[MS32 - 04] X-ray diffraction and Raman spectroscopic study of structural changes at extreme conditions. Boris Zakharov,[ab] Boris Kolesov,[bc] Elena Boldyreva,[ab]

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Multicomponent crystals with components present in a well-defined stoichiometric ratio (salts and co-crystals) attract much attention. Multicomponent crystals containing amino-acids are of special interest for studies at non-ambient conditions. They are interesting for improving our understanding of factors determining the formation of a crystal structure and its variations vs. temperature and pressure. They are also promising as new materials. A remarkable feature of most of these compounds is that very short O-H...O hydrogen bonds are present in the crystal structures. The structureforming units in these crystals are similar to those in the biopolymers and can be used as biomimetics. The main aim of this study was to follow the effects of cooling and increasing pressure on crystal structures of bis(DL-serinium) oxalate dihydrate and DL-alaninium semi-oxalate monohydrate by combination of singlecrystal X-ray diffraction and polarized Raman spectroscopy selected as main experimental techniques. The properties of several types of O–H...O hydrogen bonds in bis(DL-serinium) oxalate dihydrate and DLalaninium semi-oxalate monohydrate have been studied by a combination of variable-temperature single-crystal X-ray diffraction and polarized Raman spectroscopy. The changes in the hydrogen bonds geometry could be compared with the changes of the corresponding spectral modes. The correlation suggested by Novak [1] is roughly followed, better for medium and weak, than for short hydrogen bonds. Fine details of spectral changes differ for individual bonds. The way how H-bonds are affected by cooling depends on their environment in the crystal structure. Short O–H...O hydrogen bonds in bis(DL-serinium) oxalate dihydrate expand or remain almost unchanged on cooling, whereas in DL-alaninium semi-oxalate monohydrate all strong H-bonds are compressed under these conditions.The distortion of individual hydrogen bonds on temperature variations is correlated with the anisotropy of lattice strain [2]. In contrast to lowering temperature bis(DL-serinium) oxalate dihydrate and DL-alaninium semi-oxalate monohydrate were shown to undergo a phase transitions at high pressures (~4 and ~2 GPa respectively) with domains formation. Pressure-induced phase transitions in bis(DL-serinium) oxalate dihydrate related to lowering symmetry. A crystal structure disordering was shown by Raman spectroscopy on increasing pressure for this object and confirmed by appearance of diffuse scattering on diffraction patterns. A single-crystal to single-crystal transition in DL-alaninium semi-oxalate monohydrate without changing a space group (P21/c) was detected at a pressure between 1.5 and 2.4 GPa. During the phase transition selected hydrogen bonds switch-over and become bifurcated, whereas the others are compressed continuously. The transition is accompanied by pronounced discontinuities in the changes of cell parameters and volume vs. pressure, although no radical changes in the molecular packing are induced and no crystal breaking was detected [3]. Using this results we can conclude that polarized Raman spectroscopy complemented by single crystal X-ray diffraction provide an excellent instrument for detailed studies not only fine effects in hydrogen bonds on cooling but also for studying phase transitions and hydrogen bonds on increasing pressure.

This work was supported by a grant from RFBR (12-03-31541 mol_a), by the Ministry of Education and Science of Russia (project 14.B37.21.1093), and by a grant of President of Russia for State support of Russian leading

Scientific Schools (project NSh-221.2012.3).

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Keywords: extreme conditions; amino-acid complexes; hydrogen bonds