

ANHARMONIC VIBRATION STUDY OF POTENTIAL BARRIERS IN THE TRIVALENT Al^{3+} ION CONDUCTOR $Al_2(WO_4)_3$

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Solid electrolytes with mono or divalent mobile ion, such as Ag^+ , Cu^+ , H^+ , Na^+ , Li^+ and F^- or Ca^{2+} , O^{2-} were well known. However the diffusion of trivalent ions in solids, an aggregate of charged particles, has been considered extremely difficult. Recently trivalent ion conduction have been demonstrated by our group. In the present study potentials around Al^{3+} were investigated with the X-ray analysis of anharmonic thermal vibration (AHV) to exhibit diffusion paths and potential barriers of Al^{3+} . 5677 reflections were measured at room temperature with a four-circle diffractometer. Relativistic atomic orbitals were calculated for W and were transferred to scattering factors. AHV of Al^{3+} and O^{2-} ions were analyzed with the method based on the classical statistics. The analysis revealed Al^{3+} in $Al_2(WO_4)_3$ locates in a very shallow and anisotropic potential-well with cols. That of Al^{3+} in Al_2O_3 at 2170 is very deep and isotropic having no cols. The potential barriers on 100, 010 and 001 planes are 0.280, 0.690 and 0.750×10^{-19} J, almost comparable with $kT/2=0.206 \times 10^{-19}$ J, proving Al^{3+} is mobile in $Al_2(WO_4)_3$ crystal.

Keywords: TRIVALENT ION CONDUCTOR ANHARMONIC THERMAL VIBRATION POTENTIAL BARRIER

INFLUENCE OF CRYSTALLINE STRUCTURE AND SURFACE TREATMENT OF TiO_2 PARTICLES ON THEIR INTERACTION WITH POLAR ORGANIC MOLECULES

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Optically pure titanium dioxide with different crystalline structure (anatase, rutile) were produced by thermal hydrolysis. These samples have been investigated by X-ray phase analysis, IR and Raman spectroscopy methods. Their surface modification was carried out by different temperature treatment and by metal cations adsorption (Mn, Cu, Cr, Co, Ni, Fe). As spectroscopic data revealed, TiO_2 powders had different amount of hydroxyl and hydrate covering and surface active centers. Quantity and types of these active centers have been additionally investigated by pyridine adsorption method. These factors have a great influence on molecular interactions with the surface of TiO_2 particles. Such interactions are found to be sensitive to the type of doping cation. This is due to different electron configurations of these ions, which have non-paired d-electrons from 5 for Mn to 2 for Ni. The strength and character of the surface interactions determine changes in IR spectral parameters and correlate with the values of ionization potentials of the studied metal row.

We used benzophenone, nitrobenzene and 4-pentyl-4-cyanobiphenyl (5CB) liquid crystal as dispersive media for TiO_2 particles. These polar molecules acted as specific organic probes for investigations of surface functional groups. Molecular interactions in these heterogeneous systems occur mainly by forming of hydrogen bonds. In the case of benzophenone, they are of the benzene π -electrons...HO-Ti type. Nitrobenzene molecules interact through nitro groups, and 5CB via phenyl ring p-electron systems creating hydrogen bonds with the surface hydroxyl covering. CN-groups are also affected and form weaker bonds of Van-der-Vaals type. At that a part of physisorbed water is found to be displaced by organic molecules. Surrounding of TiO_2 particles with polar molecules also results in changes of structure polarizability. These processes are clearly reflected in the corresponding Raman and IR spectra.

Keywords: TiO_2 , SPECTROSCOPY, INTERACTIONS

HYDROGEN BONDS: FURTHER EVIDENCE FOR THE CAUSE OF THE COLOR CHANGE OF NITROSYLPENTAAMMINECHROMIUM COMPLEXES

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Recently, we have reported the X-ray structures of nitrosylpentaamminechromium chloride (red-orange), chloride perchlorate (brown) and perchlorate (green)[1], where we discussed the cause of the color change of the complexes with the change of the outer sphere anions using the X-ray structural data of the complexes. We report here the X-ray structures of new compounds: nitrosylpentaamminechromium hexafluorophosphate (red) and chloride hexafluorophosphate (brown). Both the complex cations in the hexafluorophosphate and chloride hexafluorophosphate have distorted octahedral structures with linear Cr-N-O moieties. The structures of the cations are close to those of the cations in the complexes that we have reported before [1]. Large differences, however, are observed among the distances of O(nitrosyl)-N(ammonia in the adjacent cation) with the change of the counter anions. The distance between the complex cations in each crystal increases in the order: hexafluorophosphate (2.409 Å), chloride (2.749 Å), chloride perchlorate (3.127 Å), chloride hexafluorophosphate (3.262 Å), and perchlorate (3.595 Å). Large differences are also observed among the peak positions of reflection spectra of the complexes. The peak position of each complex shifts to longer wavelengths in the order: hexafluorophosphate (579 nm), chloride (588 nm), chloride perchlorate (598 nm), chloride hexafluorophosphate (603 nm), and perchlorate (623 nm). It is clear that the change of the strength of hydrogen bonds between O(nitrosyl) and N(ammonia in the adjacent cation) with the change of outer sphere anions causes the color change of the complexes in the solid states.

[1] H. Akashi, et al., Inorg. Chim. Acta, in press.

Keywords: NITROSYL COMPLEX, CHROMIUM HYDROGEN BONDING

CHANGES IN THE STATE OF AGGREGATION OF THE Pfk-2 ENZYME INDUCED BY MgATP

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The connection between monomer-oligomer equilibria and allosteric phenomena has been observed in a number of biological systems. The most commonly reported appears to be that in which the binding of a ligand to an enzyme together with a change in its catalytic properties is accompanied by an association-dissociation process. This is the case of Pfk-2, a dimeric E. coli phosphofructokinase isoenzyme which is inhibited by the MgATP ligand that binds to an allosteric site and promotes the tetramerization of the dimeric enzyme. The Pfk-2 enzyme is a particularly simple system for the study of molecular aggregation and ligand binding because it only exists as dimers or tetramers and its ligand-binding mechanism and catalytic properties are well characterized. Our SAXS experiments demonstrated that, when MgATP binds to an allosteric site, simultaneous conformational changes occur in both the tertiary and quaternary structure. Furthermore, we have studied the tetramerization process as a function of MgATP concentration. The tetramerization was observed only when more than three MgATP molecules were present in solution for every two dimeric Pfk-2 molecules. We also studied the effects of binding fructose-6-phosphate at the active site of Pfk-2 and, in this case, a clear conformational change within each subunit was observed. Dissociation of Pfk-2 tetramers, induced by temperature changes from an initial solution containing an excess of MgATP was also observed, suggesting that the stability of the Pfk-2 tetramer is affected above 40°C. Structural models are proposed based on a combination of homology methods and SAXS data.

Keywords: OLIGOMER SAXS CONFORMATIONAL CHANGE