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Low Frequency Infrared Absorption Bands of Water of Crystallization at Low Temperature

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The low temperature infrared absorption spectra of water of crystallization of $BaCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$, which have water of crystallization in different bound states, were measured and compared with the room temperature spectra. Corresponding to the change of temperature of the samples, remarkable change in frequencies and intensities was observed for the bands due to the lattice vibrations associated with water of crystallization.

Water of crystallization is classified into several types on the basis of its type of bonding with surrounding ions, electron acceptor or donor groups.[1] The infrared spectra of water of crystallization in the low frequency region vary with the difference of its bound state in the crystals, and they were investigated for aquo complexes by Nakagawa and Shimanouchi[2] and for several inorganic hydrates by van der Elsken and Robinson,[3] respectively. The author carried out calculations of optically active lattice vibrations of $BaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot 2D_2O$,[4] $K_2C_2O_4 \cdot H_2O$, $K_2C_2O_4 \cdot D_2O$,[5] $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$[6] crystals, which are different from each other in the type of bonding of water of crystallization, and obtained information about the bound state of the water of crystallization. A remarkable change in the far infrared spectra of certain kinds of water of crystallization with change of temperature has been reported.[7] In the present investigation, this change of infrared spectra with change of temperature has been studied for the crystals containing water of crystallization in different bound states.

Experimental

The samples were prepared by recrystallization of $BaCl_2 \cdot 2H_2O$ of Wako Pure Chemical Industries. Ltd., $CuCl_2 \cdot 2H_2O$ of Koso Chemicals Co., Ltd., and $K_2C_2O_4 \cdot H_2O$ of Koso Chemicals Co., Ltd. from their aqueous solutions, respectively. The infrared spectra of the samples in Nujol mull in the 700—60 cm^{-1} region were measured at low temper-

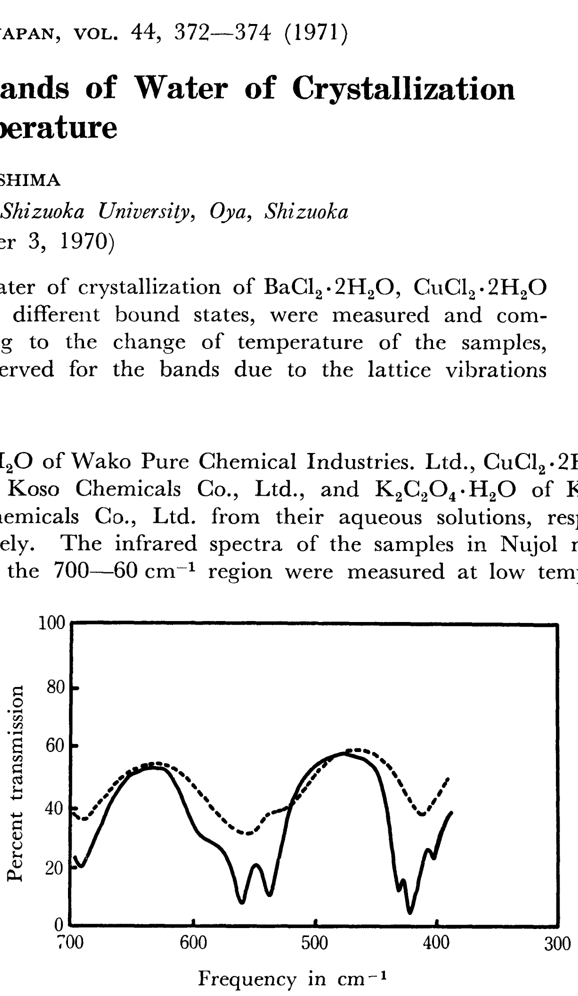

Fig. 1. Infrared spectra of $BaCl_2 \cdot 2H_2O$ at −150°C (solid line) and at room temperature (dotted line).

