

Substitution of praseodymium by lead in $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ at 850°C

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This study analyzed the substitution of lead ions with praseodymium ions in sodium lead apatite. Two techniques, X-ray diffraction analysis and infrared spectroscopy, were used to examine the substitutions. The examination was based on the equation: $2\text{Pb}^{2+} + \nu \rightarrow 2\text{Pr}^{3+} + \text{O}^{2-}$. The results were solid solutions with the composition $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ ($0.0 \leq x \leq 1.0$). Lead sodium apatite samples produced at 850°C ranged from $x=0.0$ to $x=0.6$. The following methods were used to determine the limits of the Pb substitute for Pr in lead sodium apatite: the method for determining the dependency of unit cell parameters and the vanishing phase method.

Keywords: apatite structure, solid solutions, lead, praseodymium, sodium.

Заміщення празеодиму на свинець у $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ при 850°C. Mohammed A. B. Abdul Jabar, A. V. Ignatov, A. O. Zhgailo

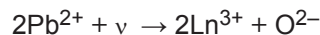
Проаналізовано заміщення іонів свинцю іонами празеодиму в апатиті натрію свинцю. Для дослідження заміщень використовували дві методики: рентгенівський дифракційний аналіз та інфрачервону спектроскопію. Обстеження базувалося на рівнянні: $2\text{Pb}^{2+} + \nu \rightarrow 2\text{Pr}^{3+} + \text{O}^{2-}$. Результатом були тверді розчини складу $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ ($0,0 \leq x \leq 1,0$). Зразки апатиту натрію свинцю, отримані при 850°C, коливалися від $x=0,0$ до $x=0,6$. Для визначення меж заміни Pb на Pr в апатиті натрію свинцю використовували такі методи: метод визначення залежності параметрів елементарної комірки та метод зникаючої фази.

1. Introduction

Solid solution compounds, including various apatite compounds, have attracted the interest of specialized researchers for various reasons, including their ability to modify the properties of the crystal structure, the distances between atoms, the nature of the chemical bond, and others [1-3]. Internal substitutions provide compounds' structures with several vital modifications and properties [4]. Identical substituents are an essential component of the crystal chemistry of compounds with apatite-like structures since different apatite compounds may have different structural arrangements of their structural units [5-8] because apatite,

an essential element that affects a material's chemical and physical properties, changes its crystal structure as structural units in the material undergo substitution [9-13].

Lead sodium apatite compounds, which are one of the types of apatite compounds with the formula $\text{Pb}_{8-x}\text{Na}_2\text{Ln}_x(\text{PO}_4)_6\text{O}_{x/2}$ are substituted according to the following scheme



where ν is a vacancy in the system, are considered essential compounds whose various substitutions with rare earth elements have not been sufficiently studied by researchers [14-16].

Although lead's ionic radius is similar to alkaline earth ions, literature regarding substi-

