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## High pressure structural and vibrational studies of $\beta$ - and $\alpha$ -In<sub>2</sub>Se<sub>3</sub>-like Ga<sub>2</sub>S<sub>3</sub>

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Tetradymite  $\alpha$ -Bi<sub>2</sub>Te<sub>3</sub> (space group (S.G.) R-3m, centrosymmetric) is well known to be found in a few group-V A<sub>2</sub>X<sub>3</sub> compounds (A=As, Sb, Bi) at room conditions (RC). Under high temperature (HT), this R-3m can be obtained in the In<sub>2</sub>Se<sub>3</sub>, the  $\beta$  phase [1], which belongs to the group-III A<sub>2</sub>X<sub>3</sub> compounds (A=Al, In, Ga). A few theoretical works have shown that this  $\beta$ -In<sub>2</sub>Se<sub>3</sub>-like structure is stable above the theoretical T<sub>c</sub> calculated, following a tendency of Al<sub>2</sub>X<sub>3</sub> > Ga<sub>2</sub>X<sub>3</sub> > In<sub>2</sub>X<sub>3</sub> [2], starting from the  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>-type structure (s.g. R3m, non-centrosymmetric), which is stable at RC. Such structure is dynamically stable for all this family at RC [2], unlike the  $\beta$ -In<sub>2</sub>Se<sub>3</sub>-like structure [3]. The seeking of centrosymmetric and non-centrosymmetric structures, together with the easiest way to switch between them, are being studied for ferroelectric, pyroelectric, and piezoelectric applications, among others.

Multiple high-pressure works on such A<sub>2</sub>X<sub>3</sub> compounds, both from V and III groups have been released for years, where in situ high-pressure x-ray diffraction (HP-XRD) measurements have been deployed to characterize the phase transitions (PTs) observed and the related structural changes. In addition, other experimental techniques are employed, supported by DFT calculations, to fully understand these PTs. In this sense,  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> undergoes a PT to  $\beta$ -In<sub>2</sub>Se<sub>3</sub> at above 10-12 GPa, after transforming into  $\beta'$ -In<sub>2</sub>Se<sub>3</sub> at 1 GPa [4]. Very recently, Ga<sub>2</sub>S<sub>3</sub> transforms into this  $\beta$ -In<sub>2</sub>Se<sub>3</sub>-like structure was observed at about 16 GPa [7]. Evidence of such PT has been stressed in subsequent works [8, 9]. What is more unexpected, after this  $\alpha'$ - $\beta'$ PT on Ga<sub>2</sub>S<sub>3</sub>, two other polymorphs have been synthesized upon decreasing pressure, at 9.0 and 3.0 GPa, respectively [8]. However, further information about the nature of both polymorphs was not given.

In this work, we have confirmed this  $\beta'$ -Ga<sub>2</sub>S<sub>3</sub> under HP via XRD and Raman measurements, joint theoretical simulations. Upon decreasing pressure,  $\alpha$ -In<sub>2</sub>Se<sub>3</sub>-like structure matches quite well with the 1st polymorph observed at 9.0 GPa ( $\phi$ -Ga<sub>2</sub>S<sub>3</sub>). Raman signatures and pressure dependence of structural parameters have allowed us to discern such  $\beta'$ - $\phi$  PT. The 2nd polymorph below 1.0 GPa has been identified with a disordered zincblende ( $\gamma$ -Ga<sub>2</sub>S<sub>3</sub>). To complement our results, we discuss the relation between the PTs of both Ga<sub>2</sub>X<sub>3</sub> and AGa<sub>2</sub>X<sub>4</sub> compounds.

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[2] J. Liu et al., *2D Mat.* 2019, 6, 025001.

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[7] X. Lai et al., *J. Appl. Phys.* 2014, 116, 193507.

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[9] S. Gallego-Parra et al., *Phys. Chem. Chem. Phys.* 2021, 23, 6841-6862.

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