

NOVEL HUME-ROTHERY PHASES IN SP METALS AND ALLOYS UNDER HIGH PRESSURE

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The classical Hume-Rothery phases in the noble metal alloys have the structures controlled by the average number of valence electrons within the range 1 to 2 el/at. Application of high pressure yields the formation of phases in sp metals and alloys in the range up to 5 el/at. The concept of Brillouin zone - Fermi sphere interaction is employed to explain the stability of the novel Hume-Rothery phases observed under high pressure. Recent experimental high-pressure studies on binary alloys based on In and Sn provide the data on tetragonal phases with a specific variation of c/a along the alloy composition [1,2]. This sequence involves tetragonal phases presenting the structural fcc - bcc transformation, known as Bain path. Correlation of c/a with the electron/atom ratio implies that the valence electrons exert a driving force for a tetragonal distortion in these phases. Intermediate phases with a complex oC_{16} - $Cmca$ structure are observed under pressure in the binary Bi alloys with In, Pb and Sn [3,4]. The reasons of formation of this complex structure are related to that of the Hume-Rothery γ -brass phase.

References

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Keywords: PHASE TRANSITION BINARY ALLOYS BRILLOUIN ZONE**TRANSITION TO A RELAXOR-LIKE PHASE IN LEAD ZIRCONATE TITANATE (PZT) AT HIGH PRESSURE**J. Haines¹ J. Rouquette¹ V. Bornand¹ M. Pintard¹ Ph. Papet¹ R. Astier² J. M. Leger³ F. Gorelli⁴¹Universite Montpellier II Lpmc Umr Cnrs 5617 Place E. Bataillon Cc003 MONTPELLIER 34095 CEDEX FRANCE ²Institut Gerhardt, Universite Montpellier II, Montpellier, France ³LPMTM, UPR CNRS 9001, Universite Paris-Nord, Villetaneuse, France ⁴LENS and INFN, Sesto Fiorentino, Italy

The perovskite solid solution between lead zirconate and lead titanate $PbZr_{(1-x)}Ti_xO_3$ (PZT) is of great interest due to its very high piezoelectric response near what is termed the 'morphotropic phase boundary' between ferroelectric rhombohedral (space group $R3m$), monoclinic (space group Cm) and tetragonal (space group $P4mm$) phases for x values of close to 0.48. The dielectric and piezoelectric properties of PZT ceramics, which are mainly governed by domain wall motion, are known to be sensitive to stress induced by external elastic or electric fields and in this respect it is also very important to understand the effect of hydrostatic pressure on the phase diagram of this material. Tetragonal $PbZr_{0.52}Ti_{0.48}O_3$ was studied up to 18 GPa by angle-dispersive, x-ray diffraction using an imaging plate and by Raman spectroscopy. A novel phase transition was found in this system at close to 5 GPa. Whereas the x-ray diffraction data indicated no deviation from cubic symmetry above this pressure, a strong Raman signal was present in this phase. The Raman spectrum obtained is similar to those observed for ferroelectric relaxors and is in sharp contrast with the forbidden first-order Raman spectrum, which would be expected for a cubic paraelectric phase, such as that observed at high temperature and ambient pressure. This process involves a change from long range order in the ferroelectric phase to short range order in the high-pressure phase.

Keywords: HIGH PRESSURE PHASE TRANSITION FERROELECTRIC**HIGH-PRESSURE PHASE TRANSITION IN THE CHEVREL-PHASE $SnMo_6S_8$** W. Depmeier¹ L. Ehm¹ K. Knorr¹ A. Krimmel² P. Bouvier³ M. Mezouar³¹University of Kiel Institut fuer Geowissenschaften Olshausenstrasse 40 KIEL D-24098 GERMANY ²Lehrstuhl Experimentalphysik 5, Universitaet Augsburg, D 86159 Augsburg ³European Synchrotron Radiation Facility, F 38043 Grenoble Cedex

The Chevrel-phase $SnMo_6S_8$ is build of Mo_6S_8 clusters, in which a Mo_6 octahedron is inscribed into a S_8 cube. The tin atoms are located at the origin of the rhombohedral unit cell ($a = 6.515(2)\text{\AA}$, $\alpha = 89.6(1)^\circ$), thus retaining one Mo_6S_8 per unit cell forming a simple pseudo cubic array [1]. An important feature of these compounds arises from the interconnection of Mo_6S_8 clusters giving interesting electronic properties and making these Chevrel-phases high-field superconductors with a relatively high T_c [2]. The application of high-pressure to these compounds is of interest, because of possible changes in the electronic structure and associated properties.

The high-pressure experiments were performed at beamline ID30 at the ESRF, using a diamond anvil cell and a mar345 image plate detector. Powder diffraction patterns were collected in the pressure range from ambient pressure to up 38 GPa. At approximately 2.8 GPa the onset of a structural transition from the rhombohedral to an orthorhombic phase can be observed. The phase transition is not accompanied by a discontinuity in the unit cell volume. The pressure dependence of the unit cell volume can be fitted with a single Birch-Murnaghan equation of state [3], resulting in 70(3) GPa for the bulk modulus K , and 3.8(4) for its pressure derivative K' .

References

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Keywords: CHEVREL PHASES HIGH PRESSURE PHASE-TRANSITION**THE PHASE DIAGRAMS OF MERCURY HALIDES**M. Hostettler¹ V. Dmitriev² H. P. Weber² D. Schwarzenbach¹
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The mercury halides, HgX_2 ($X = Cl, Br, I$), form solid phases which can be interpreted as close packed anions with mercury atoms filling interstitial sites. At ambient conditions, the thermodynamically stable phase of HgI_2 presents a tetragonal layered structure ($P4_2/nmc$) made of corner-shared HgI_4 tetrahedra. $HgBr_2$ adopts an orthorhombic structure ($Cmc2_1$) showing straight Br-Hg-Br molecules and a strongly deformed octahedral Hg-coordination, while $HgCl_2$ shows straight Cl-Hg-Cl molecules in the mirror plane of the space group $Pnma$ and a deformed rhombohedral Hg-coordination.

At ambient pressure, the tetrahedral phase of HgI_2 undergoes a reconstructive transition at 400 K into a monoclinic polar phase ($P2_1$) similar to the $Cmc2_1$ structure of $HgBr_2$, but with bent I-Hg-I molecules. The orthorhombic phase of $HgBr_2$ is stable for all temperatures up to the fusion, while $HgCl_2$ undergoes a transition to a cubic phase just a few degrees before its fusion.

Spectroscopic studies of the HgX_2 system [D.M. Adams & R. Appleby, J.C.S. Chem Comm. (1976) 975-976] have revealed the existence of a variety of high-pressure phases, the structures of which have not yet all been determined. We undertook powder diffraction studies, as a function of temperature and/or pressure, to obtain structural information. Newly identified phases of HgX_2 have monoclinic, orthorhombic, trigonal and rhombohedral symmetries. Several of the phase transformations are reconstructive, leading to changes in the packing of the anions. An overview of all diverse structures, symmetries and types of transitions observed in our studies of HgX_2 will be presented.

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