Resolving ^{71}Ga NMR Signals of Ga_2Se_3 Using QMATPASS at 35.2 T

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Introduction

Chalcogenide crystals and glasses are technologically important materials that can be suitably designed to exhibit many interesting physical properties including high transparency in the infrared range, low phonon energy, high optical non-linearity, large photo-sensitivity and high ionic conductivity. Beyond the usual systems based on Ge-Sb-Se or Ge-As-Se moieties, one of the pseudo-binary systems that display glass-forming ability over a significant composition range is Ga_2Se_3-$GeSe_2$. One of the most powerful ways to improve the properties of these gallium and germanium selenide glasses is through the determination of structure-activity relationships. Hence, it is critical to have a precise understanding of the atomic-level structure. Various techniques, including Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Extended X-rAy Fine Structure (EXAFS) as well as ^{77}Se and ^{71}Ga solid-state NMR spectroscopy have been used to probe the atomic-level structure of these gallium and germanium selenide glasses [1]. Nevertheless, there are still unsettled questions about the atomic-level structure of these glasses. Solid-state NMR is a powerful local characterization technique to identify molecular motifs in glass. We present in this report the NMR study of gallium and germanium selenide glasses by first assigning the NMR signals of parent crystalline compounds, such as Ga_2Se_3.

Experimental

^{71}Ga NMR spectra of Ga_2Se_3 were acquired at B_0 = 35.2 T using the series-connected hybrid (SCH) magnet at the NHMFL. The sample was packed in a 3.2 mm rotor and spun at 18 kHz. 2D ^{71}Ga Magic Angle Turning Quadrupolar Phase Adjusted Spinning Sideband (QMATPASS) [2] was used to resolve spinning sidebands produced by second-order quadrupolar interaction. Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) multiple-echo detection [3] was used to enhance the sensitivity.

Results and Discussion

Even at 35.2 T field and 18 kHz MAS frequency, the spinning sidebands of ^{71}Ga NMR central transition of Ga_2Se_3 overlap (Fig. 1 top). These spinning sidebands were separated using 2D QMATPASS experiment (Figs. 2 and 1 bottom). The signal from the cubic phase of Ga_2Se_3 concentrates mostly in the centerband due to its relatively small quadrupolar coupling. The signal from the monoclinic phases spreads over seven spinning sidebands from the large and anisotropic second-order interaction.

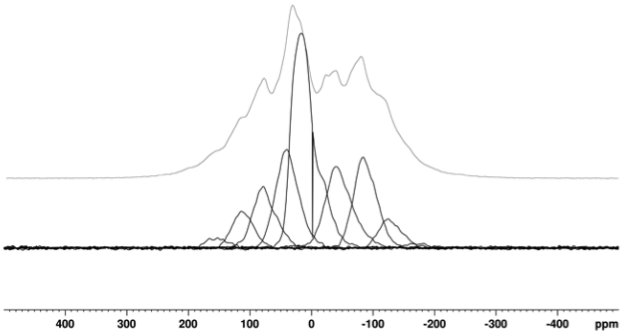

Fig.1 1D ^{71}Ga NMR spectrum of Ga_2Se_3 obtained by the summation of QCPMG echoes (top) and sidebands extracted from the 2D ^{71}Ga QMATPASS spectrum of Fig. 2 (bottom).

Conclusions

We acquired the ^{71}Ga NMR spectrum of Ga_2Se_3 at B_0 = 35.2 T and MAS frequency of 18 kHz. The uses of high magnetic field and QMATPASS are essential to separate the signal of cubic phase and the sideband pattern of monoclinic one.

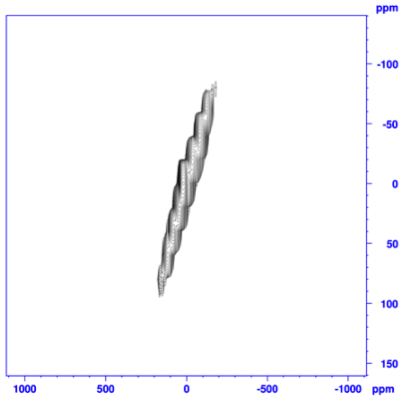

Fig.2 2D ^{71}Ga QMATPASS spectrum of Ga_2Se_3 at 35.2 T.

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