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Study of thermal disordering of the $KSc(WO_4)_2$ crystal structure by Raman spectroscopy

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Raman spectra of $KSc(WO_4)_2$, exhibiting three reversible phase transitions from a trigonal phase to monoclinic and triclinic structures, have been studied in the temperature region of 100–294 K. The measurements have revealed the presence of significant broadening of librational and translational modes of the WO_4^{2-} ions with increasing temperature. This broadening was explained as a result of anisotropic activation of the complex ion reorientations.

Key words: thermal disordering, Raman spectroscopy, molecular-ionic crystals, disordered phase

1. Introduction

Crystals of binary molybdates and tungstates of alkali metals with the general formula $M^{I}M^{III}(M^{VI}O_4)_2$, where M^{I} is Na, K, Rb, Cs; M^{III} = In, Sc, Al; M^{VI} = Mo, W belong to the type of molecular-ionic crystals. Their structure incorporates a rigid complex ion $M^{VI}O_4^{2-}$ whose atoms are mutually bonded by a covalent bond. In its turn, the $M^{VI}O_4^{2-}$ complex ion is connected with the rest of the ions of the crystalline lattice by a weaker electrostatic interaction [1]. The crystals undergo a series of thermal phase transformations [2–11].

Many of the important characteristics of similar crystals may be determined by the state of orientational ordering as well as by translational and rotational mobility of the complex ion. Increasing the translational mobility of the $M^{VI}O_4^{2-}$ ion in the crystal lattice may result in phase transition of the displacive type. The change in orientational ordering and the rotational mobility of the complex ion is of an activation character (i.e., it requires overcoming of potential barriers) and may be accompanied by phase transitions of the order-disorder type. In this case the “melting” (activation of rotations) of rotational degrees of the complex ion freedom with temperature increase may occur stepwise, through a series of intermediate, partially disordered phases differing by various orientational ordering and the state of dynamic mobility of this ion.

The stepwise “melting” of the rotational degrees of freedom of the complex ion can be detected by the temperature dependence of Raman spectra in the low frequency region, where the librational vibrations of $M^{VI}O_4^{2-}$ are located. Disruption of the correlated vibrational movement of $M^{VI}O_4^{2-}$ ions in the crystal caused by individual, incorrectly oriented $M^{VI}O_4^{2-}$ ions or their individual reorientations of a certain type should lead to broadening, relative decrease of intensities, whereas in the limit when correlation is completely disrupted, to blurring out to the unstructured wing of the Rayleigh line of the respective lines of librational vibrations of the complex ion. The lines in the Raman spectrum pertaining to librational vibrations of the complex $M^{VI}O_4^{2-}$ ion around different axes of inertia, due to the difference in the values and temperature behaviour of orientation barriers in respect to different axes of inertia, may broaden differently and be blurred to the wing of Rayleigh line as the temperature increases [12].

The orientational disordering of the complex ion WO_4^{2-} was studied by the Raman spectra in the structure of $KSc(WO_4)_2$ crystal in the temperature interval of 100–294 K. $KSc(WO_4)_2$ is a convenient object for studying the rotational motion and orientational ordering of the complex WO_4^{2-} ion by the Raman spectra, since in the spectra of trigonal phase only internal and external vibrations of WO_4^{2-} reveal themselves. The vibrations of the K^+ and Sc^{3+} ions should not make themselves evident in the Raman spectrum since these ions occupy in the structure the positions at the centre of inversion [11, 13] and for these vibrations no change in the polarizability of the crystal unit cell occurs. In a ferroelastic phase, the situation is a little bit more complicated since the K^+ ions are no longer located at the centre of inversion and the respective vibrations become Raman-active. However, these vibrations are very weak [11].

2. Experimental

Single crystals of $KSc(WO_4)_2$ were grown by cooling of the molten mixture containing $KSc(WO_4)_2$ and solvent ($K_2W_2O_7$) in a ratio 1:1. The cooling rate was 2 K per hour. Back-scattering Raman spectra were obtained with a triple-grating spectrometer of additive dispersion (Jobin Yvon, T6400) and with a spectral resolution of 2 cm^{-1} (more experimental details can be found in our previous paper [11]).

