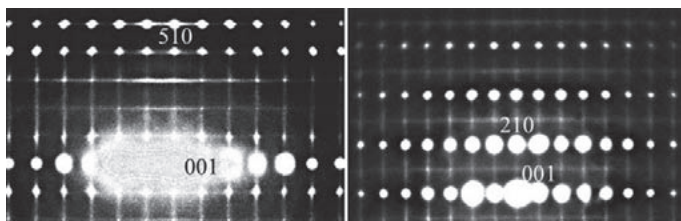


P08.14.129*Acta Cryst.* (2008). A64, C458**Structured diffuse scattering and polar nano-regions in BaTiO₃ doped relaxor ferroelectric systems**Ray L Withers¹, Yun Liu¹, Xiaoyong Wei², John D Fitz Gerald³

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BaTiO₃-doped, relaxor ferroelectric systems exhibit broadened but still large peaks in dielectric permittivity as a function of temperature. The observation via electron diffraction of relatively sharp G+{001}* sheets of diffuse intensity (see Fig.1) arising from the large amplitude excitation of 1-d inherently polar modes of distortion in such systems shows that the polar nano regions (PNRs) in these RF materials correspond to the same highly anisotropic <001> PNRs as are characteristic of the normal ferroelectric end member BaTiO₃ itself. The correlation length along the chains of these 1-D PNRs is estimated to be ~ 4-5 nm. The role of the dopant ions is not to directly induce PNRs but rather to set up random local strain fields preventing the condensation of long wavelength homogeneous strain distortion of the unit cell thereby suppressing transverse correlations of the inherent <001> chain dipoles and the development of long range ferroelectric order.



Keywords: relaxor ferroelectrics, diffuse diffraction, dielectrics

P08.14.130*Acta Cryst.* (2008). A64, C458**Crystal structure and nonlinear optical behavior of N-(2 or 3-nitrobenzalidene)2,4-dimethylaniline**Ayhan Elmali¹, Asli Karakas², Huseyin Unver³

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N-(2-nitrobenzalidene)2,4-dimethylaniline (**1**) and N-(3-nitrobenzalidene)2,4-dimethylaniline (**2**) have been synthesized for the studies of their third-order optical nonlinearities. The structural characterizations have been determined by X-ray diffraction measurements. The maximum one-photon absorption (OPA) wavelengths evaluated theoretically using the configuration interaction (CI) method are shorter than 450 nm, giving rise to good optical transparency in the visible and near IR regions. To test the microscopic third-order nonlinear optical (NLO) behavior, linear and second (hyper)polarizabilities of the studied compounds may be considered rather adequate. We have computed both dispersion-

free (static) and also frequency-dependent (dynamic) linear polarizabilities and second hyperpolarizabilities at 825-1125 nm and 1050-1600 nm wavelength areas using time-dependent Hartree-Fock (TDHF) method. The *ab-initio* calculation results with non-zero values on (hyper)polarizabilities indicate that the synthesized molecules might possess microscopic third-order NLO phenomena.

Keywords: X-ray diffraction, third-order nonlinear optics, time-dependent hartree-fock

P08.14.131*Acta Cryst.* (2008). A64, C458**Crystal structure and nonlinear optical properties of n-(3-hydroxybenzalidene)4-bromoaniline**Huseyin Unver¹, Asli Karakas², Ayhan Elmali³

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N-(3-hydroxybenzalidene)4-bromoaniline has been synthesized and characterized by X-ray diffraction analysis. To understand the relationship between structure-property and nonlinear optic (NLO) of the examined compound, our study has been extended to compute the one-photon absorption (OPA) wavelengths, linear and second (hyper)polarizabilities. We have calculated both dispersion-free (static) and also frequency-dependent (dynamic) linear polarizabilities and second hyperpolarizabilities at 825-1125 nm and 1050-1600 nm wavelength areas using time-dependent Hartree-Fock (TDHF) method. According to the calculation results obtained by means of configuration interaction (CI) method on the linear optical behavior, the maximum OPA wavelengths are estimated in the UV region to be shorter than 450 nm, showing good optical transparency to the visible light. The *ab-initio* calculated non-zero (hyper)polarizability values imply that the examined compound might possess microscopic third-order NLO behavior.

Keywords: crystal structure, nonlinear optics, second hyperpolarizability

P08.14.132*Acta Cryst.* (2008). A64, C458-459**Virtual chemistry - The game we all play**

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The only real things in chemistry are the nuclei and the electron density; everything else is virtual: orbitals, resonance, hybridization, ionic and covalent bonds, electronegativity, bond-order (-strength, -number, -valence, -energy), even bonds themselves, and for condensed matter, atoms are nothing more than concepts we impose on the nuclei and electron density in the hope of making sense of what we see there. None of these concepts arises naturally from the electron density and none of them has a unique definition. Some of these concepts are useful because they have predictive power, but others lead to more confusion than enlightenment. Manipulating these virtual concepts to interpret chemical structure is a game we

all play. Although we are all using the same ball, confusion reigns because we each play the game according to our own set of rules. A good chemical model requires well defined concepts that lead to quantitative predictions. The ionic model meets these criteria. The electroneutrality rule (the sum of all atomic valences in a compound is zero) is the only assumption the model makes and it applies to all compounds that obey this rule (mostly inorganic compounds, but also aqueous chemistry, hence much of biological chemistry). From the Coulomb field of the ionic model one can derive rigorous concepts of atom, bond, atomic valence, bond valence and electronegativity as well as Lewis acid and base strength. The result is a predictive model expressed in terms of the familiar chemical concept of localized bonds linking nearest-neighbour atoms.

