

Isomorphous Substitutions in the Electron-Ion Conductor $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$

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ABSTRACT

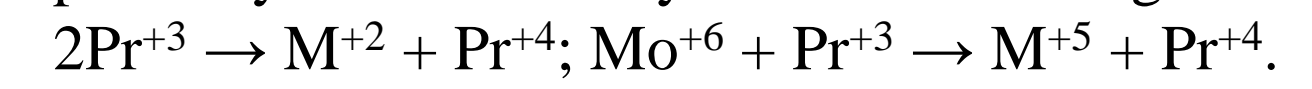
Compounds with fluorite structure are the most common fluorine or oxygen ionic conductors. This is facilitated by the features of the composition and structure: the high ratio of anions to cations in the formula, the ease of structural defects formation, the large size of cations forming cubic closest packing, a significant amount of voids in the structure. Fluorite-like molybdates $\text{Ln}_3\text{Mo}_3\text{O}_{16+\delta}$ have high ionic conductivity due to the presence of superstoichiometric oxygen-ions compared with fluorite CaF_2 . Such molybdates were first synthesized for neodymium and their composition is presented as $\text{Nd}_{14}\text{Mo}_8\text{O}_{45}$ [1]. Later, the composition of the compound is defined as $\text{Nd}_5\text{Mo}_3\text{O}_{16}$ [2].

Oxide ion conductivity in compounds $\text{Ln}_3\text{Mo}_3\text{O}_{16+\delta}$ for the first time was found and described by Tsai [3].

The excess oxygen content was determined using chemical analysis. The crystal structure was first defined by Hubert [2] and later investigated by XRD on monocrystals and by neutron diffraction [4,5]. The conductivity of the oxidized $\text{Ln}_3\text{Mo}_3\text{O}_{16+\delta}$ molybdates is proportional to the REE size, which is due to an increase in interatomic distances and, as a consequence, to a decrease in steric obstacles to the oxygen ions movement. The cubic fluorite-like structure is formed under oxidizing conditions only for praseodymium and neodymium molybdates. Praseodymium may have a variable oxidation state in $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$,

which determines the presence of electronic conductivity and the using possibility as an electrode material in fuel cells [6].

The value of electronic conductivity is insufficient for practical use, but it can be improved through heterovalent isomorphous substitutions with charge compensation of elements in lower oxidation states for praseodymium and molybdenum according to the schemes:



However, other schemes with charge compensation are valid:



To verify this, in this research we studied isomorphous substitution of calcium for praseodymium and niobium for molybdenum in the $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$.

EXPERIMENTAL PART

The samples of the molybdates $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$ ($x = 0 - 1$) and $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$ ($x = 0 - 2$) systems were prepared by a solid state reaction from the metal oxides. The final temperature was 1100 °C for 20 h. X-ray diffraction analysis was performed using DRON-3 diffractometer (CuK α -radiation, Ni-filter). The results were processed using the Match program and PDF-2 database (ICDD). To obtain data for crystal structure refinement by the Rietveld procedure the samples were scanned in steps of 0.02° (2 θ), exposure time 3 s in the range 10° ≤ 2 θ ≤ 140°.

JSM-6490LV (JEOL, Japan) scanning electron microscope and INCA Penta FETx3 (Oxford Instruments, England) energy-dispersive spectrometer were used for investigation of morphology and elemental content of samples.

The samples were investigated by FTIR-spectroscopy using Bruker Optics IR spectrometer in the 400-4000 cm⁻¹ range. Electrical resistivity was determined using LCR DE-5000 at frequency of 1 kHz within the temperature range of 300-700 °C in increments of 20° at a heating rate of 2 °/min.

CRYSTAL STRUCTURE

The $\text{Ln}_3\text{Mo}_3\text{O}_{16+\delta}$ compounds have a fluorite-like structure and crystallize in the space group Pn-3n. The structure of fluorite is distorted as a result of the presence of cations significantly different in both size (for example, $r(\text{Nd}^{+3}) = 1.109 \text{ \AA}$, $r(\text{Mo}^{+6}) = 0.41 \text{ \AA}$) and charge. This leads to the displacement of oxide ions from the positions of the ideal fluorite and the formation of MoO_4 tetrahedra. In addition, fully oxidized compounds have superstoichiometric oxygen relative to fluorite (the ratio of the number of cations to anions in fluorite is 4 : 8, in these REE molybdates – 8 : 16.5), which ensures high ionic conductivity.

