

transition metal elements TM = E8 – E10. In the system Ba – Ni – Ge, two homogeneity ranges with different Ni content are structurally characterized, which are both related to the clathrate-I structure. Compounds with low Ni content, $\text{Ba}_8\text{Ni}_x\text{Ge}_{42\pm 1}$ ($0 < x \leq 0.6$), can be considered as solution of Ni in the binary $\text{Ba}_8\text{Ge}_{43}\square_3$ (space group $Ia-3d$, $a = 21.307(2)$ Å). The subcell with space group $Pm-3n$ is observed for the compositions $\text{Ba}_8\text{Ni}_x\text{Ge}_{42\pm 1}$ ($0.6 < x \leq 4.2$). The change in Ni content is associated with the respective change in lattice parameters ($a = 10.657(1) - 10.681(1)$ Å), but also confirmed by microprobe analyses.

[1] Carrillo-Cabrera W., Budnyk S., Prots Y., Grin Yu., *Z. Anorg. Allg. Chem.*, **2004**, 630, 2267

Keywords: clathrate-I; defects; supercell

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Valence Tautomerism of a Novel Polymeric Mn(II) Species. Francesco Caruso^a, Elizabeth Chacon-Villalba^b, Miriam Rossi^c. ^a*Istituto di Chimica Biomolecolare, CNR, Piazzale Aldo Moro 5, 00185, Rome, Italy.* ^b*CEQUINOR, U.N.L.P. La Plata 1900, Argentina.* ^c*Vassar College, Department of Chemistry, Poughkeepsie, NY, 12604-0484, USA.*

E-mail: caruso@vassar.edu

$\text{Mn}(\text{Lap})_2$, HLap = lapachol, is a polymeric compound showing extended conjugated double bonds, where the 3 O atoms of lapachol act in a novel way, two chelating one Mn and the 3rd generating a coordinative bond towards another metal unit. X-ray structure determinations at 125K, 197K and 300K describe the progressive trend of a Mn contribution to Mn-O1 bond length as a function of T. The Mn-O1 bond distance increases with temperature and may be therefore associated with a lapachol semiquinone action at low T by the carbonyl O1 donor (and corresponding to Mn(III)). It transforms to a more classical coordinative bond at room T and stabilizes a Mn(II) species; this is a reversible phenomenon involving Mn(II)-Mn(III) oxidation states. A related UV-visible band shows in the near IR spectrum. The extended network of mesomerism allows for potential transfer of charge through the whole crystal. There are few precedents of this phenomenon in the literature [1].

[1] AS. Attia, C. G. Pierpont, *Inorg. Chem.* **1998**, 37, 3051.

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Structural Analysis, Magnetic Properties of the $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{2-x}\text{Co}_x)\text{O}_{8+d}$ System. N. Boussouf^a, M. F. Mosbah^a, A. Amira^b, T. Guerfi^c. ^a*Université Mentouri de Constantine, Laboratoire de Couches Minces et Interfaces, Campus de Chaabet-Erssas-25000 Constantine- Algérie.* ^b*Laboratoire des Essais Non Destructifs (LEND), Université de Jijel. B.P. 98, 18000 Jijel, Algeria.* ^c*Université de Boumerdes,*

Faculté des Sciences, département de Physique.

E-mail: boussoufnora@yahoo.fr

The effects of Co substitution on the structural and superconducting properties of the $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{2-x}\text{Co}_x)\text{O}_{8+d}$ compound have been studied. as a function of doping concentrations. The $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{2-x}\text{Co}_x)\text{O}_{8+d}$ samples were prepared by conventional solid state reaction method and characterized by X-ray diffraction (XRD), DC resistivity, AC susceptibility,. XRD investigations showed multiphase in the Co-substituted samples with slight reflection peaks of impurity and Bi2201 low-Tc (LTc) phase, these configurations suggest the insufficient ionic diffusion to form the superconducting crystals [1]. The refinement result for XRD data shows that the a-axis expands, while the c-axis contract slightly with increasing of Co. The value Tc increased significantly with increasing the Co concentration in the system. The relation between Tc and the c-axis lattice parameter suggests that the change of Tc is correlated with a redistribution of holes between the Bi-O layers and the Cu-O planes [2].

