

# Structural Peculiarities Of Compounds Of Double Phosphates And Vanadates Of Rare Earth Elements

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**Abstract:** In this work, structural studies of double vanadates and phosphates of rare-earth elements with potassium and sodium are carried out, which are among the promising materials of electronics. It is shown that REE - potassium double phosphates are built on a trigonal basis and are a somewhat deformed glaserite structure. Moreover, the main reason for its distortion is a certain slope of the phosphate tetrahedron (point symmetry Ci) on the third-order axis of the original structure. The structural features of the compound of potassium double vanadates — REE of the beginning of the lanthanide series — were synthesized and studied for the first time. It has been shown that double potassium vanadates of rare-earth elements can be divided into three clearly distinct subgroups: vanadates of the elements La, Pr, vanadates Sm, Eu, Gd, Tb, Dy and, finally, vanadates of elements from Ho to Lu. The neodymium compound lattice has its own characteristics and is closer to the Sm – Dy double vanadate group.

**Index Terms:** glaserite, isotype, monoclinic, phosphate, potassium, radiography, rare earth element, single cap, single-phase, sodium, trigonal, vanadate.

## 1 INTRODUCTION

Obtaining new inorganic compounds with optimal dielectric properties is an urgent problem, since, based on traditionally used multicomponent compositions, based on mechanical mixtures of simple, double compounds and their solid solutions, it is not possible to meet the growing demands of the industry for electronics materials, including and reproducibility, stability of physical properties. A number of recent publications have shown the promise of obtaining new binary compounds based on rare-earth elements (REE), elements I and V of the periodic system and using them for these purposes. This is connected with the scientific and practical interest in studying the physicochemical principles of obtaining new inorganic compounds, their electrical properties, due to the peculiarities of their crystalline structure. In particular, such compounds include complex oxide compositions possessing the required dielectric parameters. Metal oxides in recent years have been the subject of numerous studies, due to the urgency of the problem of studying the electrical properties of solids and the establishment of an internal connection between electrical and magnetic characteristics. In transition metal oxides, this problem is directly related to clarifying the reasons for the different behavior of d- and f-electrons. The increasing attention of researchers is attracted by oxide compounds in abnormal oxidation states, which are stable under certain conditions.

## 2 RESEARCH METHODS

X-ray studies were carried out according to the powder method using a focusing chamber — a monochromator of the Guinier-de-Wolf type; CuK $\alpha$  radiation. The unit cell parameters were refined using the OLS using the “powder” program. Structural analysis was performed on a KAD-4-SDP auto diffractometric system, MoK $\alpha$  — radiation, graphite monochromator w / 20-scan. Neodymium atoms are found from the analysis of the three-dimensional distribution of the Petterson function.