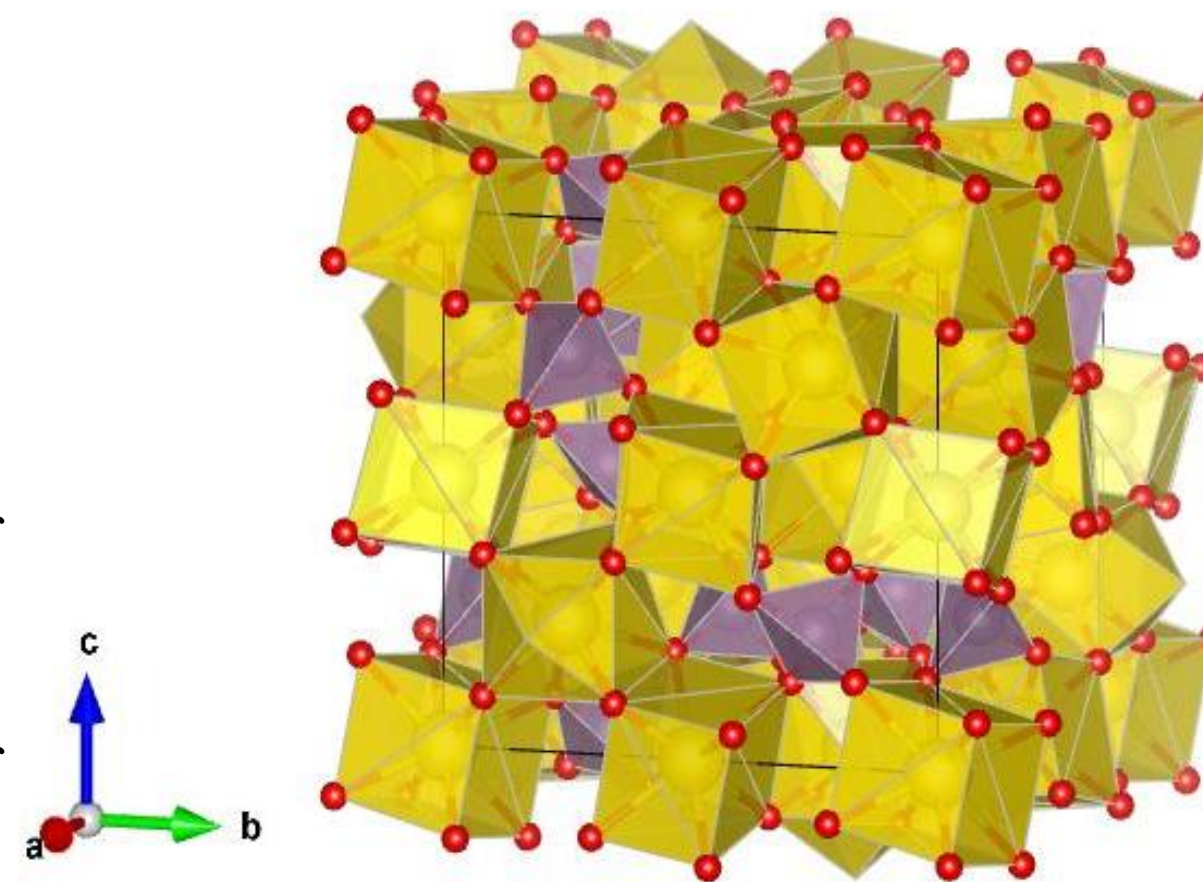


Fig. 1 Unit cell of $\text{Ln}_3\text{Mo}_3\text{O}_{16+\delta}$ fluorite-like compounds

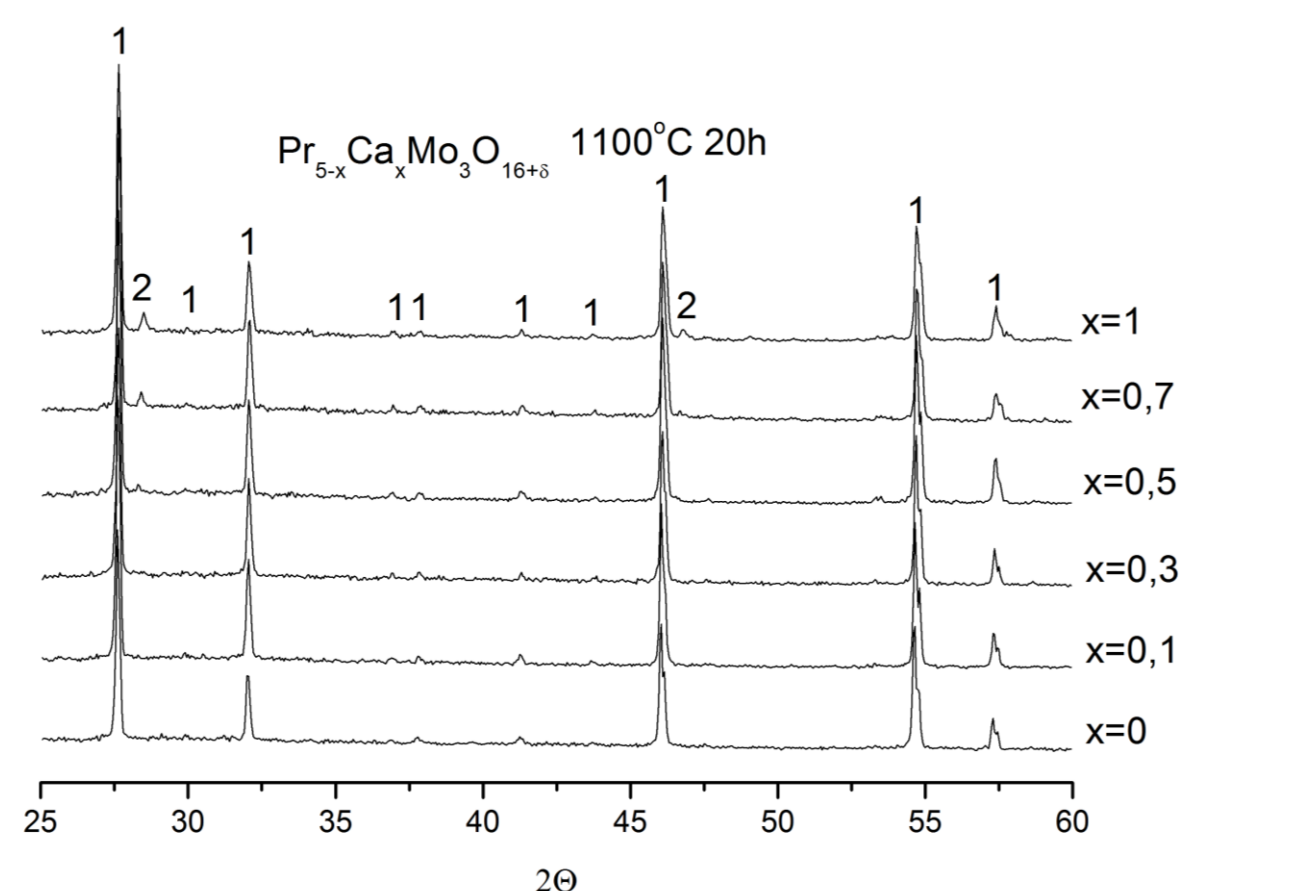


Fig.2 X-ray diffraction patterns of $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$ 1 - $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$ phase; 2 - CaMoO_4 .