3. Discussion

As the temperature increases, the $KSc(WO_4)_2$ crystal undergoes three reversible phase transitions P1←(T = 124 K) → C2/m or C2/c ← (T = 288 K) → monoclinic, incommensurate ← (T = 307 K) → P3m1 [2–11], the mechanism of which remains unclear. There are grounds to believe that the phase transitions are primarily due to changes in the translational and activation rotational mobility of the WO_4^{2-} ion in relation to its axes of inertia with increasing temperature.

Raman spectra of $KSc(WO_4)_2$ have been studied in [3–5, 11]. The spectra obtained by us are shown in Figs. 1 and 2. The vibrational spectrum of this crystal can be split into two groups of lines corresponding to internal and external vibrations of the crystal lattice. Internal vibrations (valent and deformational vibrations of the complex WO_4^{2-} ion) are visible in the regions 800–1100 and 300–400 cm^{-1}, respectively. In the low-frequency region (0–60 and 60–200 cm^{-1}) the external vibrations, i.e. librational and translational vibrations of the complex ion as a whole and translational modes of K^+ ions are located. The assignment of vibrations into the discussed groups is fairly justified since the respective lines in the spectrum are separated from one another by a sufficiently large energy gap (~150 cm^{-1}), which points to a weak interaction of one group of vibrations with those of the other group.

It is evident from Fig. 2b that in the temperature range studied no distortion of valent bonds in the complex ion occurs, since the frequency of valent semi-symmetrical vibrations (n_{wo} ~1010 cm^{-1}), characterizing the rigidity of the chemical bond W–O, does not change with temperature. In the region of deformational vibrations of the complex ion at the temperature above 250 K, more significant changes are observed: all the lines in the spectrum are noticeably widened and, moreover, the lines of frequencies ~350 and 370 cm^{-1} diminish in intensity (see Fig. 2a). However, only small changes in vibrational frequencies were observed herewith. Such behaviour of line parameters of valent and deformational vibrations of the complex ion may be above all caused by the activation mechanism – anisotropic reorientations of the WO_4^{2-} ion around the respective axis of inertia. Therefore, the most broadened should be the lines corresponding to the vibrations occurring perpendicular to the axes of respective reorientations. On this basis it may be assumed that reorientations of the complex ion in the crystal structure occur predominantly around the W–O axis.

The change in the reorientational motion of the WO_4^{2-} complex ion is observed clearly with the increase of temperature in the region of librational vibrations located in the low-frequency part of the spectrum. It is evident from Fig. 1 that with the increase of temperature, the librational line in the Raman spectrum broadens gradually. Such a behaviour of the line is the evidence of anisotropic activation of the complex ion reorientations in the structure of $KSc(WO_4)_2$ crystal at the 124 K temperature phase transition.

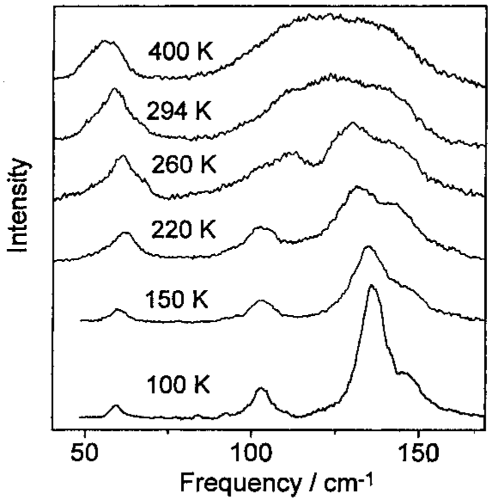

Fig. 1. Temperature-induced changes in the Raman spectrum of $KSc(WO_4)_2$ crystal in the frequency range of librational and translational vibrations of the WO_4^{2-} complex ion