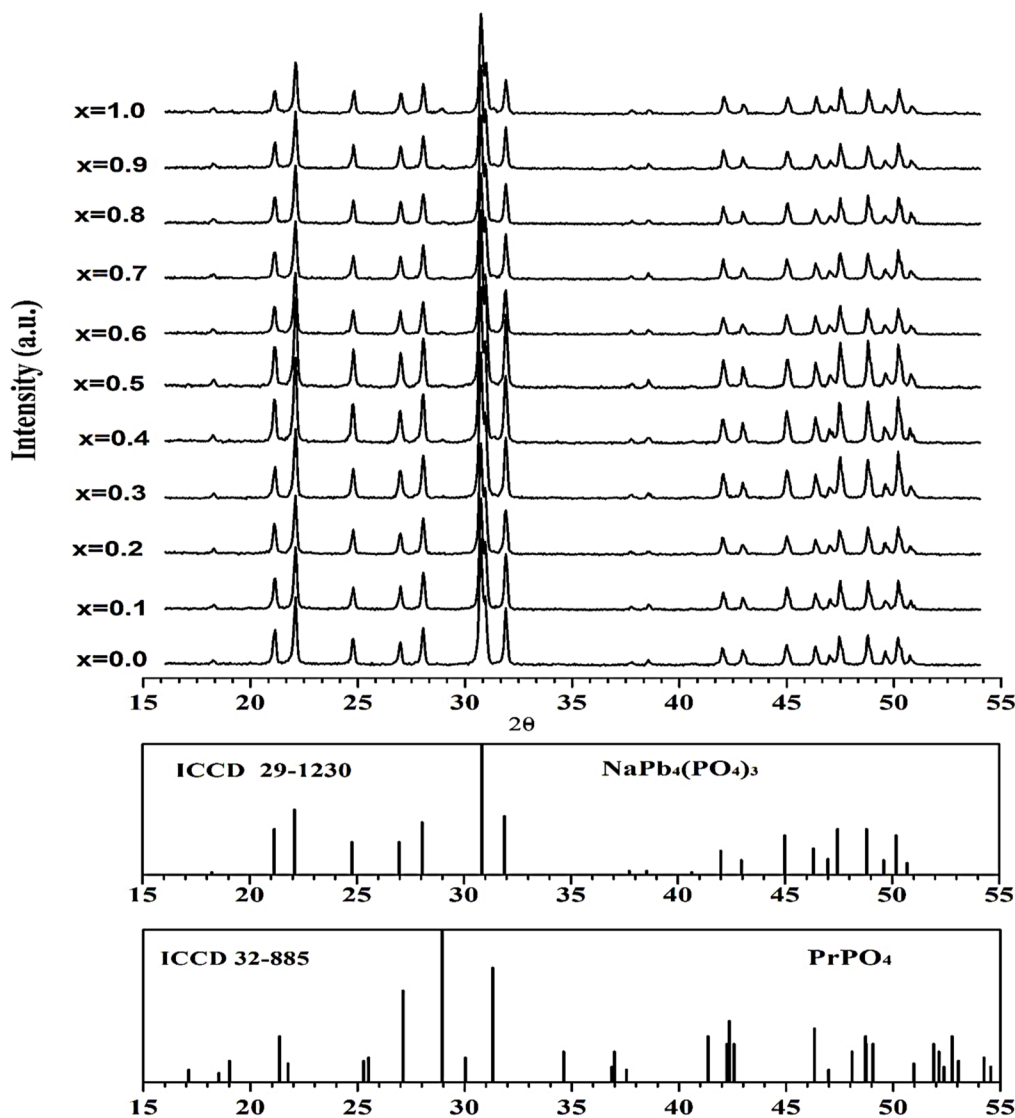


Fig. 1. X-ray diffraction patterns of $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ samples and a $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ X-ray diffraction pattern constructed from the pdf-2 (ICDD) database.

tuting lead with rare earth elements (REE) in the $\text{Pb}_{8-x}\text{Na}_2\text{Ln}_x(\text{PO}_4)_6\text{O}_{x/2}$ material is scarce. One potential benefit of employing lead apatites in systems is achieving a lower synthesis temperature for lead sodium apatites than alkaline earth apatite compounds. This characteristic expedites the synthesis process and aids in the production of refined grains [17]. Alkali metals have been used simultaneously as a substitute for lead in many publications. It is acceptable to assume that the possibility of substituting lead with REE will increase if lead ions are largely substituted by monovalent metal ions (Na^+ , K^+ , Ag^+) [18-20].

Many previous investigations showed that at low temperatures between 800 - 850 °C, lead-

sodium apatite compounds could have been substituted with rare earth elements [21-23].

During our ongoing inquiry, we analyzed the substitution of lead with praseodymium in the $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ compound at a temperature of 850 °C. We have studied different compositions ranging from $x=0.0$ to 1.0.

2. Experimental

Synthesis

To synthesize samples of the system $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ ($0 \leq x \leq 1$), PbO (chemically pure), Pr_6O_{11} , Na_2CO_3 (chemically pure), and $(\text{NH}_4)_2\text{HPO}_4$ (analytical grade). Compositions with $x = 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90$, and 1.0 were investigated.

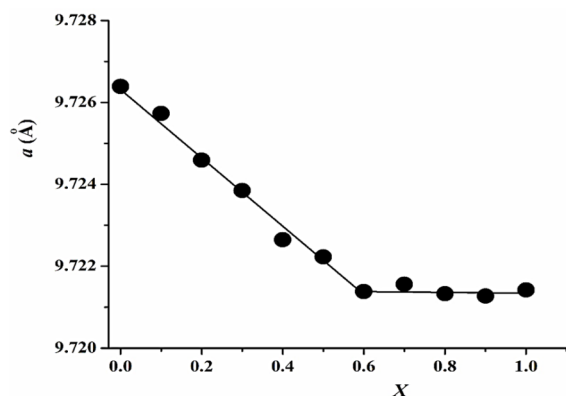
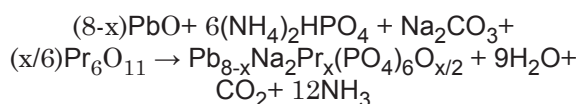


Fig. 2. Unit cell parameters a of samples of $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$, the structure, which depends on the composition.

