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^{71}Ga-^{77}Se connectivities and proximities in gallium selenide crystal and glass probed by solid-state NMR

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ABSTRACT

We introduce two-dimensional (2D) ^{71}Ga-^{77}Se through-bond and through-space correlation experiments. Such correlations are achieved using (i) the *J*-mediated Refocused Insensitive Nuclei Enhanced by Polarization Transfer (*J*-RINEPT) method with ^{71}Ga excitation and ^{77}Se Carr-Purcell-Meiboon-Gill (CPMG) detection, as well as (ii) the *J*- or dipolar-mediated Hetero-nuclear Multiple-Quantum Correlation (*J*- or *D*-HMQC) schemes with ^{71}Ga excitation and quadrupolar CPMG (QCPMG) detection. These methods are applied to the crystalline β-Ga_2Se_3 and the $0.2Ga_2Se_3$-$0.8GeSe_2$ glass. Such glass leads to a homogeneous and reproducible glass–ceramic, which is a good alternative to single-crystalline Ge and polycrystalline ZnSe materials for making lenses transparent in the IR range for thermal imaging applications. We show that 2D ^{71}Ga-^{77}Se correlation experiments allow resolving the ^{77}Se signals of molecular units, which are not resolved in the 1D ^{77}Se CPMG spectrum. Additionally, the build-up curves of the *J*-RINEPT and the *J*-HMQC experiments allow the estimate of the ^{71}Ga-^{77}Se *J*-couplings via one and three-bonds in the three-dimensional network of β-Ga_2Se_3. Furthermore, these build-up curves show that the one-bond $^1J_{^{71}Ga\text{-}^{77}Se}$ couplings in the $0.2Ga_2Se_3$-$0.8GeSe_2$ glass are similar to those measured for β-Ga_2Se_3. We also report 2D ^{71}Ga Satellite Transition Magic-Angle Spinning (STMAS) spectrum of β-Ga_2Se_3 using QCPMG detection at high magnetic field and high Magic-Angle Spinning frequency using large radio frequency field. Such spectrum allows separating the signal of β-Ga_2Se_3 and that of an impurity.

1. Introduction

Chalcogenide 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 [1–7]. 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-$GeSe_2$ [8]. Previous studies using Raman, X-ray photo-electron (XPS), extended X-ray absorption fine-structure (EXAFS), as well as ^{77}Se and ^{71}Ga solid-state NMR (SS-NMR) spectroscopies have shown that the structures of these gallium and germanium selenide glasses (denoted GGS hereafter) are composed predominantly of a network of corner-sharing (CS) $GaSe_4$ and/or $GeSe_4$ tetrahedra and a small fraction of edge-sharing (ES) $GaSe_4$ and/or $GeSe_4$ tetrahedra, in which the Ga, Ge, and Se atoms are covalently bonded to 4, 4, and 2 neighboring atoms, respectively [9–13]. The tetra-coordinated Ga and Ge sites and the di-coordinated Se ones are denoted Ga^{IV}, Ge^{IV} and Se^{II} hereafter. XPS and ^{71}Ga SS-NMR spectroscopy have demonstrated that the addition of Ga_2Se_3 increases the deficiency in Se and leads to the formation of Ge-Ge bonds and $(Se^{II})_3$-Ge-Ge-$(Se^{II})_3$ units, which are distributed in such way that any clustering of these units is avoided [11,12]. Furthermore, Raman spectroscopy and ^{77}Se SS-NMR studies, including two-dimensional (2D) ^{77}Se MATPASS/CPMG (Magic-Angle Turning-Phase Adjusted Spinning Sidebands with Carr-Purcell-Meiboon-Gill detection) experiments, have shown the formation of tri-coordinated Se atoms (Se^{III}) in GGS glasses with high content of Ga_2Se_3 (>25% mol) [12,13]. The

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formation of these sites provides another mechanism to accommodate the deficiency in Se atoms. These Se^{III} species mainly replace the Se^{II} ones in the CS $GaSe_4$ and/or $GeSe_4$ tetrahedra.

