General and Inorganic Chemistry

Synthesis of K—Zr phosphates by the molten salt method

A. V. Barabanova,[a]* *P. V. Afanas'ev,*[b] *B. G. Kostyuk,*[a] *and V. V. Lunin*[a]

[a]*M. V. Lomonosov Moscow State University, Chemical Department,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 939 4575. E-mail: knn@cge.chem.msu.su
[b]*IRC, 2 av. A. Einstein, 69626 Lyons, Villenrbanne, Cedex, France.*
E-mail: afanas@catalyse.univ-lion1.fr

Phosphates of K and Zr of a layered, microporous structure have been obtained by the molten salt method in a potassium nitrate medium in the temperatures range 573—823 K. Dependences of the product composition on the P/Zr atomic ratio and the temperature of synthesis were studied. The substances obtained have been characterized by XRD, ^1H and ^{31}P NMR, and IR spectroscopy, and scanning electron microscopy.

Key words: phosphates of potassium and zirconium, molten salt method, physicochemical properties.

In recent years, the chemistry of phosphates of tetravalent metals attracts significant attention. Zirconium phosphates are known to be insoluble inorganic ion-exchangers, ionic conductors, and the catalysts of acid-base and redox reactions.[1—3]

Two types of zirconium phosphates that are different in structure have been described. The structure of phosphates of the NASICON type, whose prototype is $NaZr_2(PO_4)_3$, has a rigid three-dimentional framework of a "mixed" type, formed by $[PO_4]$ tetrahedra and $[ZrO_6]$ octahedra[4] and containing cationic voids of two types, that allow for ionic conductivity. α-Zirconium phosphate, $\alpha\text{-}Zr(HPO_4)_2 \cdot H_2O$ (below α-ZrP), has a layered structure, and each layer consists of zirconium atoms that are in the same plane and are linked by the tetrahedral $[PO_3—OH]$ groups that are located alternately above and below the plane of the zirconium atoms.[5] The layers are bound to each other only by the van der Waals interaction, which makes possible a wide variety of possible replacements for this structural type.

As has been shown for α-ZrP,[6] the reactivity and hydrolytic stability of zirconium phosphates change depending on the degree of crystallinity. Therefore, a procedure of synthesis plays a key role for the structural parameters and reactivity of the compounds obtained. Conventional methods of the preparation of zirconium phosphates are solid-phase synthesis,[7] hydrothermal synthesis,[8] and the sol-gel method.[1—5] Substituted modifications of α-ZrP are prepared by the ion-exchange method.[2]

In this work, a novel procedure of preparing double zirconium phosphates using a melt of potassium nitrate as a specific non-aqueous reaction medium is proposed. The molar composition of the reaction medium and the temperature of synthesis are optimized. The crystal substances, $KZr_2(PO_4)_3$ and $K_2Zr(PO_4)_2$, are characterized by XRD, ^{31}P and ^1H NMR, and IR spectroscopy, and scanning electron microscopy.

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Experimental

The starting compounds for the preparation of a reaction mixture were zirconium oxychloride octahydrate (chemically pure grade), ammonium hydrogen phosphate (chemically pure grade), and potassium nitrate (reagent grade purity). Thoroughly mixed starting reagents with the Zr : P : K = 1 : 4 : 10 mole ratio were placed in a pyrex reactor and heated to the reaction temperature at a rate less than 5 deg min^{-1}. The reaction was carried out in the temperature range 573—823 K for 2—5 h. The compounds obtained were separated from soluble salts by washing with distilled water at 373 K and dried in air at 393 K.

The phase composition of the samples was monitored by XRD on a DRON-2 diffractometer with Cu-Kα radiation.

The chemical composition of the samples was determined by atomic emission analysis.

The NMR spectra were registered on a Bruker MSL-300 spectrometer (81.035 MHz). The chemical shifts of phosphorus-containing compounds were measured with a 85% H_3PO_4 solution as the external standard.

The IR spectra of samples (pellets with KBr) were recorded on a Specord M-80 spectrophotometer in the 500—2500 cm^{-1} region.

The surface area of samples was measured by low-temperature adsorption of N_2. The relative error of measurements was 10%.