All samples were synthesized by the solid phase reaction, which can be expressed by the equation below:



The ingredients were initially weighed in stoichiometric ratios and subjected to stirring in an agate mortar for 20 minutes. Subsequently, all samples were placed in ceramic crucibles made of aluminum at 300 degrees Celsius for approximately 3 hours. We then gradually raised the temperature to 850°C, and the heat treatment process of the samples continued for 5 to 8 hours. All samples underwent heat treatment at 850°C, followed by homogenization of the samples for subsequent analysis using X-ray diffraction (XRD). As mentioned above, the series of procedures was repeated until a state of equilibrium was achieved. Consequently, the overall duration of calcination at a temperature of 850 °C amounted to 30 hours.

Characterizations

The experiment involved X-ray phase analysis using a modernized DRON-3 diffractometer equipped with electronic control and results processing. The diffractometer utilized monochromatic Ni-filtered Cu K α radiation. During survey shooting, the counter's rotation speed to determine the samples' phase composition was 2 θ /min. The X-ray diffraction shapes of the examined samples were determined using several internationally approved programs and databases, including the Match program version 4.0, Origin lab program version 9.85, the PDF-2 database (ICCD), and the PDF-4 database (ASTM) [24-26].

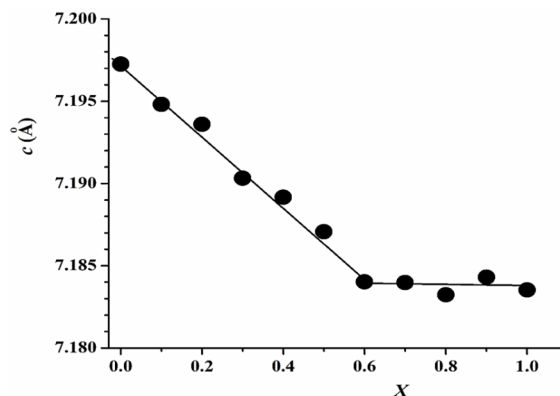


Fig. 3. Unit cell parameters c of samples of $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$, the structure, which depends on the composition.

A least-squares process was used to obtain a suitable fit of unit cell parameters according to 16 independently indexed and independently re-scanned reflections at 1° (2)/min in the $16 \geq 2\theta \geq 54^\circ$. The silicon worked as a separate source of reference standards.

IR-Fourier spectrometer TENSOR 27 (Bruker Optics) (4000-400) cm^{-1} was used to capture infrared spectra. The samples were heat treated at 600°C to extract the absorbed water from the atmosphere; 1 mg was crushed with 600 mg of KBr and compressed into tablets (compression pressure was 900 MPa).

3. Results and discussion

According to the X-ray phase analysis data (Fig. 1), a lead sodium apatite compound ($\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$) occurs within the entire region of the investigated compositions. According to X-ray phase analysis data, solid solutions with the apatite structure are generated in the entire range of the examined compositions. The X-ray data obtained showed the presence of phase reflections consistent with the apatite structure up to $x = 0.3$. In samples with $x = 0.3 - 0.5$ composition, X-ray diffraction patterns indicate one reflection with an intensity of 3-4% less than the maximum intensity of the apatite structure reflection. Because its intensity is practically independent of x , it may be inferred that this is either a superstructure reflection or a reflection of a non-isomorphic component included in the apatite compound [27, 28]. X-ray diffraction (XRD) manners examinations revealed several reflections specific to the structure of the praseodymium phosphate (PrPO_4) compound within the compositional range $x = 0.6 - 1.0$. The strength of these reflections rises linearly with the value of x . This X-ray diffraction pattern

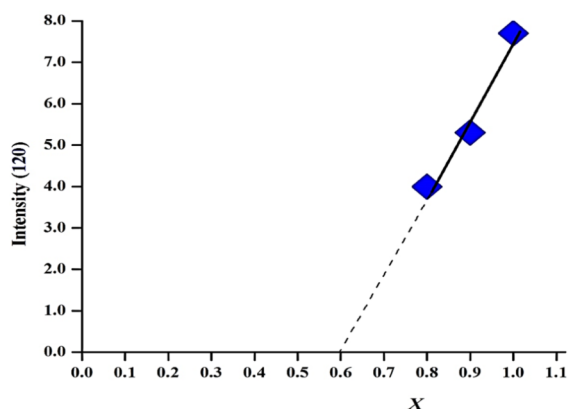


Fig. 4. The reflection intensity of the 120 phase of praseodymium phosphate PrPO_4 is contingent upon the composition x .

indicates that the isomorphic substitution limit corresponds to a composition with $x \leq 0.6$.