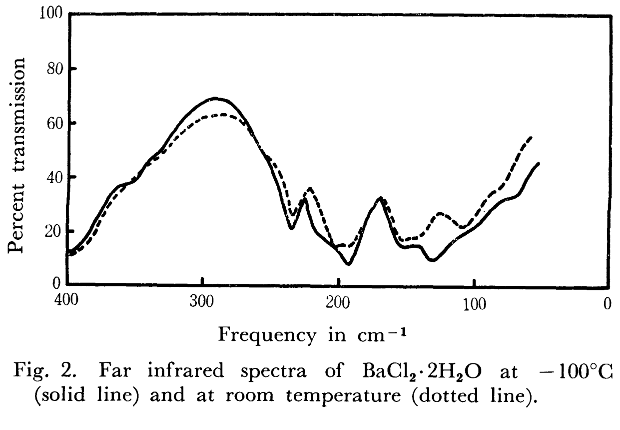

Fig. 2. Far infrared spectra of $BaCl_2 \cdot 2H_2O$ at −100°C (solid line) and at room temperature (dotted line).

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[1] R. Chidambaram, A. Sequeira, and S. K. Sikka, *J. Chem. Phys.*, **41**, 3616 (1964).

[2] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

[3] J. van der Elsken and D. W. Robinson, *ibid.*, **17**, 1249 (1961).

[4] K. Fukushima and H. Kataiwa, This Bulletin, **43**, 690 (1970).

[5] K. Fukushima, *ibid.*, **43**, 1313 (1970).

[6] K. Fukushima, to be published.

[7] Y. Kuroda, M. Nagasaki, and M. Kubo, presented at Symposium on Molecular Structure, Fukuoka, Japan (1969).

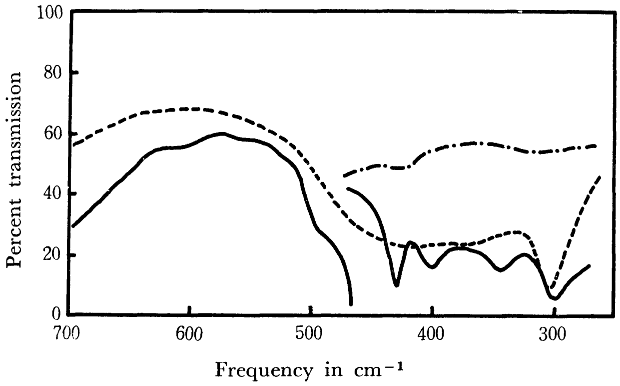

Fig. 3. Infrared spectra of $CuCl_2 \cdot 2H_2O$ at −95°C (solid line) and at room temperature (dotted line); (broken line, Nujol placed between polyethylene plates at −95°C).

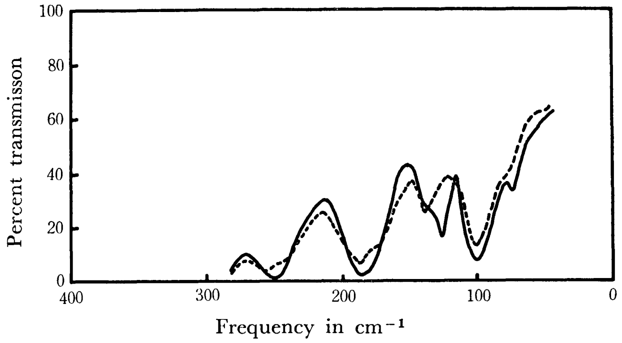

Fig. 4. Far infrared spectra of $CuCl_2 \cdot 2H_2O$ at −100°C (solid line) and at room temperature (dotted line).

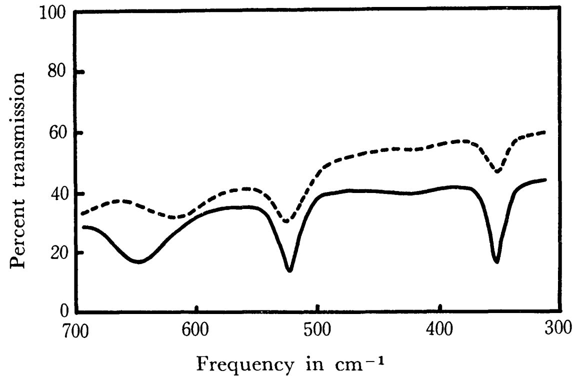

Fig. 5. Infrared spectra of $K_2C_2O_4 \cdot H_2O$ at −75°C (solid line) and at room temperature (dotted line).