Results and Discussion

It has recently been shown[9] that the KNO_3—$NaNO_3$ eutectic is an alternative nonaqueous medium for obtaining pure ZrO_2 and ZrO_2—$[PO_4]$-supported systems with special structural properties. The possibility of the formation of not only the oxide but also zirconium phosphates in a molten salt was first shown[10] when compound $K_{0.1}Na_{0.9}Zr(PO_4)_2$ was obtained in a medium of the KNO_3—$NaNO_3$ eutectic at 723 K. Interestingly, both ZrO_2 and $K_{0.1}Na_{0.9}Zr(PO_4)_2$ were synthesized under the same conditions except that the molar composition of the reaction medium was varied. Thus, the phase composition of the reaction products is determined by the P/Zr ratio in the reaction mixture.

We studied the effect of the P/Zr ratio and the temperature of synthesis on the composition of reaction products, while retaining a 10-fold molar excess of KNO_3 relative to the Zr-containing component of the mixture (Table 1). When P/Zr < 1, a great portion of phosphorus, according to the chemical analysis data, enters the composition of the solid reaction products. When P/Zr = 0.1, the reaction product (samples **1**, **5**), according to XRD, contains only the tetragonal modification of ZrO_2, and the phosphate groups are anchored at the surface of ZrO_2.[9,11] The modification of the ZrO_2 surface by phosphate groups results in a significant increase in the surface area of the sample (see Table 1) (the surface area of ZrO_2 prepared under similar conditions, without phosphate groups, was equal to 130 m^2 g^{-1}). Similar stabilization of the dispersed ZrO_2 by multivalent oxoanions occurs when sulfate and molybdate ions are introduced into a molten salt.[11] When the P/Zr ratio is increased to 0.3, peaks related to the K—Zr phosphate phase (samples **2**, **6**) appear. In this case, the reaction product is a mixture of the double zirconium phosphate with unreacted ZrO_2. These samples are inhomogeneous due to the fact that the amount of phosphate is insufficient for the formation of the pure phase. The pure crystal phase can be obtained when P/Zr = 4 (samples **3**, **4**, **8**—**10**). Thus, one can conclude without resorting to quantitative evaluations, that it is necessary to create a specified concentration of phosphate ions in a melt to form the K—Zr phosphate phase, and the P/Zr ratio in the reaction mixture determines the composition of the reaction products.

If the molar excess of phosphate groups in the reaction mixture is retained, then the reaction temperature becomes a key parameter determining the composition of the solid reaction product. The phase and chemical compositions of the samples prepared when the Zr : P : K = 1 : 4 : 10 molar composition of the reaction mixture was retained are presented in Table 2. According to the XRD data, the main reaction product in the temperature range 573—723 K is $KZr_2(PO_4)_3$ (ASTM

Table 1. Dependence of phase composition of the solid reaction product on the molar composition of the reaction mixture and the temperature of synthesis

Sample	T/K	P/Zr	Chemical composition of the solid reaction product	Phase according to XRD	S/m^2 g^{-1}
1	623	0.1	$K_{0.03}Zr(PO_4)_{0.078}$	ZrO_2 (broad line)	116
2	623	0.3	$K_{0.11}Zr(PO_4)_{0.23}$	ZrO_2 + NASICON	58
3	623	4	$K_{1.01}Zr(PO_4)_{3.02}$	NASICON	4
4	623	10	$K_{1.00}Zr(PO_4)_{3.00}$	NASICON	5
5	773	0.1	$K_{0.06}Zr(PO_4)_{0.09}$	ZrO_2 (T)	200
6	773	1	$K_{0.71}Zr(PO_4)_{0.88}$	ZrO_2 + NASICON + ZrP	70
7	773	4	$K_{1.91}Zr(PO_4)_{1.94}$	ZrP + NASICON	15
8	773	10	$K_{1.94}Zr(PO_4)_{1.96}$	ZrP + NASICON (traces)	17
9	773	4*	$K_{1.99}Zr(PO_4)_{1.98}$	ZrP + NASICON (traces)	15
10	823	4*	$K_{2.01}Zr(PO_4)_{2.02}$	ZrP	12

* Time of reaction is 20 h.