## 3 RESEARCH RESULTS AND DISCUSSION

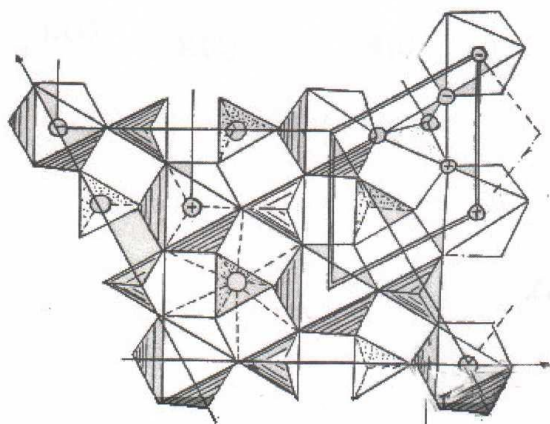
The structure of double phosphates and sodium vanadates - REE. In this group of compounds, vanadates are the most studied, possibly due to the great simplicity of their preparation. The study of phosphate and arsenate at first was carried out only to confirm one or another of the properties of vanadates put forward when discussing. As already noted, the studied phases can be considered as derivatives of glaserite. Crystallographic data on nine main structural types are summarized by the authors [1]. The parameters of the elementary cells of these phases are associated with the parameters of glaserite by elementary relations. All structures of low-temperature forms can be described on the basis of glaserite, either through the  $\beta$ -K $2S04$  type for large REE ions, or through the Na $2C04$  type for REE ions with smaller radii [2]. Historically, the first double vanadate Na $3Nd(V04)2$  was obtained in the process of studying a complex ternary system [3]. Later, this group of substances was studied in detail and it was established that the double vanadates of light REE (La, Nd) have only one crystalline modification, and the majority of double vanadates Na $3Ln(V04)2$  (Ln = Dy-Lu) have three crystalline modifications each. Full X-ray structural study of Na $3Ln(V04)2$  a = 5.58; b = 14.24; c = 19.42 Å showed that the structure can be described as an ordered superstructure  $\beta$ -K $2S04$ . It is composed of isolated V04 tetrahedra forming its core. The atoms La (1) and La (2) occupy positions X with eight-dimensional coordination. Na (1) and Na (2) are the central M-octahedron with coordination 6, while Na (3), Na (4), Na (5) and Na (6) populate the Y-positions with the sixth coordination. In this case, rows are formed parallel to the b axis and composed either by alternating sodium and

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lanthanum atoms, or by sodium atoms and VO<sub>4</sub> tetrahedra. This leads to a doubling of the parameters *a* and *c* of the structure ( $\beta$ -K<sub>2</sub>SO<sub>4</sub>). The formula can be written as X<sub>2</sub>Y<sub>4</sub>M<sub>6</sub>(TO<sub>4</sub>)<sub>2</sub>. The authors of [4,5] develop the previously proposed general topological approach to complex compounds of the type A<sub>x</sub>B<sub>y</sub>(EO<sub>4</sub>)<sub>x+y/2</sub> with tetrahedral groupings. Such a large amount of research into the structure of binary vanadates is related to the fact that these compounds have found application in applied fields. Recent examples can be the preparation of compounds mixed in REE cation, which can be used for the conversion of IR radiation in the visible region [4]. Double vanadates phosphates, potassium - REE. The double compounds K<sub>3</sub>Ln(EO<sub>4</sub>)<sub>2</sub> of this type of complex are studied in the most detail. Already the first radiographic studies, using the powder method, showed that all these compounds are built on a trigonal basis.

#### Compounds can be divided into three structural types:

1. The first structural type includes the double phosphates of potassium lutetia and potassium-scandium. At the same time, there is an increase in the unit cell of glaserite three times. The structure of K<sub>3</sub>Ln(PO<sub>4</sub>)<sub>2</sub> is shown in fig. 1. In this structure, the lutetium atoms are differentiated in two positions with local symmetry C<sub>3</sub> and C<sub>3i</sub>, each of which coordinates six atoms of oxygen over the octahedron. The crystal structure of K<sub>3</sub>Sc(PO<sub>4</sub>)<sub>2</sub> is a slightly deformed glaserite structure, and the main reason for its distortion is a certain inclination of the phosphate tetrahedron (point symmetry C<sub>i</sub>) on the third-order axis of the original structure.
2. The second structural type includes compounds isostructural K<sub>3</sub>Yb(PO<sub>4</sub>)<sub>2</sub>. They are characterized by a monoclinic distortion of the K<sub>3</sub>Ln(PO<sub>4</sub>)<sub>2</sub> lattice with an increase in the cell volume of eight times. Gd-Yb double phosphates belong to this type.



**Fig. 1.** The projection of K<sub>3</sub>Lu(PO<sub>4</sub>)<sub>2</sub> on the XY plane. The single lines segregate the true K<sub>3</sub>Lu(PO<sub>4</sub>)<sub>2</sub> cell, the double ones - the ideal glaserite sub cell.

