

the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

**Keywords:** phase transitions in solids, thermodynamics, X-ray synchrotron powder diffraction

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#### Diffusion Path Formation for Cu<sup>+</sup> Ions in Superionic Cu<sub>6</sub>PS<sub>5</sub>I Single Crystal

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The knowledge of structural transformations to phases characterized by high ionic conductivity remains still very important in understanding the mechanisms and structural conditions supporting high mobility of ions in solids.

Trying to understand the mechanism for superionic conductivity of Cu<sup>+</sup> ions in Cu<sub>6</sub>PS<sub>5</sub>I argyrodite compound the detailed structure analysis based on single-crystal X-ray diffraction was performed. The main interest was focused on a new cubic superstructure F-43c, stable from 140K to 275K. In the range of this phase ordering of copper ions occurs. The final structure model is given including the detailed temperature evolution of site occupation factors of copper ions. Possible diffusion paths for the copper Cu<sup>+</sup> ions are represented by means of the atomic displacement factors and split model. Ordering process of Cu<sup>+</sup> ions with temperature lowering is found to be similar with ordering of copper in β-Cu<sub>7</sub>PSe<sub>6</sub> [1].

Comparison of the structural data with non-Arrhenius behavior of conductivity [2] indicates significant change in conduction mechanism with temperature increasing: from hopping to liquid like behavior.

[1] Gaudin E., et al., *Acta Cryst.*, 2000, B56, 402-408. [2] Beeken R.B., et al., *Journal of Physic and Chemistry of Solids*, 2003, 64, 1261-1264.

**Keywords:** ionic conductors, phase transition and structure, copper ions

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#### Tensor Distinction of Domain States in Ferroic Phase Transitions

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Distinction of domain states in ferroic phase transitions by their tensor properties is of importance in domain engineering. This is simple if the ferroic group is a halving subgroup of the parent group. In such cases there are two domains which differ only by the sign of primary transition parameter. However, even in these cases we may run into complications if the transition parameter is not a cartesian tensor components but a linear combination of such components as in cases of parent groups of tetragonal and higher symmetries. For ferroic transitions associated with two- and three-dimensional *R-ireps* we meet even more complicated relations which are a consequence of the fact that symmetry allowed tensor forms are invariants of the symmetry groups while their cartesian components are generally not invariant. The use of the ordinary transformation formulae is awkward and error inviting in these cases.

Transition parameters are generally expressed as components of tensorial covariants [1]. To find changes of cartesian components at the ferroic transition we proposed a method consisting of "labelling of covariants" followed by "conversion equations" This method facilitates the description of individual domain states in terms of cartesian tensor components and hence also their distinction.

[1] Kopský V., *Phase Transitions*, 2001, 73, No.1-2, 1-422.

**Keywords:** domain states, labelling of covariants, conversion equations

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#### Maximal Symmetry Transition Paths for Reconstructive Phase Transitions

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The transition path of a phase transition with no group-subgroup relation between their phases (as reconstructive phase transitions) can be defined as the set of atomic displacements, and strains that should occur at a local level during the transformation. The maximal symmetry transition paths are characterized by intermediate structural configurations with symmetries given by maximal common subgroups of the space groups of the two end phases. Additional symmetry constraints follow from the compatibility conditions of the occupied atomic positions at both ends of the path. By definition, the symmetry of any possible transition path must be among those maximal symmetry paths, or their subgroups. Recently, we have developed a systematic procedure for the determination of the full set of possible maximal transition paths between two structure types with no group-subgroup relations between their symmetries. A computer program has been implemented at the Bilbao Crystallographic Server (<http://www.cryst.ehu.es>) [1].

Here we present the results of our search of maximal symmetry transition-paths for some typical cases of reconstructive phase transitions (*e.g.* wurtzite to rocksalt, wurtzite to zinblende or zinblende to rocksalt structure types, *etc.*) [2].

[1] Kroumova E., Perez-Mato J.M., Aroyo M.I., Kirov A., Capillas C., Ivantchev S., Wondratschek H., *Phase Transitions*, 2003, 76, 155-170. [2] Perez-Mato J.M., Aroyo M.I., Capillas C., Blaha P., Schwarz, *Phys. Rev. Lett.*, 2003, 90, 4, 049603.

**Keywords:** reconstructive transitions, maximal transition paths, Bilbao crystallographic server

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#### Melting and Freezing of Bi Nanoclusters Embedded in Glass

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Bi-glass nanocomposites were obtained by quenching homogeneous Bi-doped soda-borate melts followed by an annealing at  $T = T_a$ . This process induces the formation of spherical Bi nanoclusters embedded in a glass matrix [1]. Since  $T_a \neq T_{mb}$ ,  $T_{mb}$  being the melting temperature of bulk Bi, we have in fact obtained liquid Bi droplets that, after cooling, became spherical nanocrystals. The nanocrystal-to-liquid transition was investigated using simultaneously the SAXS and WAXS techniques [2]. The melting temperature  $T_m$  decreases for decreasing radius and is a linear function of  $1/R$ ,  $T_m = T_{mb} - a/R$ ,  $a$  being a positive constant related to surface energy parameters. For Bi nanocrystals with  $R = 1.5$  nm, the magnitude of the melting temperature reduction is about 200 K. An additional study of the liquid-to-crystal transition was performed. The freezing temperature of bulk Bi,  $T_{cb}$ , is much lower than  $T_{mb}$ , ( $T_{mb} - T_{cb} = 150$  K). We have established that the freezing temperature also decreases linearly for increasing values of  $(1/R)$ , but at a rate lower than the melting temperature, in such a way that the magnitude of the overcooling is progressively reduced for nanodroplets with decreasing radius. The overcooling vanishes for droplets with radius close to 2 nm. The linear nature of  $T_c$  vs.  $1/R$  is explained by using a simple thermodynamic model of heterogeneous crystal nucleation at the liquid-glass interfaces.

[1] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2003, 67, 085405. [2] Kellermann G., Craievich A. F., *Phys. Rev. B*, 2002, 65, 134204.

**Keywords:** nanocrystals, melting, SAXS WAXS