

s13.m37.p11 **Crystal Structure and Physical Properties of  $Ba_{1-x}Sr_xPb_{0.7}Bi_{0.3}O_3$  and  $BaPb_{0.7-x}M_xBi_{0.3}O_3$  ( $M = Sn, Sb$ ).** Antoni Winiarski, Bronislaw Psiuk and Grazyna Chelkowska, August Chelkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland. E-mail: awini@us.edu.pl

**Keywords:** Oxides; Superconductivity; Vegard's law

$Ba_{1-x}Sr_xPb_{0.7}Bi_{0.3}O_3$  and  $BaPb_{0.7-x}M_xBi_{0.3}O_3$  ( $M = Sn, Sb$ ) compounds are interesting because they are based on non-copper oxidic superconductor  $BaPb_{0.7}Bi_{0.3}O_3$  [1], [2]. Sb influence on  $T_c$  in  $Ba(Pb,Bi,Sb)O_3$  system was investigated by R. Nagarajan [3]. The samples  $Ba_{1-x}Sr_xPb_{0.7}Bi_{0.3}O_3$ ,  $BaPb_{0.7-x}Sb_xBi_{0.3}O_3$  and  $BaPb_{0.7-x}Sn_xBi_{0.3}O_3$  were prepared by sintering of starting materials  $BaCO_3$ ,  $SrCO_3$ ,  $PbO_2$ ,  $Bi_2O_3$ ,  $SnO_2$  and  $Sb_2O_5$ . The samples were powdered and examined with the use of Siemens D5000 X-ray Powder Diffractometer. Electric resistivity and X-ray photoelectron spectroscopic (XPS) measurements were performed to explain deviations from the Vegard's law. The lattice parameters and the cell volume of  $Ba_{1-x}Sr_xPb_{0.7}Bi_{0.3}O_3$  compounds (space group Cmm2) exhibit anomalous behavior in the Sr concentration region close to  $x = 0.5$ . The  $Ba_{1-x}Sr_xPb_{0.7}Bi_{0.3}O_3$  compounds are semiconductors except of  $Ba_{0.5}Sr_{0.5}Pb_{0.7}Bi_{0.3}O_3$  which shows a metallic character. The upper limit of Pb replacement by Sn in tetragonal  $BaPb_{0.7-x}Sn_xBi_{0.3}O_3$  was found to be  $x = 0.13$ . The analysis of diffraction patterns points to increasing of the tilt angle of  $Pb(Bi,Sn)O_6$  octahedrons for increased concentrations of tin. These samples crystallize in tetragonal I4/mcm space group. Even small amounts of Sn destroy superconductivity and markedly increase electric resistivity by a few orders of magnitude. The volume of the monoclinic unit cell of  $BaPb_{0.7-x}Sb_xBi_{0.3}O_3$  reaches minimum equal to  $316.05 \text{ \AA}^3$  for  $x = 0.2$ . For this value of  $x$ ,  $T_c$  (onset) reaches maximum equal to 13.3 K. It is clearly visible that deviation from the Vegard's law is connected with the change in electric resistivity while compression of the unit cell volume may lead to superconductivity. We discuss such behavior in terms of overlapping electron orbitals.

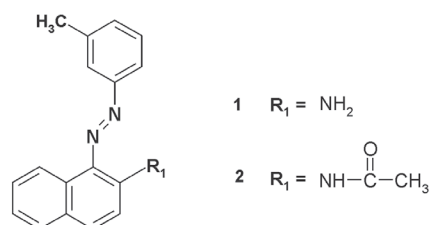
- [1] Hashimoto, T., Hirasawa, R., Kobayashi, T., Hirai, H., Tagawa, H., Mizusaki, J., Toraya, H., Tanaka, M. & Ohsumi, K. (1997) *Solid State Commun.* **102**, 561-564.
- [2] Winiarski, A., Wübbeler, G., Scharfschwerdt, C. & Neumann, M. (1991) *Fresenius' Journal of Analytical Chemistry* **341**, 296-300.
- [3] Nagarajan, R., Vasanthacharya, N.Y., Gopalakrishnan, J. & Rao, C.N.R. (1991) *Solid State Commun.* **77**, 373.

s13.m37.p12 **Solid State Structure of 1-(3'-Methylphenylazo)-2-naphthylamine and its Acetamide.** Irena Wolska<sup>a</sup>, Dorota Maciejewska<sup>b</sup> and Violetta Kowalska<sup>b</sup>, <sup>a</sup>Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland, <sup>b</sup>Faculty of Pharmacy, Medical University of Warsaw, Banacha 1, 02-097 Warsaw, Poland. E-mail: iwolska@amu.edu.pl

**Keywords:** Azoaminonaphthalenes; Conformational inter-conversion; Structural problems in solid state

Tautomerism, polymorphism and various conformational rearrangements were analyzed for azobenzenes in solution and in solid state, but hardly ever for azonaphthalenes. On the basis of detailed studies of the  $^{15}N$  NMR and X-ray diffraction data of azobenzenes it was concluded, that the azo group  $N=N$  is seen to be disordered between the two *trans* conformations. It is, therefore, expected that a similar process would also occur in solid azoaminonaphthalenes.

So, we have decided to analyze the structures of the arylazo-2-naphthylamine and its acetamide (**1**, **2**) using solid-state  $^{13}C$  CP/MAS NMR, 1D and 2D solution-state  $^1H$  and  $^{13}C$  NMR, X-ray diffraction and theoretical DFT calculations in an attempt to understand their conformational interconversion.



On the basis of X-ray data, we could claim that in the molecule of **1** the azo group adopts *trans* conformation with six-membered ring formed by the intramolecular hydrogen bond. In the solid state  $^{13}C$  CP/MAS NMR spectrum of **1** and its acetamide derivative **2**, only for **2** the double signals were found. It is due to the presence of two energetically similar conformations, which could exist in solid state as conformers with different orientation of *trans*  $N=N$  azo bond stabilized by two types of the intramolecular hydrogen bond forming six-membered and five-membered rings. It correlates with the theoretical calculations at DFT level. The conformers with the  $NH$  amide proton involved in the intramolecular hydrogen bond as a part of a six-membered ring are more stable. For **2** the computed energy differences between both conformers is smaller than for **1** and the azo group is seen to be disordered between the two *trans* conformations.