1. Structural type K<sub>3</sub>Nd(PO<sub>4</sub>)<sub>2</sub>. The crystal structure of this compound has been fully decoded according to the data obtained on a single crystal. The main structural units of this phosphate are isolated PO<sub>4</sub> tetrahedra and NdO<sub>7</sub> decahedrons. Each PO<sub>4</sub> - a tetrahedron is associated with three neodymium atoms, and each neodymium atom with six PO<sub>4</sub> tetrahedra, forming two-dimensional {Nd (PO<sub>4</sub>)}<sub>2x</sub> grids

in the *ab* plane. Moreover, there are two types of PO<sub>4</sub> tetrahedra. Atom P (1) through two atoms O combines with the Nd atom along a common edge; through two other oxygen atoms, P (1) is bound to the other two neodymium atoms along common peaks, and the remaining oxygen atom is bound to potassium. The ionicity of the K - O bond is much higher than the ionicity of the Nd - O and P - O bonds, so that the potassium atom can be regarded as a kind of filler that does not play a structure-forming role. The crystal-chemical properties of these compounds known in the literature are limited only to the lanthanides of the second half of the series, namely, from Gd to Lu. The synthesis of compounds of the first half of the lanthanoid series and the study of their electrophysical properties makes it possible to trace the correlation of physical parameters in the series of rare-earth ions Structure type K<sub>3</sub>Ln(VO<sub>4</sub>)<sub>2</sub>. X-ray phase analysis was performed for all samples from La to Lu. As a rule, these samples were single-phase, and only occasionally on the radiographs were observed weak lines identified as reflexes of the mean vanadates of LnVO<sub>4</sub>. Their number did not exceed 1%, which for real inorganic material is insignificant pollution. In the process of obtaining samples, a change in their color was sometimes noted due to the reduction of vanadium to the tetravalent state. Such spontaneous reduction is known in the literature and was, at first, discovered in the process of modifying phosphate glasses with vanadium compounds [6, 7]. Despite the X-ray picture, such samples were thrown away. The color of the sample is usually determined by the color of the compounds of the corresponding ion. Monitoring of single phase was carried out by comparing the X-ray picture with the data published in the literature [8]. These literature data on pure double vanadates are limited to compounds K<sub>3</sub>Ln(VO<sub>4</sub>)<sub>2</sub>, where Ln is represented by elements from Gd to Lu table.1. At first it seemed that the compounds corresponding to the elements of the beginning of the rare-earth series (La, Pr, Nd and Sm, especially Sm and Eu) should also be included in the group belonging to the structural type K<sub>3</sub>Ln(VO<sub>4</sub>)<sub>2</sub>. The unit cells of these compounds are monoclinically-distorted, with respect to the initial lattice of glaserite K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>, and the volume of the latter increases 2 times. However, already in [8] it was proposed to distinguish between two subgroups that differ in monoclinic angle: the K<sub>3</sub>Lu(VO<sub>4</sub>)<sub>2</sub> subgroup and the K<sub>3</sub>Dy(VO<sub>4</sub>)<sub>2</sub> subgroup. As for the X-ray phase data on our ceramics, it is valid, for ceramics on the basis of vanadates of elements from But to Lu, the data completely coincide with the literature, both in interplanar distances and in intensities. The combed lattice parameters also do not differ from the literary ones. The situation with the vanadates of the beginning of the series was more complicated. Samples based on Sm, Eu, Gd, Tb, Dy vanadates gave a similar, but not identical, published X-ray picture. In this connection, it seemed necessary to synthesize pure vanadates of these elements with potassium and re-indexing. Such a study was conducted for K<sub>3</sub>Sm(VO<sub>4</sub>)<sub>2</sub>, K<sub>3</sub>Eu (VO<sub>4</sub>)<sub>2</sub>, K<sub>3</sub>Dy(VO<sub>4</sub>)<sub>2</sub>. It was found that the reflections on radiographs are indicated on the assumption that these compounds are isotopic to double phosphates of rare-earth elements with potassium and partially with rubidium. Parameters of the grid are given in Table. 2. Further comparisons were carried out already on the basis of these new data. It should be noted that, despite the usual distribution of structural types within the rare-earth series, double potassium vanadate, neodymium, belongs to the group just considered. It is not excluded that this is one of the

