melted}$$

The α and β phases crystallize in orthorhombic cells but the actual symmetry of the α form is monochinic ($P2_1/c$). The γ and γ' phases have trigonal symmetry with parameters close to those of glaserite [8].

A polymorphic Na$_{3-3x}$Bi$_x$PO$_4$ solid solution, with structure related to that of Na$_3$Bi(PO$_4$)$_2$, has been observed for $0.5 \leqslant x \leqslant 0.62$ over 950 °C, resulting from the partial replacement 3Na$^+ \longrightarrow$ Bi^{3+}. This paper reports on investigations of structural properties of some solid solutions of this type obtained by other cationic and anionic substitutions.

2. Experimental details

Powder samples were synthesized from dehydrated (NH$_4$)$_2$HPO$_4$, Na$_2$CO$_3$, Bi$_2$O$_3$ and the oxide of the chosen element. Appropriate mixtures balancing the stoichiometry of the compounds of general formula Na$_{3-3x}$M$_{3x/n}$Bi(PO$_4$)$_2$, Na$_3$Bi$_{1-x}$M$_{3x/n}$(PO$_4$)$_2$ or Na$_3$Bi(PO$_4$)$_{2-2x}$(VO$_4$)$_{2x}$, were made respectively for the substitution of Na$^+$, Bi^{3+}, PO$_4^{3-}$ (n is the valency of the M element). They were preheated in alumina crucibles at 275 °C for 6 h in order to decompose (NH$_4$)$_2$HPO$_4$. The temperature was then slowly increased (10 °C h^{-1}) up to 800 °C with intermediate grindings at 275, 450 and 650 °C. The materials were finally air quenched.

X-ray diffractometry using a Guinier de Wolff camera (λ Cu Kα) ensured completeness of the reaction and was used to characterize the phases obtained at room temperature. Accurate cell parameter variation was measured using KCl as an internal standard.

Investigations of the thermal behaviour were carried out using high temperature X-ray diffractometry (HTXRD) with a Guinier-Lenne camera (λ Cu Kα, heating rate 20 °C h^{-1}); differential thermal analysis (DTA) was done with a Dupont de Nemours 1600 DTA cell coupled to a 1090 B thermal analyser (heating rate 300 °C h^{-1}).

The electrical properties were investigated by impedance spectroscopy using a 1174 automated Solar-

tron frequency response analyser working in the range 1–10^6 kHz under air atmosphere. Samples were pelletized (diameter 10 mm, thickness ca. 1 mm) and sintered during 4 h at about 870 °C in air. After air quenching the degree of compaction was in all cases about 85%. Gold electrodes were vacuum deposited onto both flat surfaces of each pellet.

3. Results and discussions

Seven new solid solutions with structure related to Na$_3$PO$_4$–BiPO$_4$ were identified, in addition to the first solid solution of this type already observed in the Na$_3$Bi(PO$_4$)$_2$ system. Samples within the monophasic domain display XRD patterns identical with that of the orthorhombic form (α) Na$_3$Bi(PO$_4$)$_2$, with a noticeable shift of the reflections; therefore, their patterns are indexable on this basis.

Density measurements of the original solid solution are in agreement with theoretical densities computed from the model with a constant number of anions, and a defective cationic sublattice according to Na$_{3-3x}$Bi$_x$Bi(PO$_4$)$_2$ for one unit formula [9]. A similar model was used to describe the domains of existence of the newly investigated solid solutions, which are summarized in Table 1.

As an example, Fig. 1 shows, for Na$_{3-3x}$Pb$_{3x/2}$-Bi(PO$_4$)$_2$, the dependence of the cell parameters on

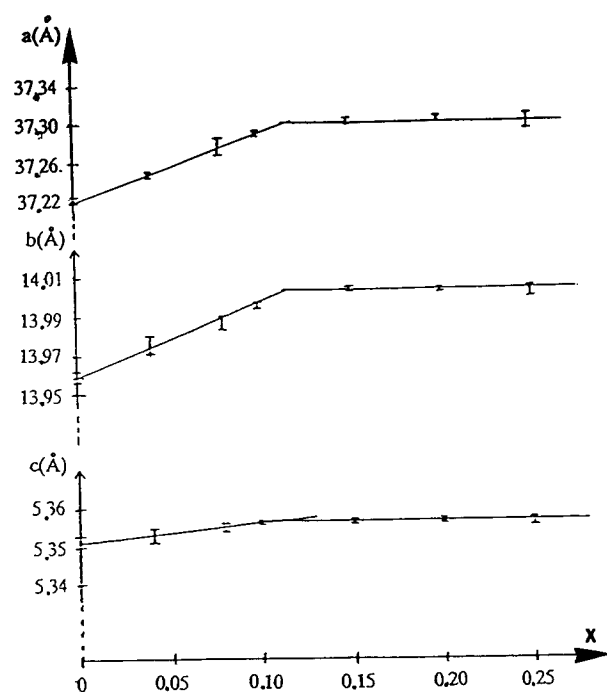TABLE 1. Stability domains at room temperature of α-Na$_3$Bi(PO$_4$)$_2$ related forms of the new solid solutions