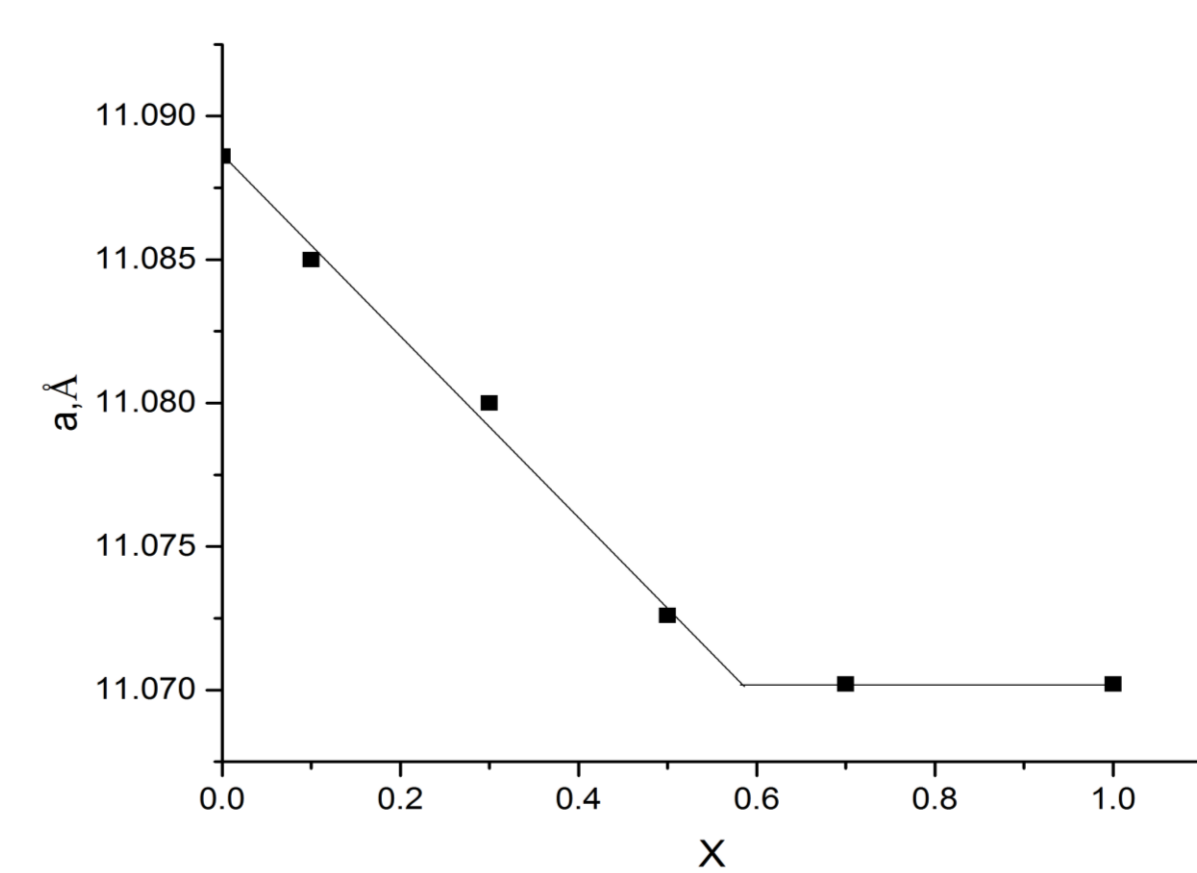


Fig. 3 Plot of unit cell parameter a vs. degree of substitution, x in $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$

The phase with a cubic structure exists in the whole concentration range of the $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$ system after calcination at 1100°C. Single-phase samples obtained in the composition up to $x = 0.5$. A phase of calcium molybdate appears with a higher content of the modifying element.

The unit cell parameter decreases with the introduction of calcium to $x = 0.5$ and does not change at higher x values which indicates the substitutional limit of calcium for praseodymium in the structure of praseodymium molybdate.

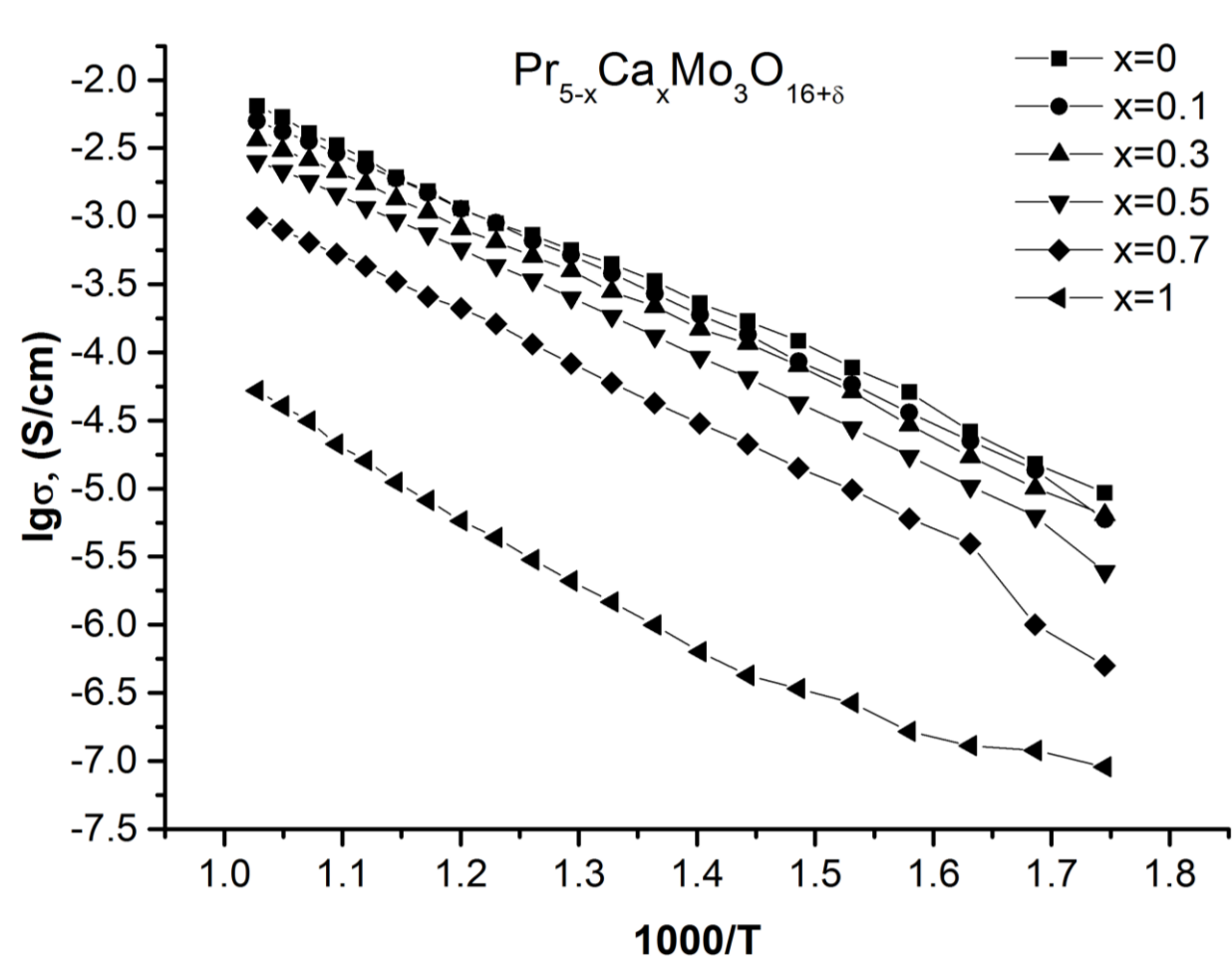


Fig. 4 Logarithm of conductivity, $\log\sigma$ ($\text{S}\cdot\text{cm}^{-1}$) as a function of $1000/T$, (10^3 K^{-1}) for $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$.