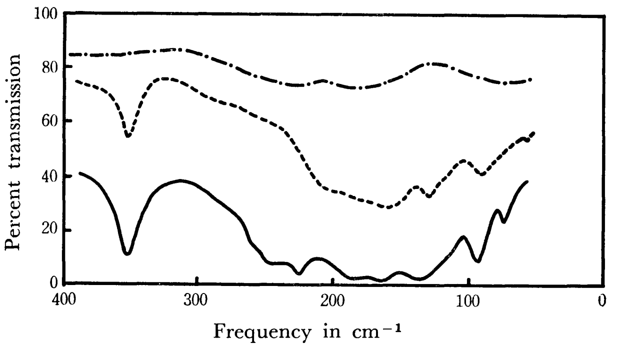

Fig. 6. Far infrared spectra of $K_2C_2O_4 \cdot H_2O$ at −100°C (solid line) and at room temperature (dotted line); (broken line, Nujol placed polyethylene at −100°C).

ature. The measurements were made using low temperature cells cooled with liquid nitrogen. The Nujol mull was placed between two CsI plates for the measurements of the infrared spectra of $BaCl_2 \cdot 2H_2O$ and $K_2C_2O_4 \cdot H_2O$ in the 700—400 cm^{-1} region, while it was placed between two polyethylene plates for the measurements of these samples in the 400—60 cm^{-1} region and of $CuCl_2 \cdot 2H_2O$ in the 700—400 cm^{-1} region, respectively. By means of a copper-constantan thermocouple recording system the temperature of the samples was found to be constant within ±2°C through the measurements. The infrared spectra were recorded with a Hitachi EPI-L spectrophotometer for the 700—400 cm^{-1} region and with a Hitachi FIS-3 far infrared spectrophotometer for the 400—60 cm^{-1} region. In the measurements of the low temperature spectra with the latter spectrophotometer, the effect of radiation of the samples and the low temperature cell was removed by the double chopping devices in the spectrophotometer. The spectra are shown in Figs. 1—6.

Results and Discussion

(A) $BaCl_2 \cdot 2H_2O$. The infrared spectra at low temperature are shown in Figs. 1 and 2, compared with those at room temperature. Among the bands in the room temperature spectra, which were concluded to be due to water of crystallization on the basis of frequency shift associated with deuteration,[4] those at 684 cm^{-1}, 555 cm^{-1} and 525 cm^{-1} become sharp at low temperature, but do not change their frequencies markedly. On the other hand, at low temperature the bands at 405 cm^{-1} and 330 cm^{-1} increase their frequencies and two other new bands appear at 432 cm^{-1} and 400 cm^{-1}. According to the results of the lattice vibration calculation[4] for the crystal structure (space group, $P2_1/n\text{-}C^5_{2h}$) determined by Padmanabhan,[8] four H_2O rocking vibrations are expected to appear in the infrared absorption spectra in the 400—300 cm^{-1} region (calculated frequencies, 398 cm^{-1}, 328 cm^{-1} (A_u species); 401 cm^{-1}, 334 cm^{-1}. (B_u species). Therefore, the appearance of the four bands is expected, and the fact that the bands in the room temperature spectra have lower frequencies than those of corresponding bands in the low temperature spectra suggests increase of the hindering potential for rocking motion of water of crystallization (the hindering potential about the C axis of H_2O molecule) at low temperature.

(B) $CuCl_2 \cdot 2H_2O$. As are shown in Figs. 3 and 4, three sharp bands appear at 425 cm^{-1}, 400 cm^{-1} and 340 cm^{-1} in the low temperature spectra instead of the one broad band in the room temperature spectra, which has been assigned as due to water of crystallization.[6] According to the calculation of the optically active lattice vibrations[6] for the crystal structure determined by Petersen and Levy,[9] three bands (one B_{1u}, one B_{2u} and one B_{3u} species) due to the rotational lattice vibrations associated with water of crystallization are expected to appear in the infrared absorption spectra. The three sharp bands seem to correspond

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[8] V. M. Padmanabhan, W. R. Busing, and H. A. Levy, *Acta Crystallogr.*, **16**, 13 (1963).