Table 2. Dependence of the composition of the solid reaction product on the temperature of synthesis at the constant molar composition Zr : P : K = 1 : 4 : 10 of the reaction mixture

Sample	*t*/h	*T*/K	Phase composition according to XRD	Chemical analysis data	*S* /m^2 g^{-1}
I	2	603	$KZr_2(PO_4)_3$, KPO_3	$K_{2.9}Zr_{1.0}P_{3.6}$	5
II	2	673	$KZr_2(PO_4)_3$	$K_{0.98}Zr_{1.0}P_{1.9}$	9
III	2	753	$KZr_2(PO_4)_3$, $K_2Zr(PO_4)_2$	$K_{1.8}Zr_{1.0}P_{2.02}$	13
IV	2	773	$K_2Zr(PO_4)_2$	$K_{2.85}Zr_{1.0}P_{2.1}$	17
V	5	823	$K_2Zr(PO_4)_2$	$K_{2.08}Zr_{1.0}P_{2.0}$	12

— 25-1206) with a structure of the NASICON type. Increasing the temperature to 773—823 K results in the interaction of $KZr_2(PO_4)_3$ with a phosphate ion to form $K_2Zr(PO_4)_2$ (ASTM — 28-857) with a structure of the α-ZrP type (reaction (1)).

$$Zr_2(PO_4)_3^- + PO_4^{3-} \longrightarrow 2\ Zr(PO_4)_2^{2-} \qquad (1)$$

The reaction product in the temperature range 723—773 K is mixture of two phosphates. The XRD data showed that at temperatures below 623 K, a significant amount of potassium metaphosphate (KPO_3), which is formed in the interaction of phosphate with molten nitrate according to reaction (2), enters the composition of the solid reaction product (sample **I**); it is difficult to separate from the reaction products due to its insolubility in water and acids.

$$NH_4H_2PO_4 + KNO_3 \longrightarrow KPO_3 + NO + 3\ H_2O + 1/2\ N_2 \quad (2)$$

Based on the XRD data, there is no KPO_3 in sample **II**, because KPO_3 begins to react with the molten nitrate according to reactions (3) and (4), when the temperature increases.

$$2\ KPO_3 + 2\ KNO_3 = K_4P_2O_7 + 2\ NO_2 + 1/2\ O_2 \qquad (3)$$

$$K_4P_2O_7 + 2\ KNO_3 = 2\ K_3PO_4 + 2\ NO_2 + 1/2\ O_2 \qquad (4)$$

However, the chemical analysis data indicate that there is more potassium and phosphorus in this sample than expected for $KZr_2(PO_4)_3$. This fact gives evidence for the presence of a slight amount of KPO_3. Only the composition of sample **V** is close to theoretical. However, as follows from XRD of the hardened melts, some number of PO_3^- ions are present in the reaction products, even if the reaction is carried out at high temperatures.

Thus, double K—Zr phosphates were synthesized for the first time in molten potassium nitrate. The structure and physicochemical properties of the compounds obtained were studied by NMR and IR spectroscopy.

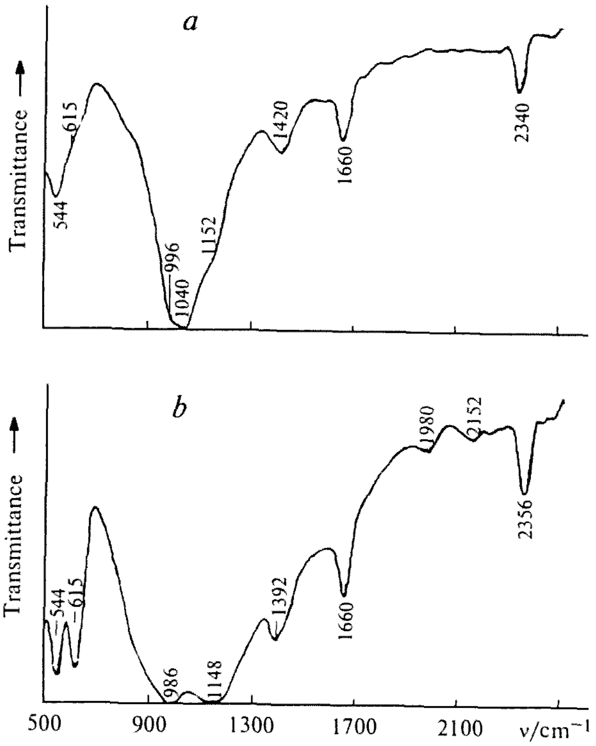

Fig. 1. IR spectra of samples **II** (*a*) and **V** (*b*).