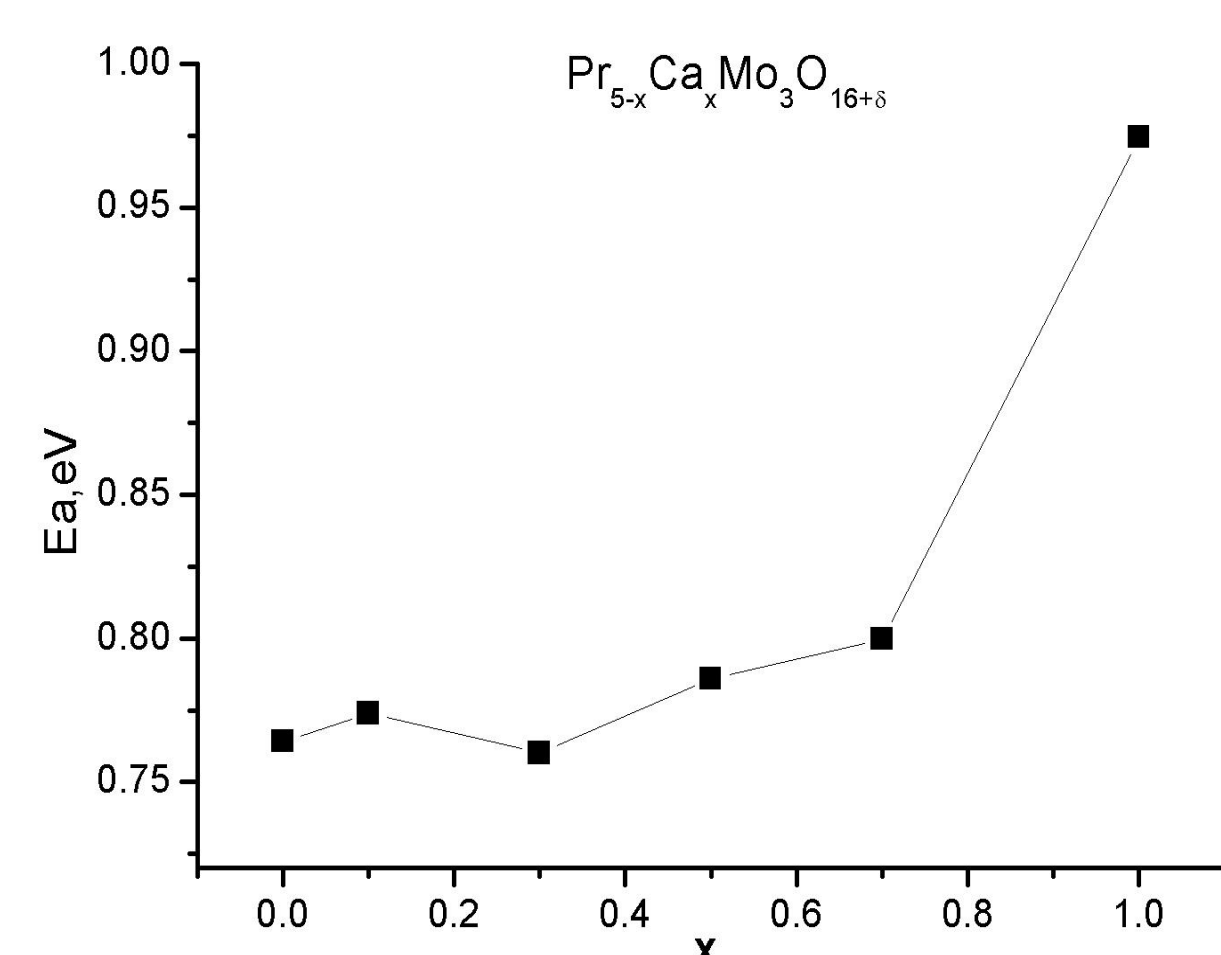


Fig. 5 The plot of activation energy of the conductivity for $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$

The activation energy does not change significantly with the introduction of calcium. A sharp increase in the activation energy for a sample with $x = 1$ is associated with the formation of an impurity: non-conducting phase of calcium molybdate.