[9] S. W. Petersen and H. A. Levy, *J. Chem. Phys.*, **26**, 220 (1957).

to the above-mentioned three vibrations. The bands at 250 cm^{-1}, 180 cm^{-1} sharpen and one at 125 cm^{-1} increase its intensity at low temperature. The calculation showed presence of optically active lattice vibrations primarily associated with translational lattice modes of water of crystallization, whose frequencies correspond well to the frequencies of the bands.[6]

(C) $K_2C_2O_4\cdot H_2O$. The bands at 624 cm^{-1} and 524 cm^{-1} in Figs. 5 and 6 in the room temperature spectra were interpreted as due to water of crystallization on the basis of frequency shift on deuteration and neutron scattering data.[5,10] At low temperature, the former band shifts to higher frequency, while the latter does not change its frequency. According to the calculation of the optically active vibrations,[5] the former band is assigned to a rotational lattice vibration primarily associated with H_2O rocking and wagging modes, and the latter to one primarily associated with an H_2O twisting mode. Therefore, it may be concluded that the degree of hindering around the principal axes, B and C, of the H_2O molecule increase at low temperature, while that around the A axis does not change. At low temperature the bands at 230 cm^{-1} and 244 cm^{-1} increase their intensities. The calculated frequencies, 224 cm^{-1} (A_u species) 208 cm^{-1} (B_u species) of the lattice vibrations associated with the translational lattice modes of water of crystallization[5] suggest an assignment of these bands to the above-mentioned vibrations.

In the crystal of $CuCl_2\cdot 2H_2O$, the H_2O molecule is bound to Cl^-'s and Cu^{2+} as is shown in Fig. 7B, and the $Cu^{2+}\cdots O$ bond is considered to be strong, as the ion-atom distance is short (1.925 Å). On the other hand, in the crystal of $BaCl_2\cdot 2H_2O$, the H_2O molecule is bound to Cl^-'s and Ba^{2+}'s as is shown in Fig. 7A. The Ba^{2+}'s are located almost in the direction of the lone-pair orbitals of the O atom (assuming sp^3 hybridization) and thus are in favorable bonding position, although the $Ba^{2+}\cdots O$ distances are rather long (2.7—3.0 Å). In the case of $K_2C_2O_4\cdot H_2O$, the K^+'s are located off the direction of the lone-pairs of the O atoms and the $K^+\cdots O$ distance is long (2.933 Å). Therefore, the H_2O molecules are differenlty bound in these crystals. Although it is very difficult to interpret the difference between the room temperature spectra and the low temperature spectra, the following comments will be made here in the present paper. In the case of $CuCl_2\cdot 2H_2O$, the water of crystallization is so-called "coordinate water", and two H_2O molecules and two Cl^-'s are bound to Cu^{2+} by covalent type bonds. They altogether form one "molecule", $CuCl_2\cdot 2H_2O$. Therefore, it is expected that in the room temperature spectra the bands due to H_2O molecules may be better described as ones of $CuCl_2\cdot 2H_2O$ "molecules" arranged in the crystal. At low temperature, however, the interactions between $CuCl_2\cdot 2H_2O$ "molecules" increase, and the state of H_2O molecules becomes similar to that of so-called "lattice water". The observed spectral change of sharpening of band width and shift of bands as a whole to lower frequency with temperature depression (see Fig. 3) may be considered as due to change of the bound state of H_2O molecule from "coordinate water" to "lattice type water". On the other hand, in the case of $BaCl_2\cdot 2H_2O$ and $K_2C_2O_4\cdot H_2O$, the water of crystallization is so-called "lattice water". The spectral change of the crystals with temperature depression is the increase of frequencies and intensities of some bands along with sharpening of bands. This may be caused by change of the degree of interactions between H_2O molecules and surrounding atoms and ions.

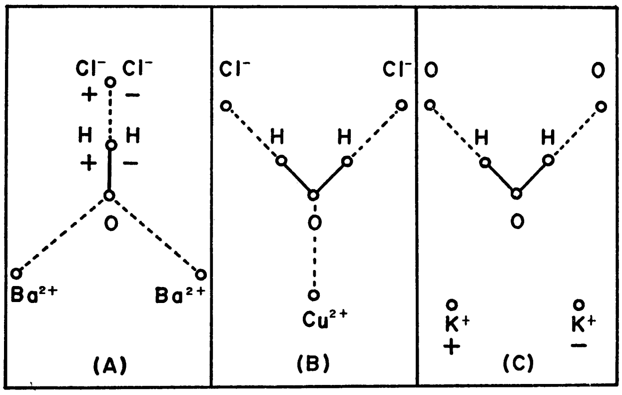

Fig. 7. Schematic representation of water of crystallization in crystals.
(+, above the paper plane; −, below the plane).

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[10] K. Fukushima, This Bulletin, **43**, 39 (1970).