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## Enthalpy relaxation in the Ag<sub>3</sub>PS<sub>4</sub> glass prepared by mechanochemical synthesis

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Mechanical milling can be used to amorphize certain kinds of crystalline materials. The thus-derived glassy materials cannot be synthesized using conventional methods, e.g., melt quenching. Despite some progress in understanding the nature of these milling-generated glasses, several important aspects such as the sub- $T_g$  relaxation, glass formation and glass transition of such glasses are still far from being understood. In this work, we explore these aspects by 1) preparing a new type of glass - the Ag<sub>3</sub>PS<sub>4</sub> glass via a high-energy ball-milling process, 2) by annealing it below  $T_g$ , and 3) by measuring the thermal responses using differential scanning calorimeter (DSC). The DSC results show an interesting sub- $T_g$  relaxation feature in the as-produced sample. i.e., the occurrence of multiple enthalpy relaxation events below  $T_g$  during a dynamic heating protocol. In this work we reveal the origin of these multiple events by analyzing structural heterogeneity, glass formation mechanism, relaxation modes, polyamorphism, and surface characteristics. We also discussed the relationship between milling energy and enthalpy relaxation. This study provides insight into the structure-functionality relation in this new type of mechanically amorphized material.

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