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For the direct determination of the microscopic local layer structure in the smectic liquid crystal under the external field, time-resolved synchrotron X-ray  $\mu$ -diffraction has become a powerful tool [1]. In this presentation, static and dynamic local layer structures and local molecular orientation in the electroclinic effect of the chiral smectic A (SmA) phase were analyzed with  $\mu$ -diffraction.

An X-ray beam size was about  $3 \times 4 \mu\text{m}^2$ . The samples were ferroelectric liquid crystals (TK-C101) and measured in the SmA phase. At the high electric field, the compound chevron structure, consisting of the curved vertical chevron and the horizontal chevron, was realized. The molecular orientation measured by the high angle halo-pattern showed the spatially-alternate molecular inclination corresponding to the layer deflection. It was shown that the anchoring effect at the alignment film played an important role for the layer structure. The layer response of the electroclinic effect was similar to that in the high electric field treatment of SmC phase, though the origin of the layer shrinkage was different between them.

[1] a) Takahashi Y., et al, *Jpn. J. Appl. Phys.*, 2001, **40**, 3294; b) *Phys. Rev.* 2003, **E67**, 051706.

**Keywords:** smectic liquid crystal, time-resolved, X-ray microbeam

#### P.11.10.1

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#### Growth and Properties of KTiOPO<sub>4</sub> Single Crystals doped with Er and Nd

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KTiOPO<sub>4</sub> (KTP) single crystals are of great interests due to their ferroelectric and nonlinear optical properties. Last time the attention is given to the investigation of KTP-family crystals doped with rare earth and codopant ions as the material for self-doubling [1,2].

In the present work single crystals of KTP codoped with Ln = Er, Nd and Me = Nb, Ta, Ba, Ca, Mg, Bi, Al, Si, KCl were grown by means of flux method and some properties were investigated.

The investigations show that an addition of Nb and Ba leads to decreasing of KTP:Ln:Me optical quality, whereas the quality increases with KCl and Bi and does not markedly depends on Ln.

Maximum luminescence intensity was observed in KTP:Er:Nb crystals. Life time of <sup>4</sup>F<sub>3/2</sub>Nd<sup>3+</sup> and <sup>4</sup>I<sub>13/2</sub>Er<sup>3+</sup> has been found as 250  $\mu$ s and 6 ms for KTP:Nd and KTP:Er respectively. In KTP:Ln:Me the life time changes in the area of 1 - 7 ms for <sup>4</sup>I<sub>13/2</sub>Er<sup>3+</sup> and 180 - 300  $\mu$ s for <sup>4</sup>F<sub>3/2</sub>Nd<sup>3+</sup> depending on the codopant of ion Me.

The presence of Ln ions in KTP:Ln:Me crystals does not strongly affect on ferroelectric phase transition temperature, but suppresses the dielectric permittivity peak caused by the above-named transition.

[1] Sole R., Nikolov V., Koseva I., et al., *Chem. Mater.*, 1997, **9**, 2745. [2] Carvajal J. J., Nikolov V., Sole R., et al., *Chem. Mater.*, 2002, **14**, 3136.

**Keywords:** crystal growth, KTiOPO<sub>4</sub>, ferroelectrics

#### P.11.10.2

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#### Second-Order Nonlinear Optical Properties of Tetradentate Schiff base Complexes

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Quadratic non-linear optical properties of new unsymmetrical Ni(II), Cu(II), Zn(II) and VO(II) complexes with [N<sub>2</sub>O<sub>2</sub>] chelate tetradentate ligands are presented. The complexes were synthesized by template condensation of 1-phenylbutane-1,3-dione mono-S-methylisothiosemicarbazone with o-hydroxybenzaldehyde or its 5-

phenylazo-derivative. The crystal structure of some complexes was determined by using synchrotron radiation (XRD1 beamline at ELETTRA, Trieste).

Large values of hyperpolarizability, as obtained for these complexes by the solution-phase dc electric-field-induced second harmonic (EFISH) generation method, together with their high stability constants, make them promising candidates for successful applications in the field of optoelectronic technologies.

The values of theoretical hyperpolarizability, calculated through both Finite Field and Time Dependent DFT methods, are also presented.

**Keywords:** transition-metal complexes, nonlinear optical properties, theoretical calculations

#### P.11.10.3

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#### Temperature Dependence of Refractive Indices in selected Borates

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The knowledge of the temperature dependence of the refractive indices of a nonlinear optical crystal play a key role for its classification as a NLO material. For example, the temperature dependence can be used as a possibility for fine tuning of the phase-matching conditions of a nonlinear optical frequency conversion process. In general it is advantageous to describe the temperature dependence of the refractive indices using the temperature dependence of the polarisation tensor [a<sub>ij</sub>] (optical dielectric impermeability tensor)  $\Delta a_{ij} = b_{ij} \Delta T + c_{ij} \Delta T^2 + \dots$ , where [b<sub>ij</sub>], [c<sub>ij</sub>], ... describe the linear, quadratic, etc. temperature dependence of the polarisation tensor. In most cases (far from phase transitions) the linear approximation turn out to be an adequate description.