As mentioned above, SS-NMR is a precious tool to characterize the local environment of atoms in GGS glasses. ^{77}Se isotope possesses a nuclear spin of 1/2, a gyromagnetic ratio similar to that of ^{29}Si nucleus ($\gamma_{77Se} \approx 0.96\gamma_{29Si} \approx 0.76\gamma_{13C}$) and a low natural abundance, $NA_{77Se} \approx 7.63\%$ [14]. As ^{29}Si nuclei, ^{77}Se isotope exhibits long longitudinal relaxation times in solids. Furthermore, ^{77}Se NMR resonances are often broad, notably for glasses. Such broadening further reduces the sensitivity since the total integrated intensity is spread over a broad spectral width. Ga element has two stable NMR-active isotopes, ^{69}Ga and ^{71}Ga, both with spin-3/2. ^{69}Ga is more abundant than ^{71}Ga ($NA_{69Ga} \approx 60.4\%$ and $NA_{71Ga} \approx 39.6\%$), but the latter possesses higher gyromagnetic ratio ($\gamma_{69Ga} \approx 0.96\gamma_{13C}$ and $\gamma_{71Ga} \approx 1.22\gamma_{13C}$) and smaller quadrupole moment ($Q_{69Ga} = 17.1$ and $Q_{71Ga} = 10.7$ fm^2). Therefore, ^{71}Ga NMR experiments are more sensitive than ^{69}Ga ones. Nevertheless, even for ^{71}Ga isotope, the quadrupole interaction can broaden the NMR resonance over hundreds of kHz and the detection of these broad powder patterns is often challenging. Finally, the detection of ^{73}Ge nuclei by SS-NMR spectroscopy remains extremely challenging owing to the unfavorable properties of this isotope: low gyromagnetic ratio ($\gamma_{73Ge} \approx 0.14\gamma_{13C}$), low natural abundance ($NA_{73Ge} \approx 7.76\%$), high spin value of 9/2, and large quadrupole moment ($Q_{73Ge} = -19.6$ fm^2). Nevertheless, ^{73}Ge SS-NMR spectra of germanium selenide glasses have been reported [15].

A major limitation of this study is the lack of resolution of 1D NMR spectra of GGS glasses since the resonances are broaden by the distribution of local environments as well as the anisotropic interactions, such as Chemical Shift Anisotropy (CSA) for ^{77}Se nuclei and quadrupole interaction for ^{71}Ga and ^{73}Ge isotopes. Recently, 2D experiments have allowed the measurement of one-bond *J*-coupling between ^{77}Se nuclei in arsenic selenide glasses [16]. Furthermore, it has been shown that the 2D MATPASS/CPMG sequence can improve the resolution of ^{77}Se signals for germanium selenide and GGS glasses by separating the isotropic chemical shift and the CSA in two distinct dimensions [13,17]. Nevertheless, to the best of our knowledge, the *J*-couplings between ^{77}Se and ^{71}Ga nuclei have not been measured so far. Similarly, neither through-bond nor through-space ^{71}Ga-^{77}Se hetero-nuclear correlation (*J*-HETCOR and *D*-HETCOR, respectively) 2D spectrum has been reported hitherto.

In this article, we introduce such ^{71}Ga-^{77}Se HETCOR 2D experiments. The sequences are first tested on β-Ga_2Se_3 crystalline sample. Using high-magnetic field (21.1 T), high Magic-Angle Spinning (MAS) frequency, $\nu_R = 62.5$ kHz, and large radio frequency (rf) field we observe for this sample two distinct ^{71}Ga signals, a broad peak and a narrow one of an impurity accounting for 12% of the total signal. Previous SS-NMR studies at lower field, MAS frequency and rf-field have only reported the observation of this narrow peak [12]. We also report a high-resolution ^{71}Ga 2D spectrum of β-Ga_2Se_3 acquired by introducing a Satellite Transition MAS (STMAS) experiment [18,19] using quadrupolar CPMG (QCPMG) detection [20] at 21.1 T and $\nu_R = 62.5$ kHz. The 2D ^{71}Ga STMAS-QCPMG spectrum allows separating the NMR signals of the impurity and β-Ga_2Se_3, but not those of the two Ga^{IV} sites in β-Ga_2Se_3 [21].