polymorphic modifications, but not quenching, nor the variation of the conditions for the synthesis of pure vanadate made it possible to distinguish a second modification that brings it closer to the lanthanum and praseodymium vanadates. The results of indexing this intermediate type are given in table. 2. Lanthan's, praseodym vanadates form a subgroup that differs only in the parameters of the monoclinic cell and, accordingly, in another set of indices hkl for this subgroup. Thus, the double vanadates of potassium-rare-earth elements can be divided into three clearly distinguished subgroups: the vanadates of the elements La, Pr, the vanadates Sm, Dy, Gd, Tb, Dy and finally the vanadates of elements from Ho to Lu. The neodymium compound lattice has its own characteristics and is closer to the Sm-Dy double vanadate group. The first two subgroups, which are isotypic to double phosphates and potassium and rubidium arsenals, the third subgroup forms an independent structural type, double potassium vanadate-lutetium K3Lu(V04)2. The structure of double potassium vanadate and neodymium. The potassium and neodymium double vanadates were similar in structure to the analogous phosphate described in [8]. Vanadium atoms (two grades) are coordinated by four oxygen atoms, each in a tetrahedron. Neodymium atoms are located in the seven vertices of NdO7, which are single-prism prisms, the "caps" are formed by oxygen atoms O22. The neodymium oxygen environment consists of five oxygen atoms, which are the vertices of the VO4 tetrahedra, and two other oxygen atoms (O11 and O12), which form the edges of the VO4 tetrahedra [7]. The structure of K3Nd(V04)2 can be considered as a derivative of  $\beta$ -K2SO4, they have the same cell vectors, however, the parameters b and c in double vanadate are reversed, due to the requirements of the standard installation pr. Gr. P2i / m.

#### 4 CONCLUSION

Thus, binary compounds of rare-earth elements with alkali metals are promising inorganic materials. They are valuable in that within a large group of single-type compounds they allow subtly changing the output physicochemical parameters, due to the contribution of rare earth ions. If necessary, using information on crystal chemical regularities, compounds of complex composition with predetermined characteristics can be obtained. The values of such materials for functional electronics cannot be overestimated. However, a significant gap is the lack of systematized information on physicochemical and physical properties. Solving this problem will make it possible to formulate purely materials-science problems based on the composition-structure-property correlations.

**Table 1.** The main characteristics of the double vanadates composition

K3Ln (V04)2 (Ln=Gd-Lu).

Compound	Grid Options			$\beta$ , deg
	a, Å	b, Å	c, Å	
K3Gd(V04)2	9,839	5,923	7,508	90,55

K3Tb(V04)2	9,847	5,954	7,504	90,55
K3Dy(V04)2	10,40	5,741	7,550	91,39
K3Ho(V04)2	10,28	5,886	7,624	89,51
K3Er(V04)2	10,25	5,883	7,595	89,52
K3Tm(V04)2	10,28	5,888	7,637	90,00
K3Yb(V04)2	10,23	5,869	7,617	89,55
K3Lu(V04)2	10,20	5,847	7,566	90,05

**Table 2.** X-ray characteristics for individual K3Ln(V04)2 double vanadates.

Compound	Lattice parameters, Å				X-ray density. g / sm <sup>3</sup>
	a	b	c	$\beta^\circ$	
K3La(V04)2	19.74	33.85	7.926	89.97	3.65
K3Pr(V04)2	19.74	35.65	7.890	89.94	3.70
K3Nd(V04)2	19.70	36.06	7.920	89.96	3.72
K3Sm(V04)2	19.89	34.74	7.604	89.96	3.77
K3Eu(V04)2	19.90	34.36	7.609	90.10	3.32
K3Dy(V04)2	10.40	5.71	7.431	90.72	3.73

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