In this work we present a technique for the measurement of temperature dependence of refractive indices based on a Jamin interferometer, which allows to measure optical path length differences as a function of temperature (temperature range: 50...280 K). The knowledge of the refractive indices at a reference temperature T<sub>0</sub> (e.g. room temperature) including the orientation of the indicatrix, and the knowledge of thermal expansion data in the same temperature range are necessary for the evaluation of the experimental data.

As results we present the [b<sub>ij</sub>] tensors of the non-centrosymmetric borate crystals: Zn<sub>4</sub>[O(BO<sub>2</sub>)<sub>6</sub>] (PG:  $\bar{4}3m$ ), Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (PG: *4mm*),  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (PG: *3m*), PbB<sub>4</sub>O<sub>7</sub> (PG: *mm2*), SrB<sub>4</sub>O<sub>7</sub> (PG: *mm2*) and BiB<sub>3</sub>O<sub>6</sub> (PG: *2*).

**Keywords:** non-centrosymmetric borates, phase-matching, nonlinear optics

#### P.11.10.4

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#### Nonlinear Optical Properties of Lithium Sulfate Monohydrate, Li<sub>2</sub>SO<sub>4</sub> · H<sub>2</sub>O

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Lithium sulfate monohydrate crystallizes in the monoclinic polar space group P2<sub>1</sub> [1]. Among the group of non-ferroelectric polar crystals, Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O possesses the highest pyroelectric coefficient as well as remarkable piezoelectric and electro-optic properties. However, there is only little known about its nonlinear optical properties [2]. Recently, the possibilities of phase-matched second harmonic generation (SHG) in Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O were analysed in detail [3]. In this work we present the results of our investigation of the SHG. Using the Maker fringe technique and four differently oriented plane slabs of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O crystals all eight independent components of the nonlinear optical susceptibility tensor [d<sub>ijk</sub>] for the fundamental wavelength  $\lambda = 1079.5 \text{ nm}$  (Nd:YAP laser) were determined. In comparison to other polar properties of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O the coefficients d<sub>ijk</sub> are surprisingly small; they are one order of magnitude smaller than those of commonly used crystals for frequency conversion of laser light, such as KTiOPO<sub>4</sub>,  $\beta$ -BaB<sub>2</sub>O<sub>4</sub>, LiB<sub>3</sub>O<sub>5</sub> or BiB<sub>3</sub>O<sub>6</sub>. The

largest value of a  $d_{ijk}$  amounts to 0.34(4) pm/V. However, in spite of the relatively small coefficients  $d_{ijk}$  there are some interesting aspects for application of  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$  as a SHG material: availability of large high-quality crystals, transparency in the UV region and possibility of phase-matching in the range from near UV to near IR.

[1] Ziegler G.E., *Z. Kristallogr.*, 1934, **89**, 456. [2] Hobden M.V., *J. Appl. Phys.*, 1967, **38**, 4365. [3] Becker P., et al., *Crys. Res. Technol.*, 2003, **38**, 881.

**Keywords:** nonlinear optics, nonlinear optical materials, optical materials

#### P.11.10.5

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##### Neutron Diffraction Study of 4-nitroaniline at 100K

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The planarity of the amino group in nitroanilines is still a matter of controversy. It has been assumed in several experimental and theoretical studies of 4-nitroaniline (pNA) [1]. Single crystal X-ray diffraction and experimental electron density analysis of pNA have been previously reported [2,3]. However, no accurate experimental coordinates and atomic displacement parameters (adps) for the hydrogen atoms are available yet. As shown by Bürgi et al. [4], accurate adps for hydrogen atoms are essential for obtaining reliable results on physical properties. With this in mind, we have carried out a single crystal neutron diffraction study of pNA at 100K. It shows a relationship between the planarity of the amino moiety and the degree of intramolecular charge transfer, as well as a hydrogen bond scheme different from that observed in other primary anilines [1].

[1] Goeta A. E., et al., *Chem Mater.*, 2000, **12**, 3342, and references therein. [2] Tonogaki M., et al., *Acta Cryst. B*, 1993, **49**, 1031. [3] Coppens P., Volkov A., *Acta Cryst. A*, 2004, **60**, 357. [4] Bürgi H. B., et al., *Chem.Eur.J.*, 2002, **8**, 3512.

**Keywords:** molecular crystals, hydrogen bonding, nonlinear optical materials

#### P.11.10.6

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##### Cation Distribution in $\text{Eu}^{2+}$ - and/or $\text{Eu}^{3+}$ -Containing Inorganic Compounds

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Divalent  $\text{Eu}^{2+}$  ( $4f^7 5s^2 5p^6 6s^2$ ) or trivalent  $\text{Eu}^{3+}$  ( $4f^6 5s^2 5p^6 6s^2$ ) ions exhibit extremely interesting electrical and optical properties in various inorganic compounds. The coordination of such ions in the crystal structure, for example, would be in control of the photoluminescence of materials used for cathode-ray tube, plasma display panels and imaging plate.