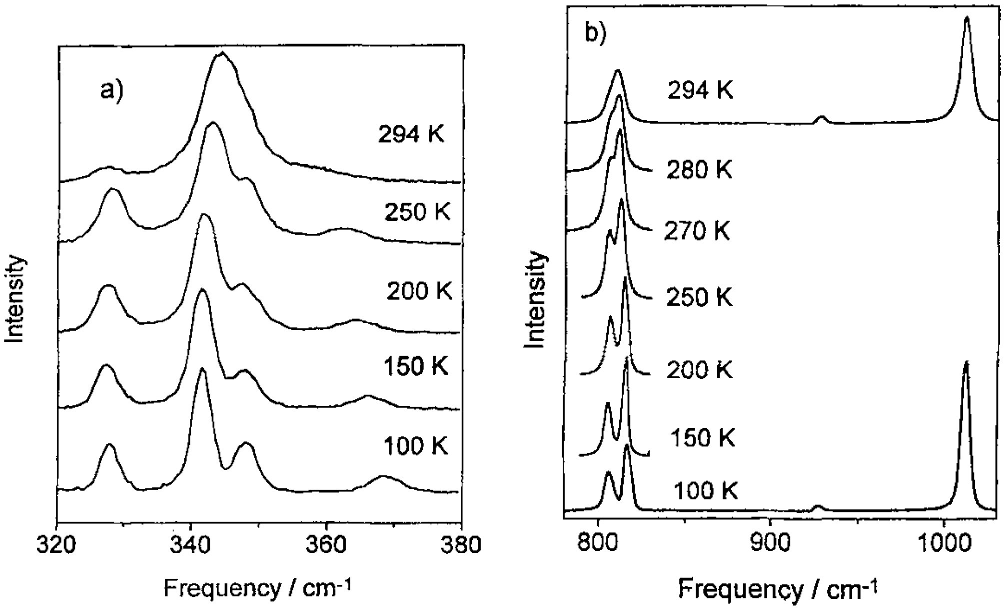

Fig. 2. Temperature-induced changes in the Raman spectrum of $KSc(WO_4)_2$ crystal in the frequency range of internal vibrations: a) the region of deformational vibrations of the complex ion, b) the region of valent vibrations of the complex ion

Reorientations of the complex ion in a phase characterized by a space group C2/*m* (C2/*c*) are activated most likely only in respect to one of the axes of inertia whereas for the two other axes a sufficiently ordered librational motion is observed. As the crystal temperature approaches the point of phase transition to the trigonal modification, the dynamic mobility of the complex ion is observed to grow further. Such effects of activation of structural units (molecules and their fragments) were earlier observed in Raman spectra of molecular crystals [12]. As regards the activation of anisotropic reorientations of complex ions in ionic crystals, similar effects were only observed in NMR spectra [14].

The reorientational movement of structural units in crystals results in loosening of the structure and facilitates the translational disordering of the structure and translational jumps (mobility) of structural units [12, 14]. In the Raman spectra, the effects of translational disordering of structural units are manifested in the region of translational vibrations of structural units. In molecular crystals similar effects of structural disordering are most clearly defined for the crystals formed by disc-shaped and globular molecules [12]. Thus, in the benzene crystal, with the increase of temperature the dynamic mobility of molecules in the benzene ring plane and simultaneously the translational diffusion of molecules in the directions also coinciding with the planes of the benzole rings are observed to increase [15].

It is clearly seen from Fig. 1 that increasing the temperature results in significant broadening of the translational lines of $KSc(WO_4)_2$ as well as a powerful deformation of the spectrum of translational vibrations of the complex ion, which may be a proof of enhanced translational diffusion of the WO_4^{2-} complex ions in the structure. Thus, it can be assumed that the phase transitions in $KSc(WO_4)_2$ crystal occur due to enhanced orientational and translational mobility of the complex ion in the structure with increasing temperature. In this case the activation of reorientations of the complex ion with increasing temperature occurs most likely stepwise and, in the first turn, during the phase transition occurring at 124 K.

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