

## Poster Sessions

to occur, the band maximum showing a non-linear blue shift with pressure.

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### MS40.P15

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#### Pressure-induced B1-B2 phase transition in AgX : revisited

Jennifer Kung, Chia-Hui Lin, *Department of Earth Sciences, National Cheng Kung University (Taiwan)*. E-mail: jkung@mail.ncku.edu.tw

A large number of known AB compounds adopt the B1 (NaCl) structure. Under pressure, most of them transform to the B2 (CsCl) structure directly or via intermediate phase(s). The computational investigations suggest that the dense B2 phase is favored at high pressure for silver halides with the B1-structure (AgX, X=Cl, Br and I). The experimental studies have shown that AgCl transforms from B1 to B2 at 17 GPa, 200 °C [1]. In-situ X-ray work [1] showed two intermediate phases existing between the B1 - B2 phase transition in AgCl, with the structure of KOH and TII, respectively. As for AgBr and AgI, both are known to undergo B1- KOH-type structural transitions [2] in the pressure range between 13 - 16 GPa. In this study, we extended the experimental conditions to higher pressure to investigate the phase transitions in AgBr and AgI and to find out if they share the same topological transition as AgCl under high pressure.

The silver halides were studied in the diamond anvil cell (DAC) by angular dispersive X-ray powder diffraction technique. The high-pressure phase transformations of AgCl, AgBr and AgI were investigated up to 28, 41 and 56 GPa, respectively. In AgCl, a phase transition sequence B1 → KOH → TII → B2 was observed at high pressure, room temperature. The pathway of transformations in AgBr was found to be B1 → (unknown phase) → KOH → TII at high pressure. The "unknown phase" observed in AgBr was found for the first time and has been detected in three consecutive runs carried out in this study. At 35.5 GPa, we applied the laser heating (estimated temperature ~ 500 °C) and found that TII-type AgBr maintained the same structure type (TII). For AgI, the KOH-type high-pressure phase was observed up to 27 GPa. Upon further compression to the pressure of 56 GPa, and after annealing by laser heating (estimated temperature ~ 500 °C), AgI did not transform to the B2 phase. Based on the current experimental results, we conclude that the topological transition of B1-KOH-TII-B2 type AgCl can be achieved by applying pressure along. The occurrence of the TII phase in AgBr at high pressures, shows that the structural transition sequence of B1-B2 in AgBr is similar to the one found in AgCl. Yet, an additional new low-pressure phase is found to exist in AgBr between the B1 and KOH phase.

Computational studies confirm the same transition sequence for the B1-B2 transition of AgI [3]. Within the experimental data resolution, KOH-type AgI is identified to be stable up to 27 GPa, at least. Compared with AgCl and AgBr, the stability range of the KOH-type AgI is surprisingly wide, an effect which has also been noted in the computational study [3]. However, our x-ray diffraction data of AgI above 40 GPa do not confirm the TII structure type, which was predicted to be the stable polymorph in the computational studies [3].

In general, the transition pressures of this multiple series of solid-solid phase transformation are increasing with decreasing ionicity of

this series of AgX compounds. The ionicities for AgCl, AgBr and AgI are 0.869, 0.847 and 0.775, respectively. The predicted pressures to reach the stability region of the B2-type structures for AgBr and AgI are above 35 GPa [4] and 105 GPa [5], respectively.

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#### Polymorphism of 1,4-diazabicyclo[2.2.2]octane complexes with HI and HBr

Anna Olejniczak, Waldemar Nowicki, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, (Poland)*. E-mail: aniao@amu.edu.pl

Materials with dielectric constant exceeding 1000 are most coveted for electronic applications in miniature devices. Such properties are exhibited by ferroelectric relaxors, which are mainly the doped lead-containing perovskite ceramics. Therefore organic relaxors are sought, which would be easier in production and more environment friendly: less energy is required for their production and deposition on substrates and they are easier for disposal. Most recently the giant dielectric response was found in NH<sup>+</sup>...N bonded 1,4-diazabicyclo[2.2.2]octane hydroiodide (dabcoHI) and hydrobromide (dabcoHBr) [1, 2].

A multitude of new polymorphs of dabcoHI has been obtained at elevated pressure and temperature [3]. The crystal symmetries identified for the nonsolvated dabcoHI crystals so far are: *P6m2*, *Pbcm*, *Pmc2<sub>1</sub>*, *Pmm2*, *Cmm2*, *P2/c*. In all the structures determined by X-ray diffraction linear or nearly linear chains of cations are linked by NH<sup>+</sup>...N hydrogen bonds. The main structural differences between the polymorphs are in the arrangement of the poly-cationic chains and iodide anions, and in the conformation of dabco cations. When crystallized from methanol, up to 1.70(5) GPa dabcoHI forms unsolvated crystals, and at higher pressure solvates could be obtained only.

Only three phases of dabcoHBr could be obtained: phase I (*Pca2<sub>1</sub>*), phase II (*Cmc2<sub>1</sub>*) and phase III (*P6m2*). The NH<sup>+</sup>...N hydrogen bonded chains, which are characteristic for all dabcoHI structures, are present only in phase III of dabcoHBr. In phases II and III they are broken and NH<sup>+</sup>...Br ionic pairs are formed. Moreover, pressure 1.30 GPa led to N-methylation of dabco.

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#### Amorphization in rare earth tungstates with modulated scheelite-type structure under pressure

N. Sabaliskis,<sup>a</sup> L. Mestres,<sup>b</sup> X. Vendrell,<sup>b</sup> E. Cerdeiras,<sup>b</sup> D. Santamaría,<sup>c</sup> V. Lavin,<sup>d</sup> A. Muñoz,<sup>e</sup> P. Rodríguez-Hernández,<sup>e</sup> J. Lopez-Solano,<sup>c</sup> E. Matesanz,<sup>f</sup> M. C. Guzman-Afonso<sup>d</sup> <sup>a</sup>*Departamento de Física Básica-Universidad de La Laguna, S/C Tenerife, (Spain)*. <sup>b</sup>*Departamento de*