Orthophosphates are convienient objects for IR-spectroscopic study due to the peculiarities of their structure (the presence of discrete tetrahedral [PO_4] groups) and to the relation between the masses of atoms and their bond energies. The IR spectra of the compounds obtained are presented in Fig. 1. The absorption bands are in good agreement with literature data.[12] The peaks at 544—615 cm^{-1} can be assigned to the triply degenerate bending vibration ($\delta_4(F_2)$) of the [PO_4] group, and the broad absorption peaks in the 810—1150 cm^{-1} region can be assigned to triply degenerate stretching vibration ($\nu_3(F_2)$).[13] The peaks in the 1380—1420 cm^{-1} region seem to be due to an admixture of nitrate ions (symmetric and antisymmetric stretching vibrations of the N=O bonds) in the solid. The peaks in the 1650—1660 cm^{-1} region give evidence for the presence of water adsorbed by the samples during washing in the coordination voids of $KZr_2(PO_4)_3$ (see Fig. 1, *a*) and in the interlayer space of $K_2Zr(PO_4)_2$ (see Fig. 1, *b*). This assumption was confirmed by studying the samples by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectra of samples **II**, **III**, and **V** are presented in Fig. 2. The broad signal in the 5 ppm region observed in all samples is due to the presence of adsorbed water, because the spectra were recorded in air. In the spectrum of sample **III**, which is a mixture of two phases, three narrow peaks at 3.27, 1.91, and 9.98 ppm are also present. The peak at 3.27 ppm (see

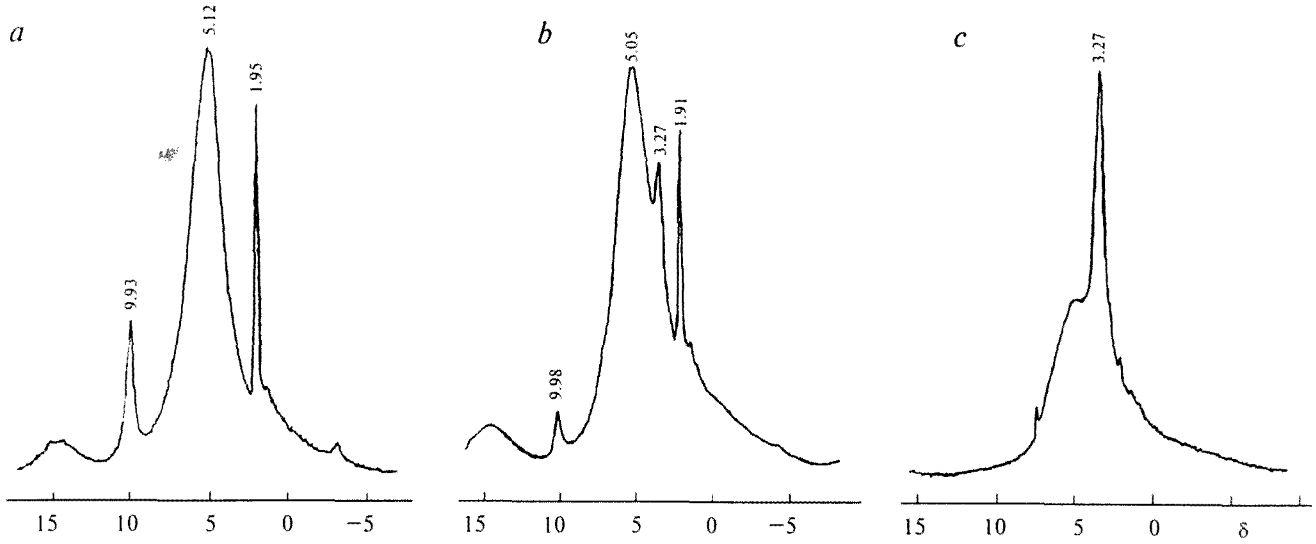

Fig. 2. ^{1}H NMR spectra of samples **II** (*a*), **III** (*b*), and **V** (*c*).

Fig. 2, *c*) corresponds to the signal of the OH groups formed when the K^+ cations in $K_2Zr(PO_4)_2$ are replaced by water protons. A layered structure of this compound contains K^+ cations of two crystallographically different types.[14] However, due to the small interplanar distance (9 Å) in the anhydrous phase obtained and to the fact that the pH value is insufficient for the beginning of intense ion exchange (during washing with water), only the more mobile K^+ cations, which occupy distorted octahedral positions,[15] are replaced. The $KZr_2(PO_4)_3$ structure contains[5] the two types of frame voids (extended octahedra and trigonal prisms), which are occupied by K^+ cations. Hence, two ^{1}H signals should exist in the spectrum of this compound. This assumption is confirmed perfectly by the presence of signals at 9.98 and 1.95 ppm (see Fig. 2, *a*). The signal at 1.95 ppm corresponds to the presence of H^+ cations in the small trigonal cavities of the $KZr_2(PO_4)_3$ structure. The large octahedral cavities are left the hydroxonium ion (H_3O^+) to be placed; this corresponds to the signal at 9.98 ppm.

