

Al coordination in bulk $\text{Al}_x\text{Te}_{1-x}$ glasses from solid-state NMR

S. Murugavel and S. Asokan*

Department of Instrumentation, Indian Institute of Science, Bangalore 560012, India

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Magic-angle-spinning NMR spectroscopic studies (^{27}Al) have been undertaken to probe the local structure of Al in Al-Te glasses and stoichiometric and nonstoichiometric crystalline Al-Te samples. The chemical-shift values obtained clearly indicate that there are two different Al environments in Al-Te glasses, corresponding to fourfold and sixfold coordinated Al. The relative proportions of the two sites vary with the composition. Though known to occur in oxide glasses, the sixfold coordination of Al has been found for the first time to our knowledge in the present study in a nonoxide, chalcogenide glass. In stoichiometric crystalline composition, only an octahedral coordination (hexagonal structure) is found, whereas the nonstoichiometric crystalline sample obtained by crystallizing the glass contains both sixfold and fourfold coordinated Al.

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I. INTRODUCTION

The local molecular structure of different chalcogenide glasses has not been fully understood, in spite of the technological applications of these materials.¹⁻³ Techniques such as Fourier transform infrared (FTIR), Raman, and Mössbauer are routinely used to probe the local structure of amorphous materials.⁴⁻⁶ However, it is usually difficult with these methods to deduce the coordination environment of a particular atom in a material. Although x-ray and neutron-diffraction techniques are used to elucidate the short-range order in amorphous materials, they provide only a partial structural information and are usually insensitive beyond the first coordination shell.⁷ This problem is exacerbated for materials containing more than a single type of atom. The solid state magic-angle-spinning (MAS) NMR technique provides a convenient means of obtaining direct information pertaining to the immediate local molecular environment in a glassy material.^{8,9}

There are many structural investigations¹⁰ in liquid alloys of group III elements with chalcogenides. However, not many studies have been undertaken on the local structure of III-VI chalcogenide glasses. In the present work, ^{27}Al MAS NMR experiments have been undertaken at 78.206 MHz, to probe the coordination of Al in Al-Te glasses of widely varying compositions. Investigation on crystalline Al-Te samples have also been undertaken to compare the coordination environment of Al in the crystalline state of the same system.

It is widely believed that Al coordinates only tetrahedrally in chalcogenide glasses,¹¹ though octahedral coordination of Al is known in oxide glasses.¹² The present results clearly indicate that in Al-Te glasses, Al resides in two different environments corresponding to tetrahedrally and octahedrally coordinated sites. In this sense, the present study underscores the ability of solid state MAS NMR chemical shifts to provide an important site differentiation in aluminum chalcogenide glasses and provides insight into the understanding of the local structure of these glasses. Also, the dual coordination of Al revealed in the present investigations, is likely to play a major role in various properties of Al-Te glasses.

II. EXPERIMENTAL

Bulk, semiconducting glasses of $\text{Al}_x\text{Te}_{100-x}$ ($17 \leq x \leq 30$) were prepared by conventional melt quenching method. As-prepared glassy samples were characterized by x-ray diffraction and differential scanning calorimetry (DSC) to determine the amorphous and glassy nature, respectively. The stoichiometric crystalline sample was formed by slow cooling of the melt and a representative nonstoichiometric crystalline sample ($\text{Al}_{23}\text{Te}_{77}$) was prepared by first forming the glass and subsequently annealing it inside an evacuated quartz ampoule (10^{-6} Torr) at the crystallization temperature (300°C) for about 2 h. Crystallized phases were identified by x-ray diffraction analysis.

Room temperature ^{27}Al MAS NMR spectra of crystalline and glassy samples were recorded with a Bruker DSX-300 spectrometer operating at 78.206 MHz. Compared to zeolites, β sialon, and other oxide systems, the chemical-shift distribution in Al chalcogenides is substantially wider, necessitating the use of extremely high spinning speeds to achieve the required resolution in chemical shifts. In this work, a cylindrical rotor with a spinning rate of 5–8 KHz was used to record the spectra. Chemical shifts were recorded with respect to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ as an external reference. Recorded spectra clearly indicate that difference between the glassy and crystalline samples.

III. RESULTS AND DISCUSSION

A. NMR studies of crystalline model compounds

Figure 1 shows the MAS NMR spectra of crystalline $\text{Al}_{40}\text{Te}_{60}$ and $\text{Al}_{23}\text{Te}_{77}$ samples. In both cases, substantial improvement in quality of the spectrum has been observed on going from a low field of 5 KHz to a high field of 8 KHz. The improvement involves the increase in intensity as well as the reduction in the width of the peak. These effects are expected and are due to the reduction in the second order quadrupolar effects at high fields.