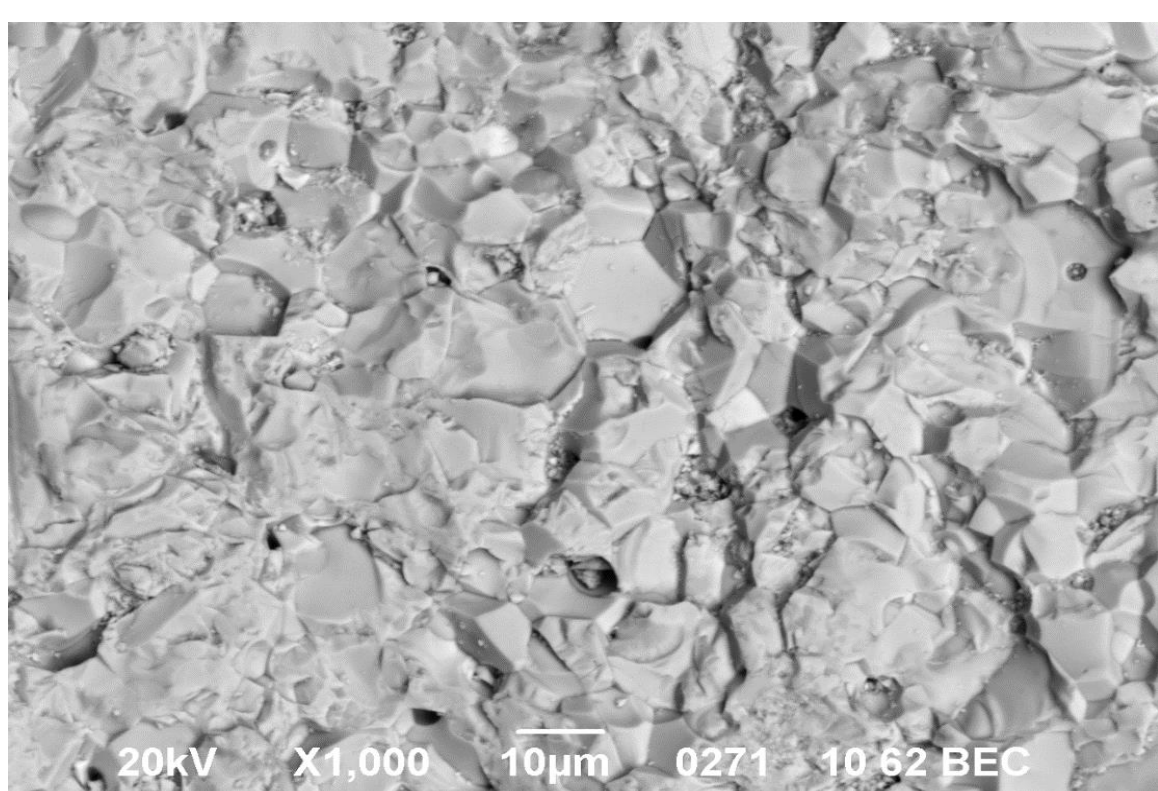
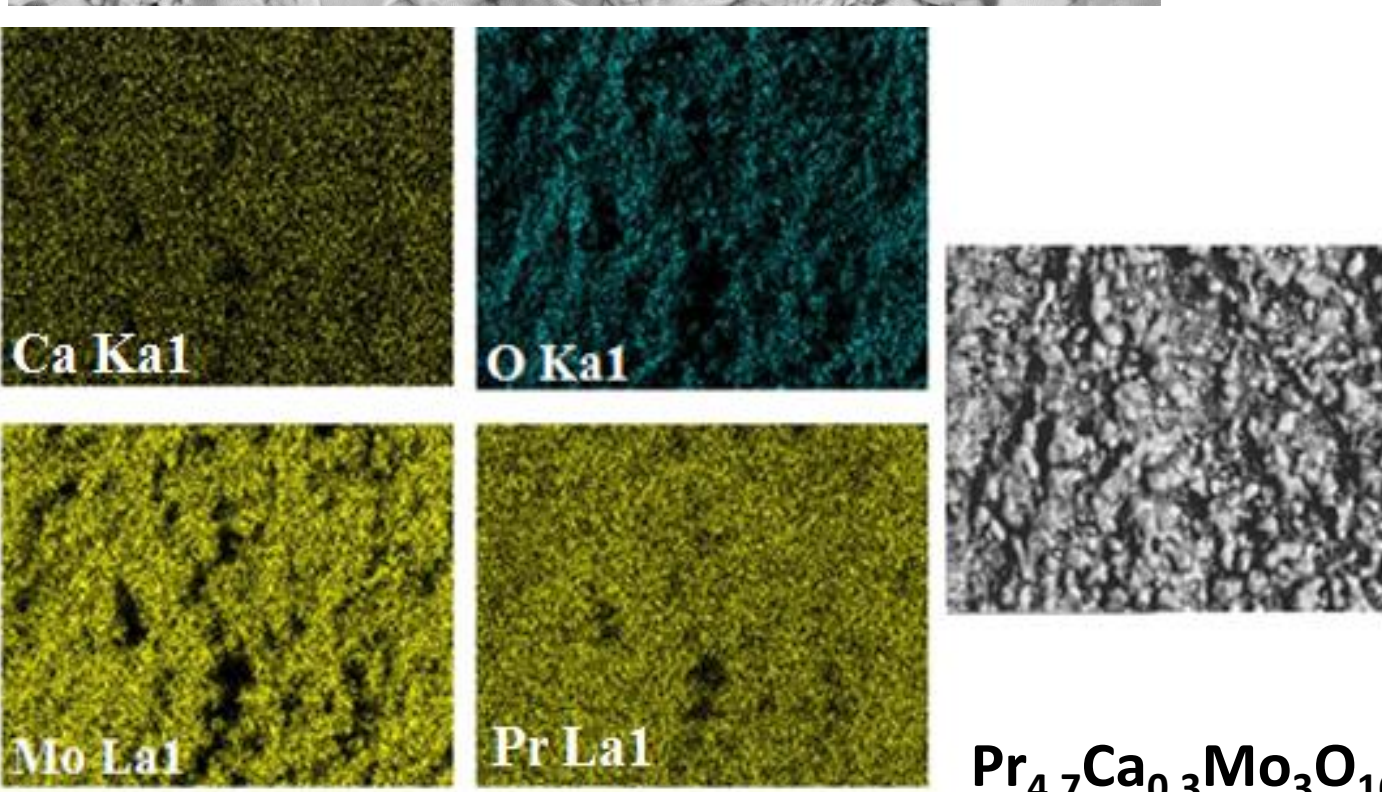


Fig. 6 Microphotograph of the sample and distribution of the elements (Ca, O, Mo, Pr) over particle's surface for $\text{Pr}_{4.7}\text{Ca}_{0.3}\text{Mo}_3\text{O}_{16+\delta}$ obtained in the characteristic X-rays.



The microphotograph shows the resulting ceramics. Under these conditions, the relative density was 89-92%. The grain size is about 10 μm . According to X-ray maps (EDS) the elements are uniformly distributed over the surface of the powder particles. Available irregularity is related to its relief.

