s3.m11.p1 **Crystallographic Aspect of the Phase Transitions in Na_2CO_3.** Alla Arakcheeva and Gervais Chapuis, *Laboratory of Crystallography, , Swiss Federal School of Technology (EPFL), Lausanne, Switzerland. E-mail: Alla.Arakcheeva@epfl.ch*

Keywords: Phase transitions; Incommensurate-commensurate; Structural aspect

From the published data related to the structure determination of phases α (hexagonal; 756 - 972 K) [1], β (monoclinic; 605 - 746 K) [1], γ (incommensurate, monoclinic; 295 K) and δ (lock-in, monoclinic; 110 K) [2] of Na_2CO_3, it appears that Na - C and Na - Na interactions are the driving forces of the phase transitions. The evolution of these interactions with temperature in phase β is reproduced along t in the incommensurate phase γ and relates different atomic groups, which are symmetrically equivalents in phase α. The triangular CO_3 anion is not a rigid unit: the C - O distances depend on additional C - Na bonds.

[1] Swainson, I. P., Dove, M. T. and Harris, M. J. (1995). *J. Phys.: Condens. Matter* **7**, 4395-4417.
[2] M. Dusek, G. Chapuis, M. Meyer and V. Petricek. *Acta Cryst*. (2003), B**59** 337-352 .

s3.m11.p2 **Crystal growth, structures and superconducting properties of cuprates in the Bi(Pb)-Sr-Ca-Cu-O system.** R. Gladyshevskii [a], E. Giannini [b], R. Flükiger [b], [a] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefidiya St., 6, UA-79005 Lviv, Ukraine;* [b] *Department of Physics of Condensed Matter, University of Geneva, 24, Quai Ernest-Ansermet, CH-1211 Geneva, Switzerland. E-mail: Roman.Gladyshevskii@franko.lviv.ua*

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Among the different chemical classes of high-T_c superconductors, Bi-based cuprates attract great interest because of their outstanding physical properties and exceptional grain morphology. They form a series with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, and their ideal crystal structures are relatively simple: body-centered tetragonal unit cells (space group I4/*mmm*) with the translation periods a ~ 3.8 Å and c ~ 24.6 (n = 1, Bi-2201), 30.9 (n = 2, Bi-2212), or 37.0 Å (n = 3, Bi-2223). The real structures exhibit different interesting features.

We have undertaken a systematic single-crystal investigation of Bi-based cuprates, including a study of the effect of Pb doping. Large, high-quality crystals (up to 3 × 2 × 0.1 mm^3) were grown by means of a newly developed Vapour-Assisted Travelling Solvent Floating Zone (VA-TSFZ) technique.

The crystal structures are characterized by an incommensurate modulation having its main component in the direction of one of the short translation vectors of the average subcell (**a** for an *A*-centered orthorhombic cell, space group *A2aa, a* ~ *b* ~ √2 × 3.8 ~ 5.4 Å, *c* being the same as for the ideal structure), however, the structures can be conveniently described in supercells. Additional oxygen atoms were found in the BiO layers. For example, in the case of Bi-2212 and Bi-2223 an additional O atom has been inserted at the level of every 9th and 10th Bi atom, respectively, which defines the translation unit of the modulation wave. The actual composition of the crystals is thus $Bi_2Sr_2CaCu_2O_{8.22}$ and $Bi_2Sr_2Ca_2Cu3O_{10.20}$, respectively This oxygen overdoping seems to be a crucial parameter for the existence of the phase in this system. Partial elimination of oxygen by annealing under reducing conditions does not remove the modulation, but produces serious structural changes. On the contrary, substitution of Bi by Pb is accompanied by an increase of the modulation period. In the case of Bi-2212, the periodicity of the structural modulation becomes infinite for a lead content close to 0.4 Pb per formula unit. The additional oxygen atoms can thus be removed by replacing 2/9 of the Bi^{3+} cations by chemically similar cations in a lower oxidation state (Pb^{2+}), keeping the same electron concentration ($Bi_{1.56}Pb_{0.44}Sr_2CaCu_2O_8$).

The superconducting transition temperature increases with increasing number of CuO_2 layers: 10 K (Bi-2201) - 90 K (Bi-2212) - 111 K (Bi-2223). Modulation-free $Bi_{1.56}Pb_{0.44}Sr_2CaCu_2O_8$ (T_c = 93 K) has an enhanced irreversibility field and a lower relaxation rate, as compared with modulated $Bi_2Sr_2CaCu_2O_{8.22}$. Moreover, the anisotropy of the Pb-doped crystals was found to be reduced with respect to undoped ones. The best pinning properties are observed for moderately Pb-doped crystals that contained lamellas of both the Bi,Pb-2212 and Bi-2212 structures. Magnetic critical current densities of $2 \cdot 10^5$ A/cm^2 were measured at T = 30 K and $\mu_0 H$ = 0 T for Bi-2223 crystals. A weak second peak in the magnetisation loops was observed in the temperature range 40-50 K, above which the critical current density was found to rapidly decrease as a function of T and H.