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VIBRATIONAL SPECTRA OF MAGNESIUM HYDROGENPHOSPHATE TRIHYDRATE AND OF ITS MANGANESE ANALOGUE

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Abstract The infrared (IR) and Raman spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and of a series of partially deuterated analogues as well as the IR spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ have been recorded and interpreted. The analysis of the IR spectra in the HOD bending region rules out the possibility of existence of H_3O^+ ions in the structure.

Key Words: Infrared spectra, Raman spectra, magnesium hydrogenphosphate trihydrate, manganese hydrogenphosphate trihydrate, newberyite, deuterated analogues.

Recorded and interpreted were the infrared (IR) spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite) and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$. Also recorded were the IR spectra of a series of deuterated analogues of newberyite and the Raman spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and its fully deuterated analogue. The close resemblance of the IR spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ is not surprising since the two title compounds are isomorphous [1,2].

Of the Raman bands present in the $\nu(\text{PO})$ region, three are due to modes localized in the PO_3 fragment (they are found above 950 cm^{-1}), whereas the $\text{P}-\text{O}(\text{H})$ stretch gives rise to the band around 892 cm^{-1} which on deuteration shifts to 877 cm^{-1} . In the IR spectrum the assignment is more difficult since the corresponding band is overlapped with the $\gamma(\text{P}-\text{O}-\text{H})$ one. The analogue of the latter band in the spectrum of the deuterated newberyite is found around 650 cm^{-1} .

The appearance of the IR bands at approximately 2200 and 2400 cm^{-1} is in line with the appreciable strength of the hydrogen bonds formed by the HPO_4^{2-} ions [1]. The presence of chains of such bonds shows that the two studied compounds are potential proton conductors. In the IR spectra of the partially deuterated analogues, bands due to $\delta(\text{HOD})$ modes are present with shapes practically identical to those of the corresponding HOH ones. The presence of these bands definitely rules out the suspected [3] possibility of existence of H_3O^+ ions in the structure of the studied compounds since in the latter case bands due to the H_2DO^+ and HD_2O^+ species would be present.

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