The 2D ^{71}Ga-^{77}Se through-bond spectra are acquired by introducing (i) the Refocused Insensitive Nuclei Enhanced by Polarization Transfer (*J*-RINEPT) experiment [22], with ^{71}Ga excitation and ^{77}Se CPMG detection [16], called ^{77}Se-{^{71}Ga}, as well as (ii) the Hetero-nuclear Multiple-Quantum Correlation (*J*-HMQC) experiment [23], with ^{71}Ga excitation and QCPMG detection, the ^{77}Se signal being indirectly detected, called ^{71}Ga-{^{77}Se}. Both ^{77}Se-{^{71}Ga} *J*-RINEPT-CPMG and ^{71}Ga-{^{77}Se} *J*-HMQC-QCPMG 2D spectra show the expected correlation between the broad ^{71}Ga signal of β-Ga_2Se_3 and the $^{77}Se^{II}$ and $^{77}Se^{III}$ signals. Furthermore, those spectra also exhibit a cross-peak between the ^{71}Ga narrow signal of the impurity and the $^{77}Se^{III}$ signals. Such observation indicates that the impurity mainly contains Se^{III} sites. In addition, by fitting the evolution of the ^{77}Se-{^{71}Ga} *J*-RINEPT and ^{71}Ga-{^{77}Se} *J*-HMQC signals as function of the defocusing and/or refocusing delays, τ and τ' (see Fig. 1), we measure for the first time the one-bond and three-bonds *J*-couplings, denoted ^1J and ^3J, respectively, between ^{71}Ga isotope and $^{77}Se^{II}$ or $^{77}Se^{III}$ nuclei. The 2D ^{71}Ga-^{77}Se through-space spectrum is acquired by introducing the ^{71}Ga-{^{77}Se} dipolar-mediated HMQC experiment (*D*-HMQC) [24,25] with QCPMG detection. The ^{71}Ga-^{77}Se dipolar couplings are reintroduced under MAS by applying the Simultaneous Frequency and Amplitude Modulation ($SFAM_1$) recoupling [26–28] during the defocusing and refocusing delays. The sensitivity of this through-space correlation experiment is compared to that of through-bond ones.

These 2D ^{71}Ga-^{77}Se *J*- and *D*-HETCOR experiments are then applied to characterize the xGa_2Se_3-$(1-x)GeSe_2$ glass with $x = 0.2$ (denoted $GGS_{0.2}$ hereafter). The GGS_x glass-ceramics are a good alternative to single-crystalline Ge and polycrystalline ZnSe materials for making lenses transparent in the IR range for thermal imaging applications. The $GGS_{0.2}$ composition leads to a homogeneous and reproducible glass–ceramic using suitable heat treatment over its glass transition temperature. For this sample, the controlled nucleation rate is assumed to be due to a specific phenomenon of phase separation [8]. The same behavior has been observed in sulfide based glasses of the same composition, highlighting the important role of gallium during the nucleation process [11,29]. The obtained glass-ceramics present enhanced mechanical properties, while keeping an excellent transparency in the mid-infrared range. The ^{71}Ga-^{77}Se *J*- and *D*-HETCOR 2D spectra permit to resolve and identify molecular units containing Ga and Se atoms in $GGS_{0.2}$ glass. Furthermore, the evolutions of ^{77}Se-{^{71}Ga} *J*-RINEPT and ^{71}Ga-{^{77}Se} *J*-HMQC signals as function of the scalar recoupling delays allow the estimate of the $^1J_{71Ga\text{-}77Se}$ couplings and indicates that the ^{71}Ga-^{77}Se covalent bonds in $GGS_{0.2}$ glass are similar to those of β-Ga_2Se_3.

2. Methods

2.1. NMR methods

2.1.1. Acquiring ^{71}Ga 1D MAS spectra

As seen below, ^{71}Ga isotope in β-Ga_2Se_3 crystal and $GGS_{0.2}$ glass is subject to large quadrupole interactions. In order to improve the spectral resolution, ^{71}Ga 1D spectra were acquired at high magnetic field, $B^0 = 21.1$ T, and high MAS frequency, $\nu_R = 62.5$ kHz, since for quadrupolar nuclei the resolution is proportional to $(B^0)^2$ and MAS can improve the spectral resolution by a factor of ca. 3–4 by partially averaging the second-order broadening, at least when the spinning sidebands are separated from the center-bands. As seen in Fig. 3b,d, the MAS averaged line-width of the central transition (CT) between energy levels ±1/2 of ^{71}Ga nuclei extends over 60 kHz in β-Ga_2Se_3 crystal and $GGS_{0.2}$ glass, and hence a high MAS frequency of $\nu_R \geq 60$ kHz is required.

2.1.2. CPMG and QCPMG

As explained in the introduction, ^{71}Ga and ^{77}Se spectra of GGS glasses exhibit wide powder patterns, which result in low sensitivity. Nevertheless, for these isotopes, the decay of the top of the echo signal for increasing spin-echo delay is often much slower than that of the Free-Induction Decay. Consequently, the sensitivity can be enhanced by acquiring multiple rotor-synchronized echoes in the form of the CPMG scheme for ^{77}Se nuclei [16] and