Formula	M	n	Compositional range (x)
Na$_{3-3x}$M$_{3x/n}$Bi(PO$_4$)$_2$	Li	1	$0 \leqslant x \leqslant 0.133$
	K	1	$0 \leqslant x \leqslant 0.2$
	Pb	2	$0 \leqslant x \leqslant 0.10$
	Er	3	$0 \leqslant x \leqslant 0.15$
Na$_3$Bi$_{1-x}$M$_{3x/n}$(PO$_4$)$_2$	Pb	2	$0 \leqslant x \leqslant 0.25$
	Er	3	$0 \leqslant x \leqslant 0.37$
Na$_3$Bi(PO$_4$)$_{2-2x}$(VO$_4$)$_{2x}$			$0 \leqslant x \leqslant 0.15$

composition refined on the basis of an (α) Na$_3$Bi(PO$_4$)$_2$ type orthorhombic cell. Figure 2 regroups the variations in volume of the unit formula with two PO$_4$ tetrahedra vs. x.

Investigation of the thermal behaviour of the samples by HTXRD and DTA allowed the variation of the transition temperatures to be observed and the equilibrium phase diagrams of some solid solutions to be determined. As examples, the DTA thermogram of Na$_{2.925}$Li$_{0.075}$Bi(PO$_4$)$_2$ and the HTXRD pattern of Na$_{2.76}$Pb$_{0.12}$Bi(PO$_4$)$_2$ are presented in Figs. 3(a) and 3(b).

The phase diagrams of the solid solutions Na$_{3-3x}$Li$_{3x}$Bi(PO$_4$)$_2$ and Na$_{3-3x}$Pb$_{3x/2}$Bi(PO$_4$)$_2$ are

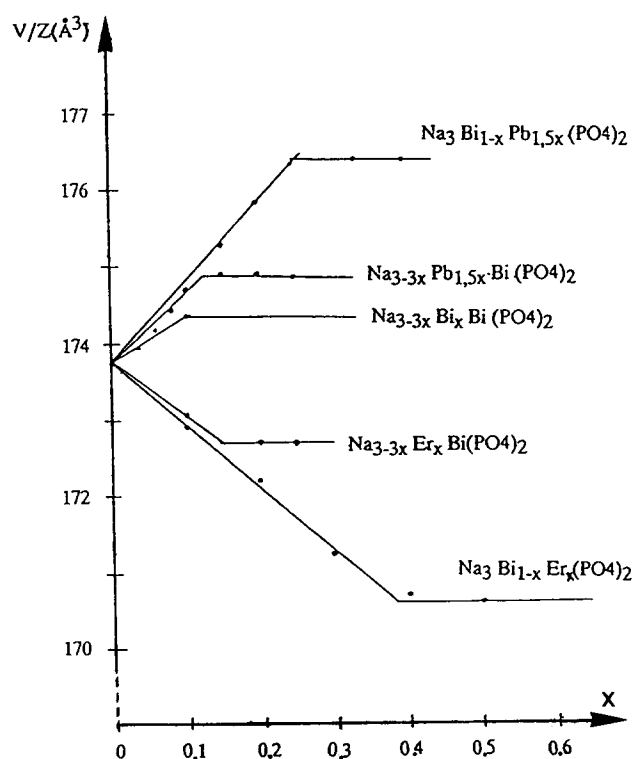Fig. 1. Dependence of cell parameters on x for the Na$_{3-3x}$Pb$_{1.5x}$Bi(PO$_4$)$_2$ solid solution.