Figure 1 indicates that in crystalline $\text{Al}_{23}\text{Te}_{77}$, there are two coordination environments for Al, namely, sixfold and fourfold coordinations, respectively. The chemical-shift val-

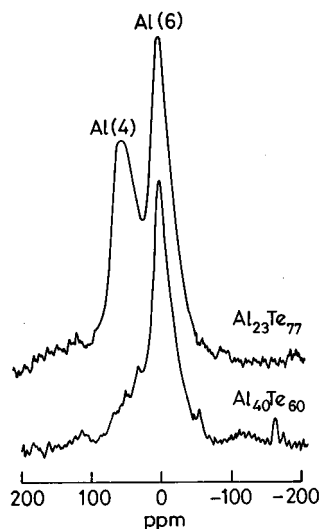


FIG. 1. Representative 76.206 MHz ^{27}Al MAS NMR spectra of crystalline compounds $\text{Al}_{23}\text{Te}_{77}$ and $\text{Al}_{40}\text{Te}_{60}$ samples with spinning speed 8 KHz.

ues of tetrahedrally and octahedrally coordinated aluminum have been found to vary between 62–66 ppm and between 5–7 ppm, respectively, on varying the field from 5 to 8 KHz. The maximum error involved in the chemical-shift measurements is less than ± 1 ppm.

It is interesting to note from the present NMR results that in the stoichiometric $\text{Al}_{40}\text{Te}_{60}$ crystalline sample, only octahedral coordination of Al is found (Fig. 1). X-ray structural reports¹³ on a crystalline Al_2Te_3 sample also indicate that this compound has an hcp structure, in which all the Al atoms can reside in an octahedral environment. NMR experiments on crystalline Al_2O_3 also indicates that only sixfold coordinated sites are possible for Al in this compound.¹⁴

As mentioned earlier, in $\text{Al}_{23}\text{Te}_{77}$ samples formed by crystallizing the glass, both tetrahedrally and octahedrally coordinated Al atoms are present. In this sense, the crystalline phases formed from the nonstoichiometric glasses by annealing, are structurally different. Earlier x-ray studies on thermally annealed Al-Te glasses also suggest the formation of a crystalline phase [ϕ -(Al-Te)] which does not correspond to the equilibrium crystalline compound Al_2Te_3 .¹⁵ Though the complete structure solution of this phase is not available, it is clear from the present NMR results that this phase is characterized by tetrahedral as well as octahedral coordination of Al.

B. NMR studies of Al-Te glasses

Figure 2 shows the composition dependent NMR spectra of $\text{Al}_x\text{Te}_{100-x}$ ($17 \leq x \leq 30$) glasses at 7 KHz. It is interesting to note that in all the Al-Te glasses studied, both fourfold and sixfold coordinated Al atoms are present. The chemical shifts values vary between 59–62 ppm for Al(4) sites and +9 to –6 ppm for Al(6) sites, which are consistent with the values obtained for crystalline samples (Fig. 1) and also those reported in literature (for zeolites).^{16–18} The small humps on the base line of the spectra are the spinning side bands arising due to chemical-shift anisotropy.

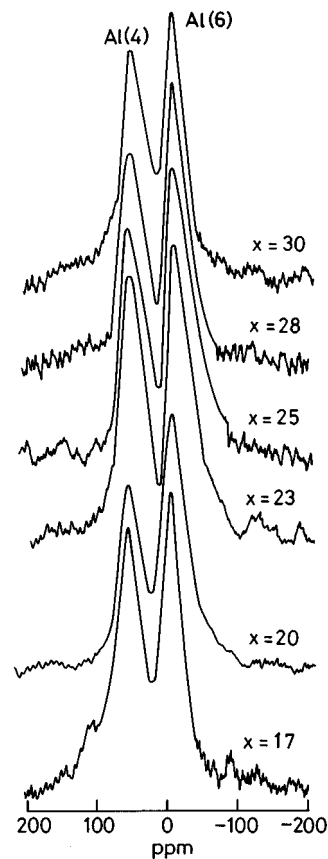


FIG. 2. Compositional dependence of the 76.206 MHz ^{27}Al MAS NMR spectra of $\text{Al}_x\text{Te}_{100-x}$ ($17 \leq x \leq 30$) glasses. The chemical shifts near 0 and 60 ppm are assigned to octahedral and tetrahedral coordinations, respectively. Other minor peaks in the spectra are spinning side bands. Spinning speed: 7 KHz.

The number of Al atoms in tetrahedral and octahedral environments are estimated from the area under the peak for each composition. Table I gives the ratio between the sixfold and fourfold coordinated Al atoms, estimated from the area under the peaks, for different compositions. In Fig. 3(a), the variation of glass transition temperature (T_g) of Al-Te glasses with composition has also been given as a reference for the reader. Figure 3(b) shows the variation with composition of the number of fourfold $\{x\text{Al}(4)/[\text{Al}(4)+\text{Al}(6)]\}$ and

TABLE I. ^{27}Al NMR chemical shifts and site quantitation in $\text{Al}_x\text{Te}_{100-x}$ ($17 \leq x \leq 30$) glasses and crystalline compounds. Chemical shifts δ are in ppm with respect to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, within the error of ± 1 ppm.