^{31}P NMR spectroscopy can be used to study zirconium phosphates due to the high sensitivity of the chemical shifts of phosphate groups to their local environment.[16] The number and electronegativity of the neighboring ligands exert a pronounced effect on the chemical shift. The ^{31}P NMR spectra of samples **II**,

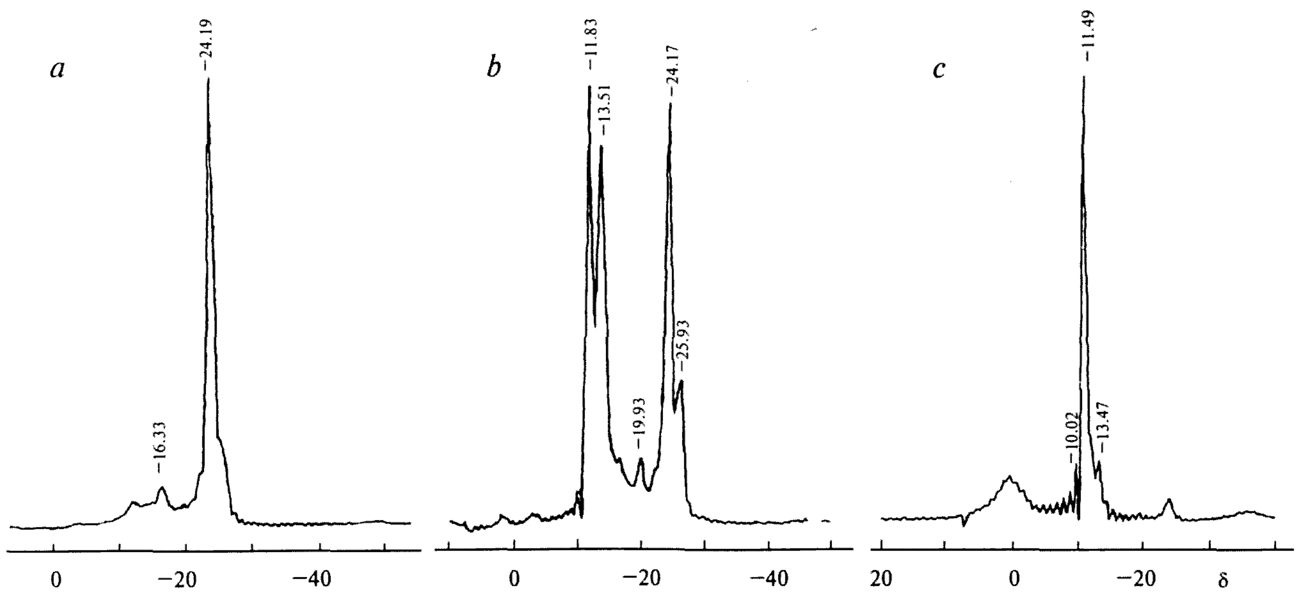

Fig. 3. ^{31}P NMR spectra of samples **II** (*a*), **III** (*b*), and **V** (*c*).

III, and **V** are presented in Fig. 3. The presence of one narrow peak (see Fig. 3, *a,c*) gives evidence that the structures of all these compounds include phosphate species of only one type. In the case of $KZr_2(PO_4)_3$, the signal at −24.19 ppm (see Fig. 3, *a*) indicates that the symmetrical local environment of the phosphorus atom consists of four oxygen atoms bound to Zr atoms; this can be schematized as $P(OZr)_4$.[17] The signal of $K_2Zr(PO_4)_2$ is registered at −11.49 ppm (see Fig. 3, *c*); this is due to the fact that the number of multicharged cations in the environment of phosphate groups in $K_2Zr(PO_4)_2$ is different from that in $KZr_2(PO_4)_3$. The absence of one zirconium atom in the local environment of a phosphorus atom, which can be schematically described as $P[(OZr)_3O^-]$, causes a decrease in the bond strength of the oxygen atoms in the phosphate groups, favoring a change in the chemical shift. The structure of α-ZrP is known to contain two phosphate groups that are identical chemically but different crystallographically; they have the same isotropic shift and different anisotropy. ^{31}P NMR does not distinguish between them in the case of the protonated α-ZrP species.[18] However, deprotonation results in a change in their chemical shifts due to the presence of the K^+ ion, the absence of hydrogen bonds, and the change in the lattice parameters during intercalation. For this reason, the signal splits into two components at −11.83 and −13.51 ppm (see Fig. 3, *b*).