Keywords: bonding, ionic model, bond valence model

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Structure of KTP crystals grown by top-seeded solution and spontaneous flux crystallization methods

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Crystals of the potassium titanyl phosphate KTiOPO_4 (KTP) family are under investigation for number years because of their application in nonlinear optics. X-Ray study of KTP single crystals grown by the top-seeded solution and spontaneous flux crystallization methods was made to evaluate the influence of growth conditions on the crystal structure and to use these results for further investigations of the structure of KTP crystals doped by isovalent and heterovalent impurities. X-Ray measurements were performed at room temperature using the four-circle CAD-4F Enraf Nonius diffractometer for the half of the sphere of reciprocal space up to $(\sin\theta/\lambda)_{\text{max}}=1.22$. Both structures were refined using the JANA2000 program up to $R=0.013$, $R_w=0.021$ for the case of the top-seeded solution method and up to $R=0.017$, $R_w=0.025$ for the case of the spontaneous flux crystallization. It was established that the electron structure of KTP crystals grown by these two methods was related with the defect structure of these crystals. The greater number of defects is shown to be formed in crystals grown by the spontaneous flux crystallization method. At the same time the similarity of potassium sublattice disordering, of cell parameters and of middle interatomic distances in structures is observed. The work was done with the partial support of the Grant for the leading scientific schools NSh-2192.2008.5 and the "Russian Science Support Foundation".

Keywords: structure and charge-density analysis, structure-properties relationships, nonlinear optical materials

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Anomalous SAXS for the morphology and metal content of a metallothionein in a metal-atom replacement

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Metallothioneins (MTs) are cysteine-rich proteins that have a high affinity with heavy metal ions. In this study, a protein unfolding-refolding process is developed to replace the metal atoms of cadmium-zinc MTs by Cu(I) or Cu(II). Using small angle X-ray scattering (SAXS) and anomalous SAXS, we have studied the changes of morphology and metal content of the MT in the designated metal-atom replacement process. The SAXS results reveal that the Cd-Zn MT has a rod-like shape and a radius of gyration $R_g = 26 \text{ \AA}$; in the solution of 4 M urea and 0.1 M β -ME, the protein is unfolded and the metal atoms are stripped from the protein, leading to a smaller R_g of 22 Å . With the unfolding environment replaced by a solution rich in Cu(I), the modified MT cannot correctly refold, but forms oligomers of a rod-like shape with a much larger R_g value of 42 Å ; when the refolding process proceeds with Cu(II), the modified MT can closely refold to the native morphology of the wild-type Cd-Zn MT. Anomalous SAXS, with the X-ray energy tuned close to the K-edge absorption of Cu, clearly indicates that the refolded MT contains Cu atoms after the refolding process. From the decrease of the ASAXS intensity, we have estimated the copper content in the modified Cu-MT. Dummy residue simulation is used to approximate the unfolded and refolded protein morphologies from the SAXS data. The Cu-S bonding observed in the X-ray absorption at the Cu K-edge and UV-VIS absorption spectra indicates clearly that Cu atoms occupy the original metal sites of the MT after the metal-atom replacement process. Corresponding changes in the circular dichroism of the MT due to the metal-atom replacement are also observed. The different influences of Cu(I) and Cu(II) in the refolding of the MT are discussed.

Keywords: anomalous SAXS, metallothionein, metal atom replacement

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Synchrotron SAXS reveals structural organization of iron oxide nanoparticles in aqueous solutions

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Iron oxide particles prepared in docosane (DOC7-PEG-PL) and octadecane OC11-PEG-PL [1] and covered with PEGylated phospholipids to make them water soluble were analyzed by small-angle X-ray scattering (SAXS). The low-resolution structures of the iron oxide cores were reconstructed *ab initio* using DAMMIN [2]. Typical shapes of the DOC7-PEG-PL (a) and OC11-PEG-PL (b) cores (inserts in Figure) yield good fits to the experimental data (curves 3). The density of the iron core of the DOC7-PEG-PL nanoparticles decreases from the center to periphery, whereas the OC11-PEG-PL sample displays a double layered structure. These differences are related to the dissimilarity of the magnetic properties of the specimens. The nanoparticles were found to form clusters containing 3-4 densely packed cores due to magnetic interactions, and their spatial organization was analyzed by the program SASREF