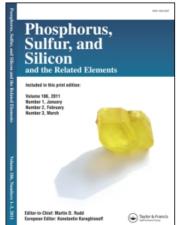
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Structure and Mobility Pattern of Proton-Containing Groups in Hydrates of Titanium, Zirconium and Tin Acid Phosphates; Their Conducting and Ion Exchanging Properties

Z. N. Prozorovskaya^a; A. B. Yaroslavtsev^a; V. F. Chuvayev^a; V. V. Parshutkin^a Mocow State University, Moscow, USSR

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STRUCTURE AND MOBILITY PATTERN OF PROTON-CONTAINING GROUPS IN HYDRATES OF TITANIUM, ZIRCONIUM AND TIN ACID PHOSPHATES; THEIR CONDUCTING AND ION EXCHANGING PROPERTIES

Z.N.PROZOROVSKAYA, A.B.YAROSLAVTSEV, V.F.CHUVAYEV, and V.V.PARSHUTKIN Moscow State University, Lenin Hills, Moscow 119899, USSR

Phosphates of tetravalent elements are practically important for ion exchange, catalysis and conductivity. This study deals with a number of hydrates of titanium, tin and zirconium phosphates. PMR data show that the structure of water molecules in hydrates is slightly distorted, and at temperatures higher than 160 K water has high translation mobility. NMR 31 P proves HPO_4^{2-} dissociation to be growing with increase of temperature. Energetic parameters of this process are determined. Close values of anion dissociation enthalpy (0,16/2/Ev) and obtained activation energy of conductivity for di- and monohydrates (0,17/2/Ev) show tunnel pattern of proton transfer along H-bond direction. This type of correlation was not observed in anhydrous compounds. That can be explained by impossibility of anion proton tunneling because of H-bond weakening. Proton conductivity of acid phosphates was studied. Ten-fold decrease of conductivity at room temperature with the loss of each water molecule proves H₂O participation in proton transport. Mechanism of this process is discussed with the use of NMR data. Dependence of water mobility and conductivity level on the degree of crystallinity is also discussed. With the help of NMR-data processes of ion exchange in tin and zirconium acid phosphates, as well as the state of developed salt forms were studied. Presence of lithium with high mobility in Li₂Sn(PO₄)₂·nH₂O was established.