Fig. 2. Dependence of the unit formula volume on x for Na$_{3-3x}$M$_{3x/n}$Bi(PO$_4$)$_2$ solid solutions.
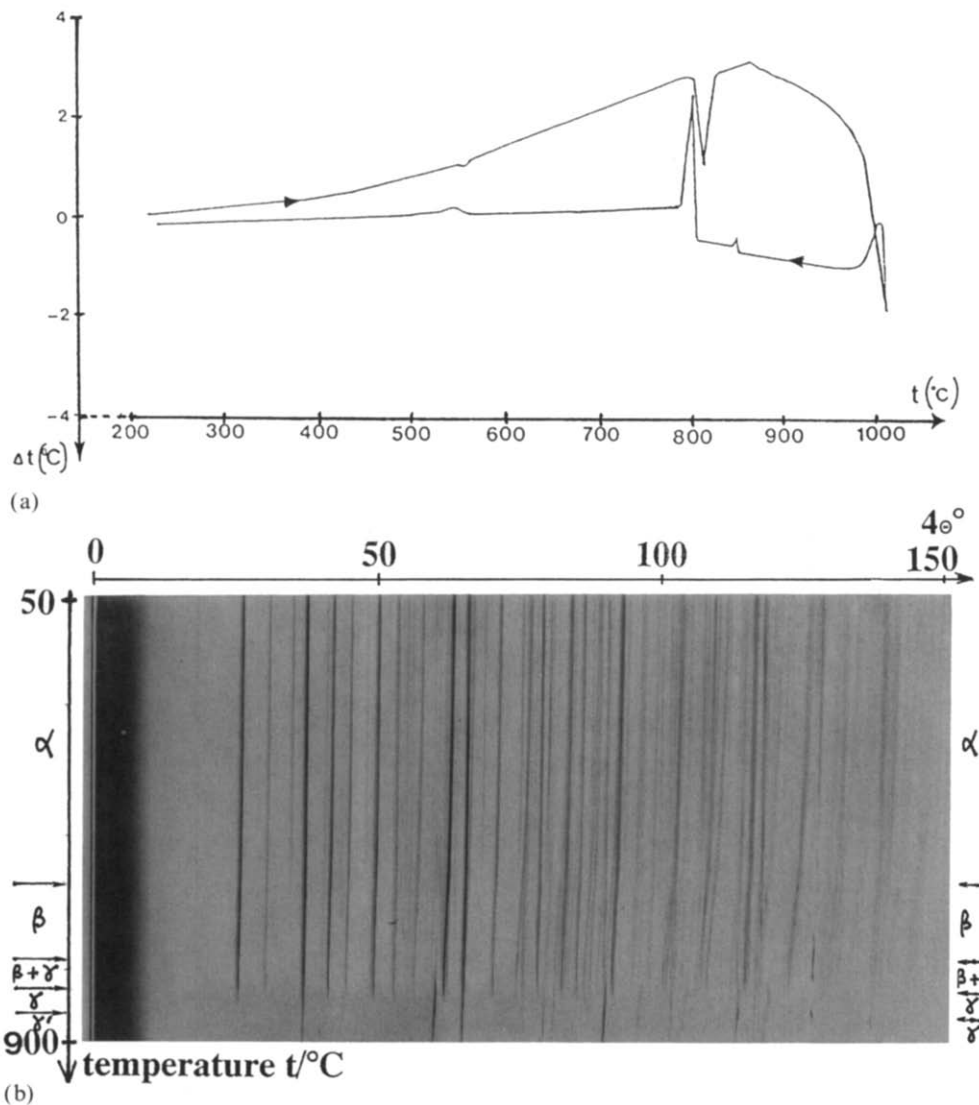
Fig. 3. Investigations of thermal behaviour: (a) DTA thermogram of $Na_{2.925}Li_{0.075}Bi(PO_4)_2$, (b) HTXRD pattern of $Na_{2.76}Pb_{0.12}Bi(PO_4)_2$.

shown in Figs. 4(a) and 4(b). These are quite similar to the phase diagram of $Na_{3-3x}Bi_xBi(PO_4)_2$, previously proposed [7]. The ranges of stability of x increase to maximum values $x = 0.275$ at 760 °C and $x = 0.17$ at 890 °C. Above these temperatures the samples are melted. Neither substitution modifies significantly the t_1 transition of $Na_3Bi(PO_4)_2$ but t_2 decreases to 720–740 °C. The t_3 transition decreases to 740 or 875 °C when Li^+ or Pb^{2+} respectively substitutes for Na^+.