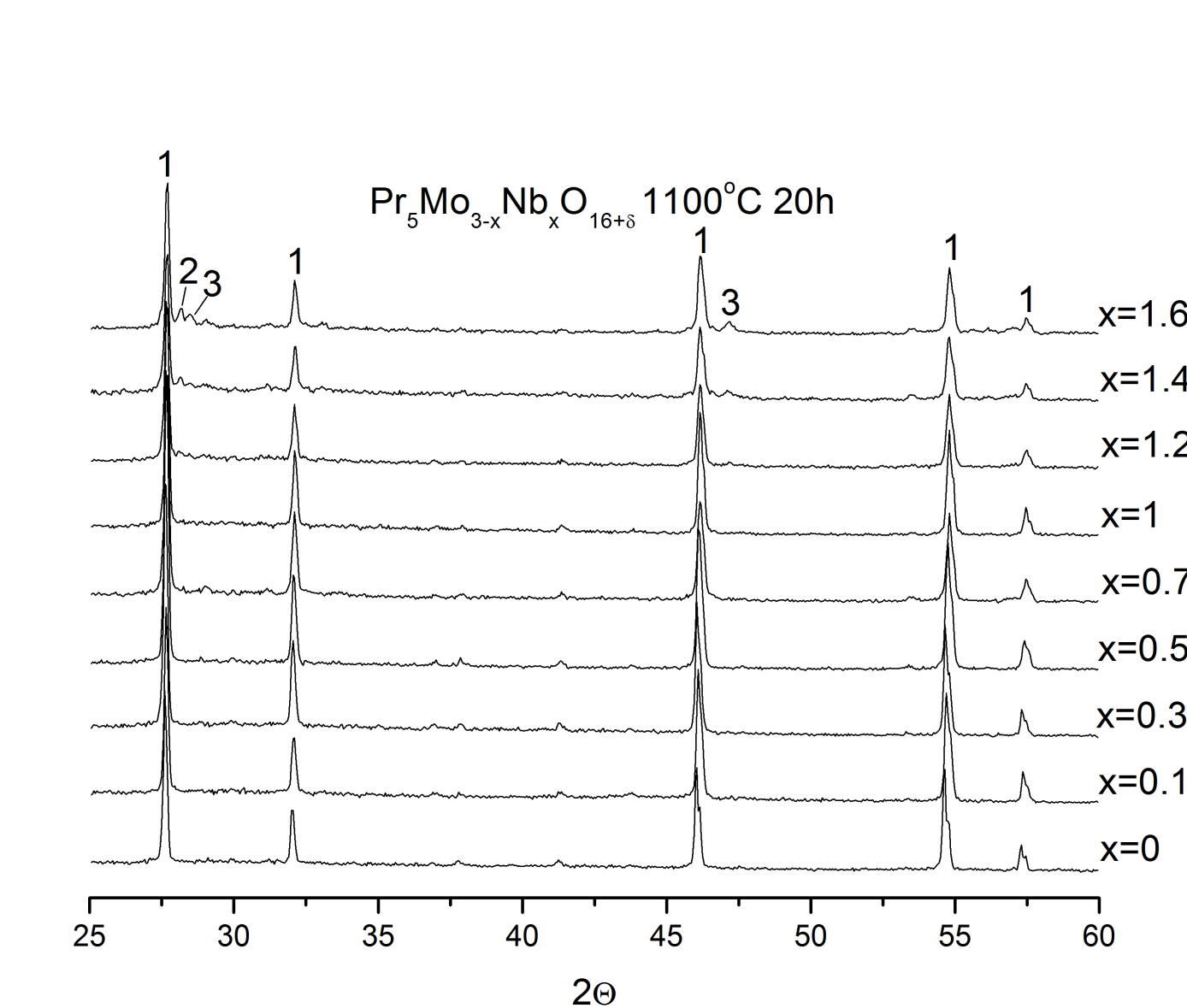


Fig.7 X-ray diffraction patterns of $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$ 1 - $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$ phase; 2 - Nb_2O_5 ; 3 - Pr_3NbO_7 .

After calcination at 1100° C, the phase with a cubic structure exists throughout the studied concentration range. For a system with niobium, the single - phase region exists up to $x=1.2$. At a higher content of niobium in the system the reflexes from the impurity phases of niobium oxide Nb_2O_5 and praseodymium niobate Pr_3NbO_7 , appear in the X-ray diffraction patterns.