The compositional dependability of unit cell characteristics in an apatite structure is illustrated in Fig. 2 and Fig. 3.

Both Fig. 2 and Fig. 3 indicate a significant decrease in parameters a and c when the value of x increases from 0.0 to 0.6. The parameters a and c remain essentially constant until x reaches a value of 1.0 when the obtained findings demonstrate that the substitution of praseodymium by lead happens at $x = 0.6$, as illustrated by the following scheme: $2\text{Pb}^{2+} + \nu \rightarrow 2\text{Pr}^{3+} + \text{O}^{2-}$. Note that these results agree well with the significant differences in dimensions of the alternative units of structure because, as is known, the crystalline ionic radius of Pb^{2+} (1.33 Å) is larger than the crystalline ionic radius of Pr^{3+} (1.13 Å) by 0.20 Å.

The “vanishing phase” method refined the praseodymium substitution limit in lead sodium apatite structure. Fig. 4 illustrates the relationship between the intensity of phase 120 of praseodymium phosphate PrPO_4 and its composition. The straight line generated is extended to the x -axis, resulting in a substitution limit value of $x=0.6$.

Fig. 5 shows sections of several samples measured by infrared spectra of the $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ structure, where the x values are 0.0, 0.1, 0.3, and 0.5.

4. Conclusions

X-ray phase analysis and infrared spectroscopy were used to investigate the isomorphic substitution of lead by praseodymium in lead sodium apatite structure. The boundaries of substitutions are determined, as are the regularities of their change based on the size of the

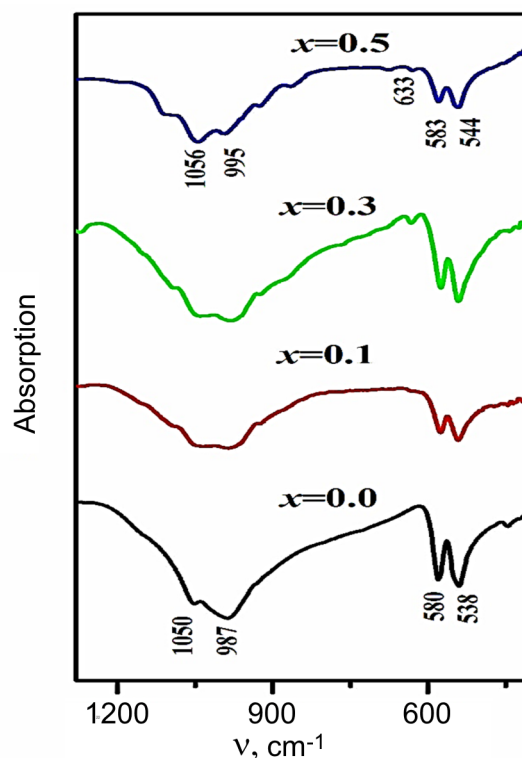


Fig. 5. Fragment of IR spectra of specimens of the $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ structure in the region 400-1300 cm^{-1} .

ions being substituted. The influence of substitutions on the crystal structure of solid solutions has been examined, allowing for the prediction of the presence of luminous characteristics. At a temperature of 850°C, solid solutions consisting of a single phase ($\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$) can be produced with a composition range of $x = 0.6$.

Two distinct methodologies were employed to assess the boundaries of lead substitution for praseodymium in the $\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$ compound. The first method depended on the relationship between unit cell parameters and the degree of substitution. As the value of x increased to 0.6, the unit cell parameters decreased because the ionic radius of Pr^{3+} (1.13 Å) was less than that of Pb^{2+} (1.33 Å). The parameters a and c virtually do not change throughout the compositions $x = 0.6 - 1.0$ range.

The second method, the vanishing phase method, reveals that when the straight line is extended to the x -axis, it shows a comparable value to the substitution limit. This value is determined based on the cell parameters, specifically at $x=0.6$.

IR spectroscopy has demonstrated that in the $\text{Pb}_{8-x}\text{Na}_2\text{Pr}_x(\text{PO}_4)_6\text{O}_{x/2}$ structure, the bands of essential vibrations of the PO_4^{3-} anion devi-

ate by 3-8 cm^{-1} toward higher wavenumbers (with an increase in the value of x), signifying the existence of substitutions in the cationic sublattice. We encourage utilizing the results of the previously mentioned study to develop new process materials, including lead sodium apatite compounds.

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