The above-mentioned partial replacement of K^+ cations by protons results in the appearance of weak signals in the spectrum at −19.93 ppm (in the case of $K_2Zr(PO_4)_2$, see Fig. 3, *b*) and at −25.93 ppm ($KZr_2(PO_4)_3$, see Fig. 3, *b*).[19] The signal at −16.33 ppm (see Fig. 3, *a*) can be attributed to the metaphosphate group of KPO_3, whose presence in samples **II** and **VI** was discussed previously.

The study performed showed that the molten salt method allows one to carry out a one-step synthesis of crystalline double zirconium phosphates under relatively mild conditions. The molar ratio P/Zr in the reaction mixture and the temperature of synthesis determine the phase composition of the solid reaction products. A peculiarity of this method is the absence of water at the main step of the reaction, which makes it possible to obtain anhydrous phases.

References

1. *Inorganic Ion Exchange Materials*, Ed. A. Clearfield, CRC Press: Boca Raton, Florida, 1982, 600 pp.
2. Y. Sadaoka, Y. Sakai, and M. Matsuguchi, *J. Mater. Sci.*, 1989, **24**, 2081.
3. A. Clearfield and D. S. Thakur, *Appl. Catal.*, 1986, **26**, 1.
4. A. A. Voronkov, N. G. Shumyatskaya, and Yu. A. Pyatenko, *Kristallokhimiya mineralov tsirkoniya i ikh iskusstvennykh analogov* [*Crystal Chemistry of Zirconium Minerals and Their Artificial Analogs*], Nauka, Moscow, 1978, 120 pp. (in Russian).
5. A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
6. A. Clearfield, *Comments Inorg. Chem.*, 1990, **10**, 89.
7. P. Nagornyi and S. Lugovaya, *Zh. Neorg. Khim.*, 1981, **93**, 2871 [*J. Inorg. Chem. USSR*, 1981, **93** (Engl. Transl.)].
8. Y. Xu, S. Feng, and W. Pang, *J. Chem. Soc., Chem. Commun.*, 1993, 1428.
9. P. Afanasiev, C. Geantet, and M. Breysse, *Int. Symp. on Soft Chemistry Routes to New Materials*, September 6—10, 1993, Nantes, France.
10. P. Afanasiev and C. Geantet, *C. R. Acad. Sci. Paris*, 1993, **317**, Serie II, 601.
11. P. Afanasiev, C. Geantet, and M. Breysse, *J. Mater. Chem.*, 1994, **4**, 1653.
12. M. E. Poloznikova and V. V. Fomichev, *Uspekhi khimii*, 1994, **63**, 419 [*Russ. Chem. Rev.*, 1994, **63** (Engl. Transl.)].
13. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley and Sons, New York—London, 1963.
14. A. Clearfield, *Chem. Rev.*, 1988, 154.
15. A. B. Yaroslavtsev, *Sostav tverdykh tel glazami khimika* [*Composition of Solids from the Chemical Viewpoint*], Izd-vo RKHTU, Moscow, 1995, 254 pp. (in Russian).
16. S. P. Gabuda, R. N. Pletnev, and M. A. Fedotov, *Yadernyi magnitnyi resonans v neorganicheskoi khimii* [*Nuclear Magnetic Resonance in Inorganic Chemistry*], Nauka, Moscow, 1988, 214 pp. (in Russian).
17. N. J. Clayden, *J. Chem. Soc., Dalton Trans.*, 1987, **8**, 1877.
18. D. J. MacLachlan and K. R. Morgan, *J. Phys. Chem.*, 1990, **94**, 7656.
19. R. J. B. Jakeman, A. K. Cheetham, N. J. Clayden, and C. M. Dobson, *J. Chem. Soc., Chem. Commun.*, 1986, 195.

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