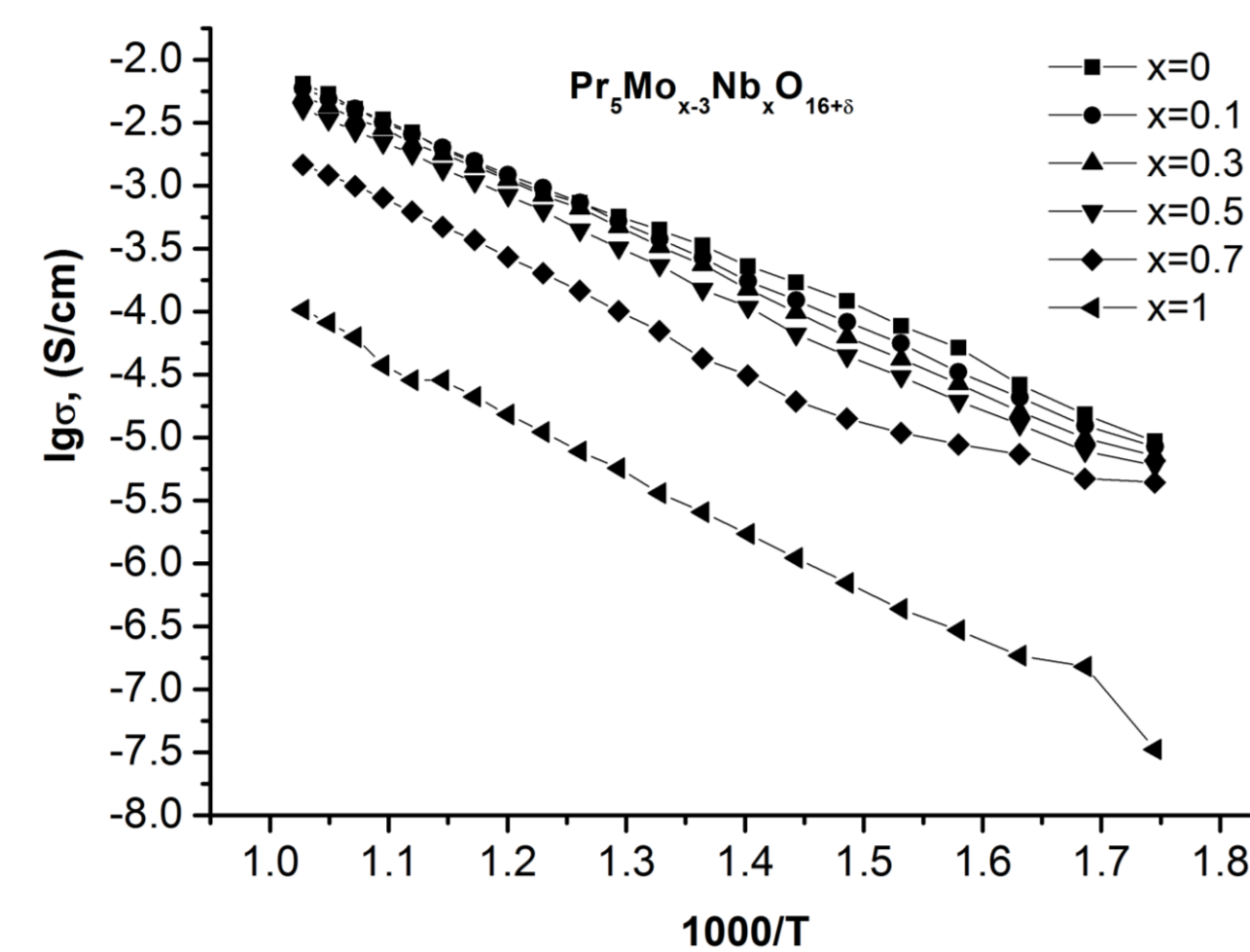


Fig. 9 Logarithm of conductivity, $\log\sigma$ ($\text{S}\cdot\text{cm}^{-1}$) as a function of $1000/T$, (10^3 K^{-1}) for $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$

The electrical conductivity of solid solutions shows the thermally activated nature of conductivity. The introduction of both calcium and niobium leads to a decrease in conductivity caused by a decrease in the number of charge carriers in the structure of praseodymium molybdate.

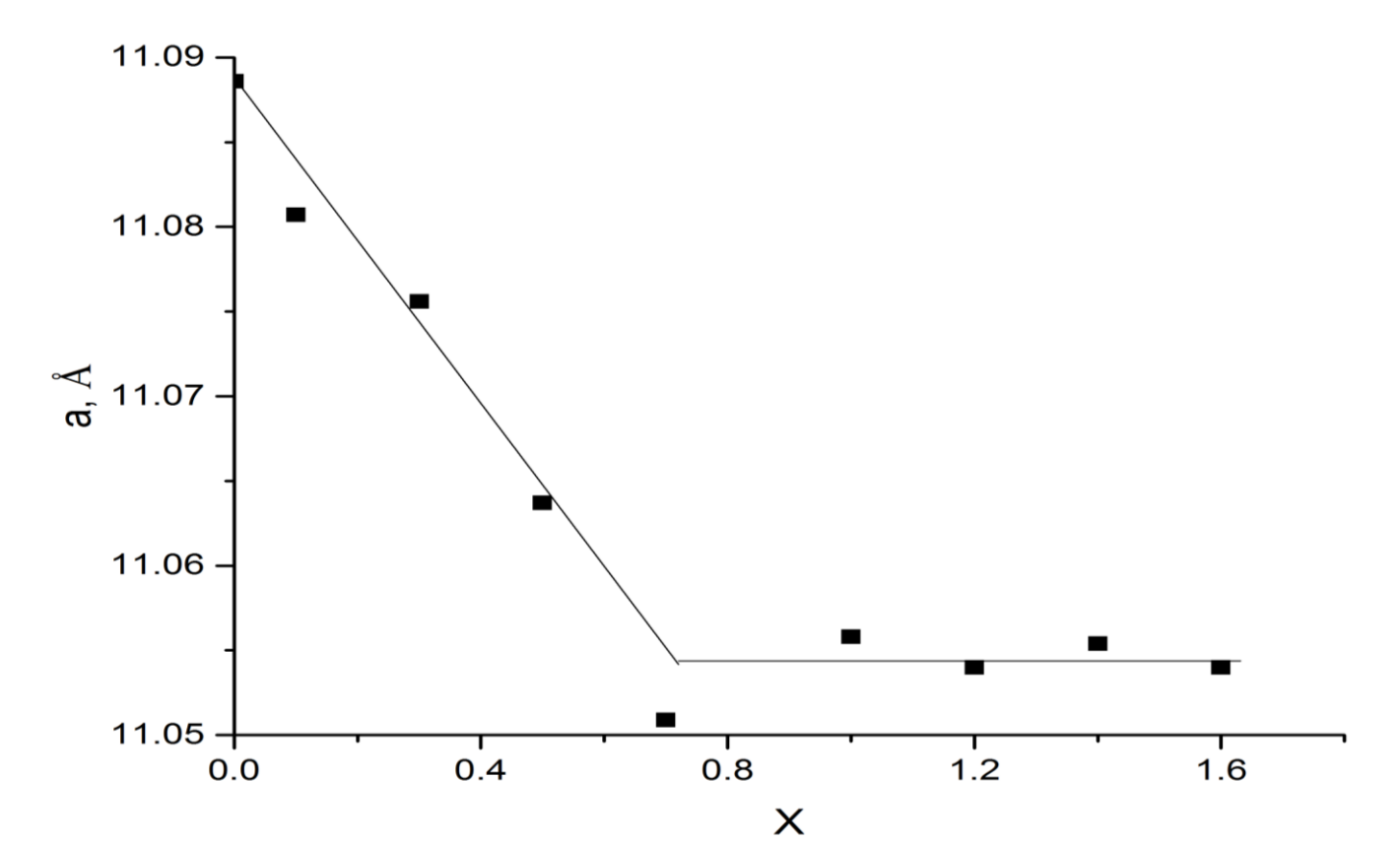


Fig. 8 Plot of unit cell parameter a vs. degree of substitution, x in $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$

Introduction of niobium leads to a significant decrease in the unit cell parameter to $x=0.7$. With a further increase in the niobium content, the cell parameter does not change, which may indicate the substitution limit in this system. However, according to X-ray phase analysis, the area of homogeneity extends up to $x=1.2$. The impact of niobium for molybdenum substitution for the unit cell parameters includes several factors. First, the substitution of niobium for molybdenum should lead to an increase in the unit cell parameter, since the ionic radius of niobium is greater than the ionic radius of molybdenum ($r(\text{Mo}^{+6}) = 0.41 \text{ \AA}$, $r(\text{Nb}^{+5}) = 0.48 \text{ \AA}$ for coordination number 4). Second, introduction of an ion with a lower charge leads to a decrease in oxygen content according to the scheme:

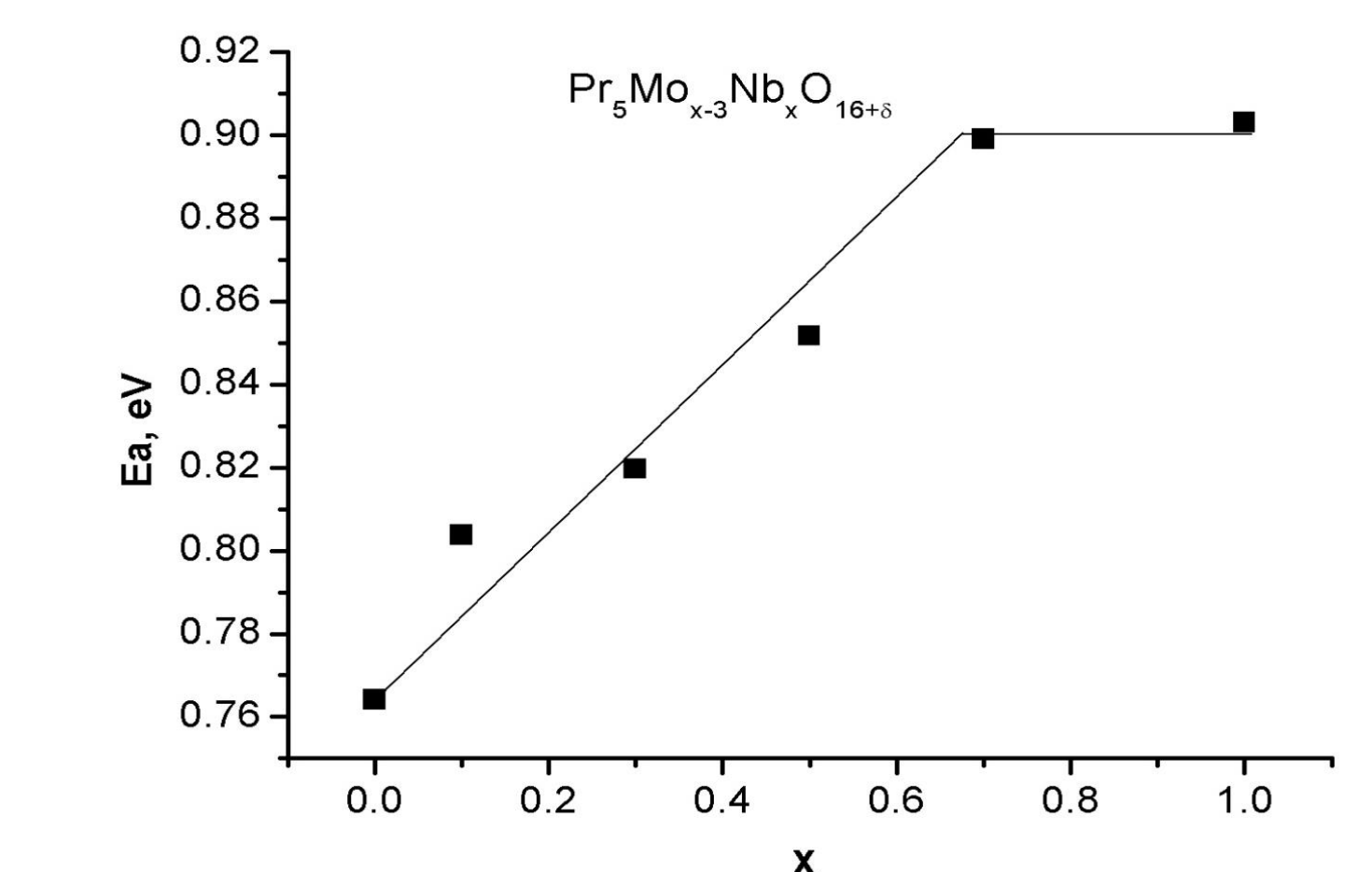
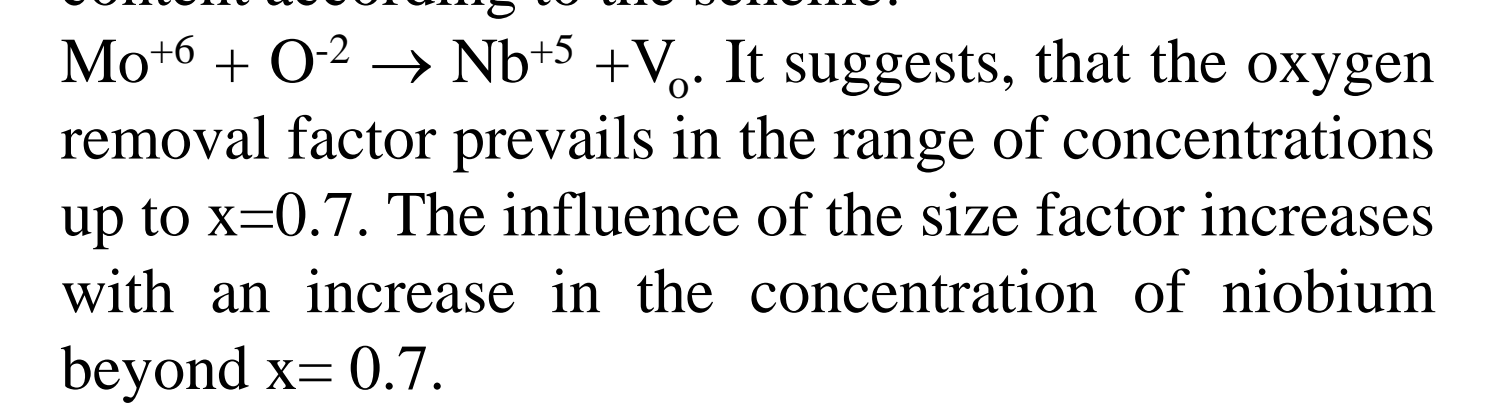


Fig. 10 The plot of activation energy of the conductivity for $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$

The activation energy of the conductivity increases as concentration of niobium increases. This is due to a decrease in the unit cell parameter, which reduces the channels in the structure and complicates the transport of oxygen in the system. When the content of niobium reaches $x=0.7$, the value of activation energy ceases to increase since the cell parameter, a does not change.

SUMMARY

1. The substitution limits in $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$ and $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$ systems have been established as $0 \leq x \leq 0.5$ and $0 \leq x \leq 1.2$ correspondingly.
2. The monotonic decrease in the unit cell parameters was found in both systems caused by the introduction of calcium and niobium.
3. The increase of the doping elements content in solid solutions results in a decrease in their conductivity and an increase in the activation energy of conductivity.
4. The mechanism of isomorphous substitution in the studied systems was established. Substitution with charge compensation occurs due to the formation of vacancies as a result of oxygen removal from the structure.

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