Atom % Al	$\delta(^{27}\text{Al})$ ppm	Area ratio %
17	61/–2	47:53
20	62/9	40:60
23	59/–5	48:52
25	59/–6	42:58
28	62/–2	46:54
30	59/–1	53:47
Crystalline $\text{Al}_{23}\text{Te}_{77}$	63/5	45:55
Crystalline $\text{Al}_{40}\text{Te}_{60}$	5	

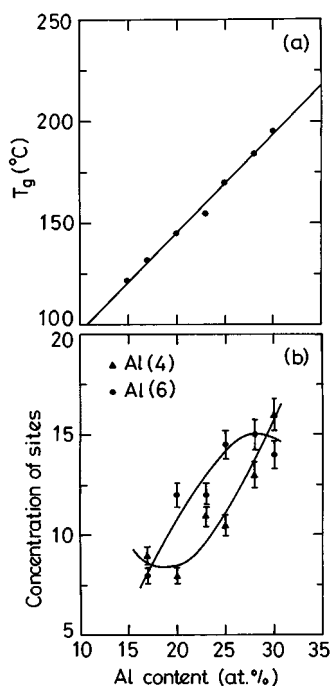


FIG. 3. (a) Compositional dependence of glass transition temperature in $\text{Al}_x\text{Te}_{1-x}$ glasses. (b) Compositional dependence of fraction of fourfold $N(4)$ and sixfold $N(6)$ coordinated Al sites in $\text{Al}_x\text{Te}_{1-x}$ glasses calculated by area under the peak $(x\text{Al}(4)/[\text{Al}(4)+\text{Al}(6)])$ and $x\text{Al}(6)/[\text{Al}(4)+\text{Al}(6)]$, respectively.

sixfold $\{x\text{Al}(6)/[\text{Al}(4)+\text{Al}(6)]\}$ coordinated Al atoms, in Al-Te glasses. It can be seen from this figure that in the composition range of glass formation ($15 \leq x \leq 30$), the number of fourfold coordinated Al ($N(4)$) increases continuously. However, the sixfold coordinated Al atoms ($N(6)$) increase with concentration and saturates around $x=28$.

It is interesting to note here that the ratio $\text{Al}(4):\text{Al}(6)$ is nearly the same in crystalline and glassy Al-Te samples (for example, 45:55 for crystalline and 48:52 for glassy $\text{Al}_{23}\text{Te}_{77}$ samples). This indicates that the local structure is similar in glassy and crystalline structures. However, the bond angle distortions in the glassy states, results broadening of the line-width.

The theoretical model¹⁹ on the dual coordination of an ionic species in a glass reveals that there exists a critical concentration above which only the coexistence of two coordination states can occur. However, this critical concentration may be too small to measure in certain systems. The

initial state in which the ionic species will reside depends on the base glass, environmental factors, and the species itself. In the Al-Te system, in the entire composition range of glass formation ($15 \leq x \leq 30$), we have the coexistence of sixfold and fourfold coordinated Al atoms. Nonstoichiometric crystalline phases obtained from the glasses also have dual coordination for Al. However, in the stoichiometric crystal, only octahedral Al sites are found. It may be concluded that there is some connection between the glass formation and the dual coordination of Al, in the Al-Te system. This aspect has to be investigated in more detail, in the future. Also, the composition dependence of relative populations of the sixfold and fourfold coordinated sites, is determined by the energy factors and their dependence on composition. Further theoretical investigations are required to understand the variation with composition, of the concentrations of tetrahedral and octahedral Al sites in Al-Te samples.

The fourfold and sixfold coordination of Al in Al-Te glasses results from the formation of a coordinate type of bonds between Al and Te, with the Al atom taking an electron from one of the neighboring Te atoms. The Te^+ which has given the electron becomes threefold coordinated. For fourfold coordination of Al, one neighboring Te becomes a C_3^+ center ($C=\text{chalcogen}$). For octahedral coordination of Al, three such C_3^+ centers have to be created. The higher coordination of Al necessarily means that there will more C_3^+ charged defect centers in Al-Te glasses, which are likely to play a crucial role in all the defect controlled properties including the electrical conductivity.

IV. CONCLUSION

The III group additives in chalcogenide glasses are generally believed to be in tetrahedral coordination. However, the present MAS NMR studies clearly indicate the coexistence of octahedral and tetrahedral Al sites in bulk Al-Te glasses and nonstoichiometric Al-Te crystalline phases. Such a high coordination is not encountered in any other metallic additive so far (e.g., Cu, Ag, Ga, Tl, etc.) in a chalcogenide matrix and it is likely to play a major role in the properties of these glasses.

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*Author to whom correspondence should be addressed. Electronic address: sasokan@isu.iisc.ernet.in

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