The site occupation of Eu ions has been mainly examined in this study. X-ray diffraction and absorption techniques were applied to such typical compounds as  $\text{YNbO}_4$ ,  $\text{Y}_2\text{O}_3\text{S}$ ,  $\text{BaMgAl}_{10}\text{O}_{17}$  and  $\text{Eu}_3\text{S}_4$ , which contain  $\text{Eu}^{2+}$  and/or  $\text{Eu}^{3+}$ . Fine powder crystals of  $(\text{Y},\text{Eu}^{3+})\text{NbO}_4$  were successfully synthesized by the polymerizable complex method and used for structural analyses with the Rietveld method. Single crystals of  $\text{Eu}_3\text{S}_4$  were synthesized from the powder sample with 0.06 g  $\text{NH}_4\text{I}$  flux by the vapor growth. The crystal structure of a mixed-valence compound,  $\text{Eu}_3\text{S}_4$  has been examined by the valence-difference contrast method of anomalous scattering at the Eu  $L_{II}$  absorption edge. The hopping character of 4f electrons between adjacent Eu sites is partially frozen between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions below  $T = 210$  K. A charge-ordered tetragonal structure was determined below  $T_c = 188.5$  K, where a half of  $\text{Eu}^{3+}$  ions occupy the whole 4a sites, while the remaining half of  $\text{Eu}^{3+}$  ions mix with all  $\text{Eu}^{2+}$  in the 8d

sites.

**Keywords:** cation distribution, structural inorganic chemistry, mixed-valence compounds

#### P.11.10.7

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##### Synthesis and Characterization of Nanocrystalline $\text{Y}_3\text{Al}_5\text{O}_{12}$ derived by a Sol-Gel Method

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Nanocrystalline pure and rare earth doped yttrium aluminum garnet (YAG) powders are promising materials for photonics

Nano-sized YAG powders were synthesized through nitrate-citrate sol-gel processing [1]. The powders were obtained by drying the YAG gel followed by calcinations at 600°C. The amorphous YAG precursor was then heat-treated at different temperatures from 900 to 1100°C. The evolution of YAG phases was investigated by X-ray powder diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The XRD pattern of powder heat-treated 3h at temperature as low as 900°C showed the formation of cubic  $\text{Y}_3\text{Al}_5\text{O}_{12}$  well-crystallized phase. No intermediate phases were observed. Integral breadth of diffraction line profile was used in order to approach the changes in crystallite size with heat-treatment. The increase of YAG crystallite size from 20 to 50nm with annealing temperature increasing from 900 to 1100°C was observed.

The FTIR measurements were found to be consistent with the YAG phase crystallization process observed by XRD.

[1] Chung B.-J., Park J.-Y., Sim S.-M., *J. Ceram. Proc. Res.*, 2003, **4**, 145.

**Keywords:** electronic photonic materials, X-ray powder diffraction, FTIR

#### P.11.10.8

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##### Structural Study of Sn-doped $\text{In}_2\text{O}_3$

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Tin doped  $\text{In}_2\text{O}_3$  (ITO) is widely used in phototronic, optoelectronic and microelectronic devices. There are numerous studies on ITO, but the understanding of its defect structure is rather incomplete.  $\text{In}_2\text{O}_3$  possesses a cubic structure, the space group  $\text{Ia}\bar{3}$ [1]. The structure contains two different six-fold-coordinated cation sites referred as sites B and D, respectively. This paper focuses on X-ray diffraction and  $^{119}\text{Sn}$  Moessbauer studies of the polycrystalline ITO samples containing 2-14 at% Sn. Nanocrystalline ITO powders were prepared by a sol-gel technique using  $\text{InCl}_3$  and  $\text{SnCl}_4$  reagent grade chemicals and annealed at 300°C for 5 h. Lattice parameter  $a$  of doped  $\text{In}_2\text{O}_3$  increased with Sn-doping level up to 8 at% and decreased above. Such behavior of lattice parameter suggests that tin substitution for  $\text{In}^{3+}$  on sites B and D is non-uniform and depends on tin content.  $^{119}\text{Sn}$  Moessbauer spectra indicated that only the  $\text{Sn}^{4+}$  state is present in ITO samples. The least square fitting of spectra was performed by assuming presence of two doublets. In accordance with [2], doublets with isomer shifts (IS) in the range 0.09–0.17 and 0.36–0.464  $\text{mms}^{-1}$ , respectively, correspond to the D and B sites in the cation sublattice of the  $\text{In}_2\text{O}_3$  structure. The area ratio of the two doublets depended on tin content.

[1] Marezio M., *Acta Cryst.*, 1966, **20**, 723. [2] Binczycka H., et al., *Phys. Stat. Sol. (B)*, 2005, in press.

**Keywords:** Sn-doped  $\text{In}_2\text{O}_3$ , X-ray diffraction, Moessbauer spectroscopy