Figure 5 presents the $Na_{3-3x}K_{3x}Bi(PO_4)_2$ solid phase diagram above 630 °C for $0 \leqslant x \leqslant 1$. X-ray investigation of quenched $Na_{3-3x}K_{3x}Bi(PO_4)_2$ samples at room temperature has shown, in addition to the α-$Na_3Bi(PO_4)_2$ type solid solution, a second single phase domain for $0.4 < x \leqslant 1$ (glaserite type solid solution). In the range $0.25 \leqslant x \leqslant 0.40$, phases of α-$Na_3Bi(PO_4)_2$ and glaserite types coexist. The glaserite type solution

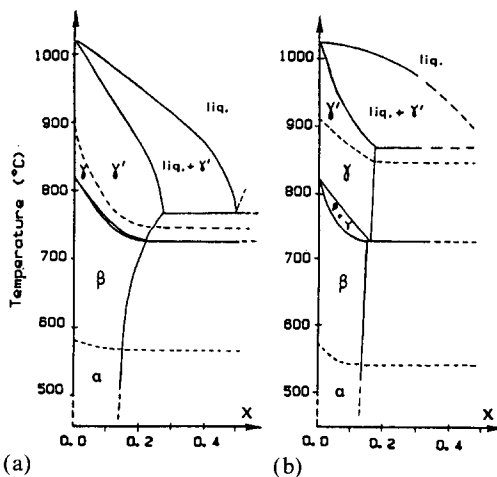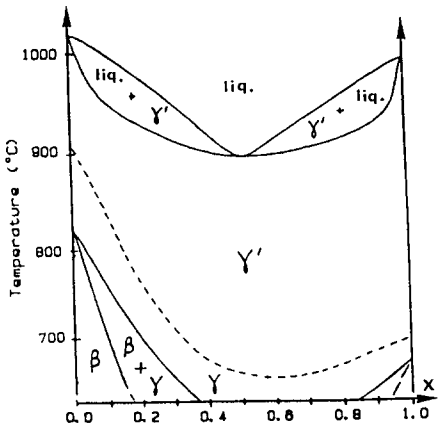Fig. 4. Phase diagrams of (a) $Na_{3-3x}Li_{3x}Bi(PO_4)_2$ and (b) $Na_{3-3x}Pb_{1.5}Bi(PO_4)_2$ solid solutions.

Fig. 5. Phase diagram of $Na_{3-3x}K_{3x}Bi(PO_4)_2$ solid solution.

$(0.4 < x \leqslant 1)$ is a quenched metastable phase; its transformation into a polyphasic material is characterized by a DTA exothermal effect at about 350 °C during the heating process. The formation of pure γ and γ' phases in the ranges of temperature of approximately 625–820 and 670–905 °C respectively is observed whatever the value of x.

Conductivity measurements were taken in the range 300–840 °C on $Na_3Bi(PO_4)_2$ and quenched samples of the solid solutions $Na_{3-3x}Bi_xBi(PO_4)_2$ ($x = 0.03, 0.08$), $Na_{3-3x}Li_{3x}Bi(PO_4)_2$ ($x = 0.15$, 0.1, 0.133) and $Na_{3-3x}K_{3x}Bi(PO_4)_2$ ($x = 0.1, 0.2$). The corresponding Arrhenius plots of the measurements taken during the heating processes are presented in Fig. 6. The linear
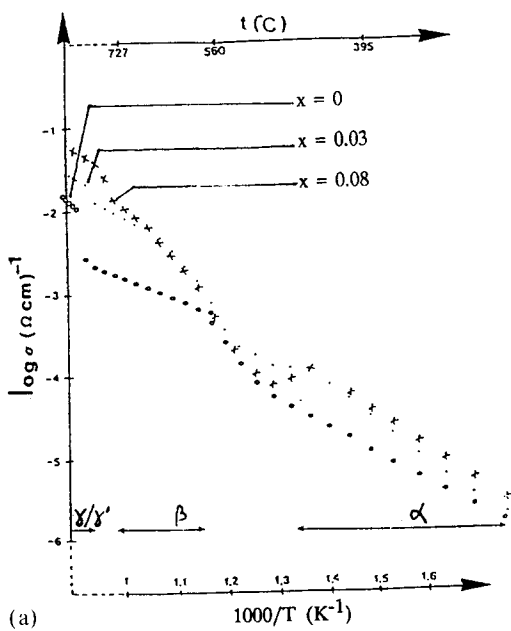
(a)
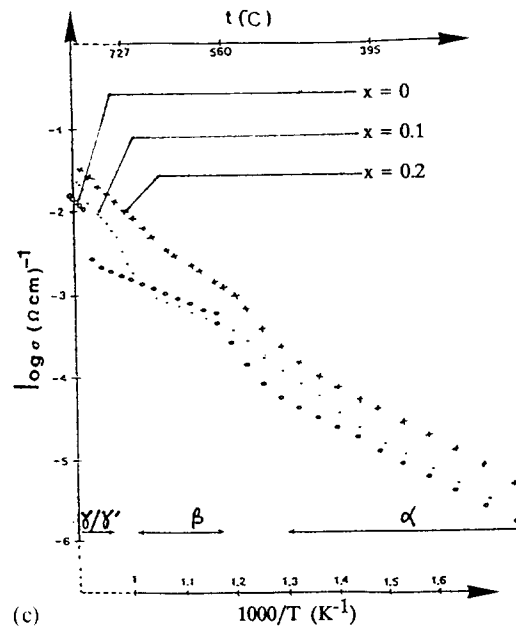
(c)
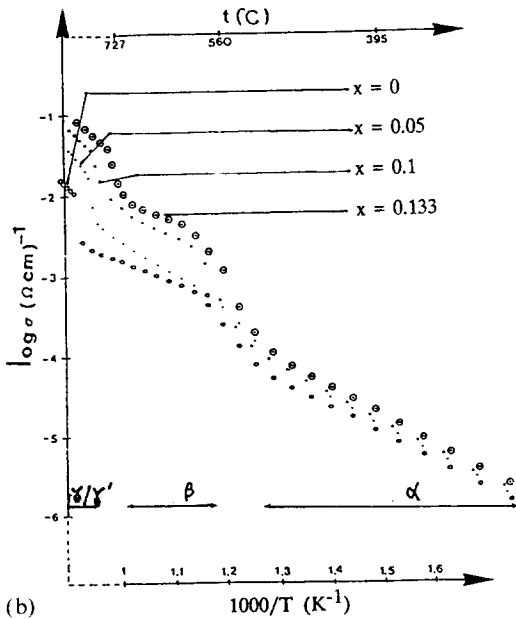
(b)

Fig. 6. Arrhenius plots for (a) $Na_{3-3x}Bi_xBi(PO_4)_2$, (b) $Na_{3-3x}Li_{3x}Bi(PO_4)_2$, and (c) $Na_{3-3x}K_{3x}Bi(PO_4)_2$.
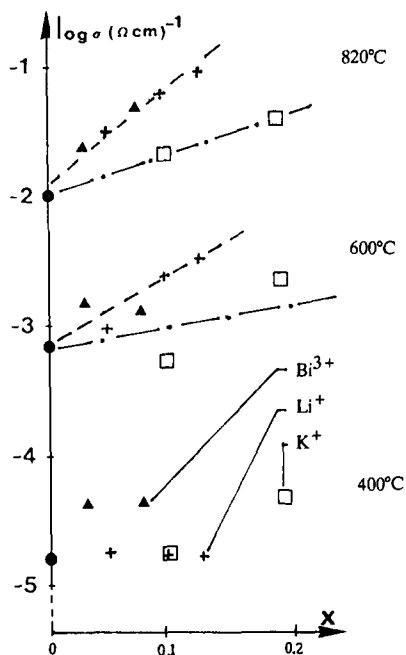
Fig. 7. Composition dependence of log σ at 400 (α form), 600 (β) and 820 °C (γ) for $Na_{3-3x}M_{3x/n}Bi(PO_4)_2$ solid solutions ($M^+ \equiv Bi^{3+}$, Li^+, K^+).

domains, drawn for each sample, characterize the α, β or γ forms of these solid solutions. Jumps of conductivity are generally observed in the temperature ranges of the $\alpha \longrightarrow \beta$ and $\beta \longrightarrow \gamma$ transitions but in the $Na_{3-3x}Bi_x Bi(PO_4)_2$ samples ($x = 0.03, 0.08$), for which a slight decrease in σ is observed between 460 and 500 °C, the $\alpha \longrightarrow \beta$ transition is not characterized. This particular behaviour can be attributed to the decomposition of the quenched solid solution which is metastable for these compositions in this temperature range.

Figure 7 shows the isothermal variation of σ at 400, 600 and 820 °C respectively for the α, β and γ varieties of the three solid solutions investigated. In all cases, the substitution of Na^+ is accompanied by an increase in conductivity.

A valuable comparison of the conductivity properties of these three solid solutions can be realized only for the β and γ forms which are true equilibrium phases. The magnitude of the conductivity gain is equivalent when Bi^{3+} or Li^+ substitutes for Na^+ in the same concentration but is lower when K^+ substitutes for Na^+. This can be related to the larger size of the K^+ cation, which cramps the motion of the conducting moities. Investigations aiming at their identification will be realized to correlate these observations with structural results.

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