

High-Temperature NMR Studies of the Glass–Crystal Transition in the $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 System

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^{133}Cs NMR and 2D-EXSY NMR and ^{51}V NMR spectra have been recorded of $\text{Cs}_2\text{S}_2\text{O}_7$ and of the catalytically important $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 mixtures in the temperature range 20–550 °C, covering both the solid and liquid region. A high mobility of the Cs^+ cations in $\text{Cs}_2\text{S}_2\text{O}_7$ was observed below the melting point (461 °C), and two crystalline modifications seem to be present depending on the method of preparation of $\text{Cs}_2\text{S}_2\text{O}_7$. ^{133}Cs and ^{51}V NMR spectra of the $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 mixtures with the molar composition $\text{Cs}/\text{V} = 2$ and 4 show, by heating from room temperature, in both cases, that the glassy samples transform to crystalline $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ around 220 °C and that further heating of the samples up to the melting point leads to a mobility of the Cs cations similar to what was found for $\text{Cs}_2\text{S}_2\text{O}_7$. For a sample with the composition $\text{Cs}/\text{V} = 1$ a similar transformation from a glassy state at around 250 °C is observed; however, here the possible compound CsVO_2SO_4 seems to be transformed to another crystalline modification by heating to 400 °C. At 550 °C in the molten state the ^{51}V NMR spectra indicate that the coordination of vanadium changes from distorted octahedral in the solid to tetrahedral in the liquid state.

Introduction

The chemistry of the $\text{M}_2\text{S}_2\text{O}_7$ – V_2O_5 ($\text{M} = \text{Na}, \text{K}, \text{Cs}$) systems has been thoroughly investigated by a number of chemical and physical methods due to their importance as precursor of the catalysts used for production of sulfuric acid. The results of earlier studies are presented in ref 1 and references therein. Later, IR spectroscopy and thermography,² ESR,^{3,4} potentiometry, cryoscopy, and spectrophotometry,⁵ combined X-ray and IR spectroscopy,⁶ Raman spectroscopy,⁷ calorimetry,⁸ and ^{51}V and ^{17}O NMR⁹ have been used to elucidate the chemical species formed in these systems. Many important features have been documented. Several crystalline compounds formed in these systems have been isolated and identified,^{6,10,11} the formation of complexes between V(V) and pyrosulfate in the melt has been suggested,^{5,9} and precipitation of catalytically inactive species of V(III) and V(IV) has been found.^{3,4,10,11} Nevertheless, many problems still remain unsolved, indicated by the lack of consistency of the results obtained by different methods. This is caused by the complexity of these systems which show pronounced tendency for glass formation. It has been demonstrated in a review paper¹² that solid-state and high-temperature NMR spectroscopy is a powerful technique for the conceptual description of the structural aspects and dynamic behavior of atoms in glasses. Since NMR is very sensitive to the local environment of the quadrupolar nuclei under study, this method is particularly well suited for the analysis of the dynamic behavior of highly disordered complex glass systems. This includes different types of motional processes such as atomic diffusion of alkali cations, restricted molecular fragments reorientation, various types of cooperative motion of the chemical bond network above the glass-transition temperature, and exchange processes in the molten state due to bond breaking and bond formation. Usually NMR studies of the molten $\text{M}_2\text{S}_2\text{O}_7$ – V_2O_5 systems are hindered both by the high temper-

atures, which are needed for these measurements, and by high electrical conductivity and high viscosity of these systems in the molten state.⁹ These systems have therefore not been studied thoroughly by NMR previously.

This paper presents the detailed results of ^{51}V and ^{133}Cs NMR studies on the $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 system of different compositions in the temperature range 20–550 °C. This temperature range includes both solid and molten states of the samples, studied by a specially constructed probe head¹³ for measuring high-temperature NMR spectra.

Experimental Section

The $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 samples of different compositions were prepared as described elsewhere.¹⁴ Pure $\text{Cs}_2\text{S}_2\text{O}_7$ was prepared by thermal decomposition of $\text{Cs}_2\text{S}_2\text{O}_8$ at 300 °C in a stream of dry nitrogen.¹⁵ None of the compounds are commercially available. V_2O_5 was from Cerac (Pure, 99.9%) and used without additional treatment. All preparations were carried out in an air-filled glovebox with a water content less than 10 ppm. For NMR measurements 2–2.5 g of $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 mixtures were sealed in quartz tubes, 10 mm o.d. and 20 mm length, under 0.5 atm of O_2 in order to prevent a possible autoreduction of V(V) to paramagnetic V(IV) at high temperatures. Before the NMR measurements were performed, all of the $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 mixtures were kept molten at 550 °C for 5 h and quenched to room temperature to produce glasses.

NMR spectra were measured on a Bruker MSL-400 NMR spectrometer (magnetic field 9.4 T, resonance frequency for ^{51}V nuclei 105.2 and 52.46 MHz for ^{133}Cs nuclei) with the home-built high-temperature probe. The probe consists of a 60 mm long and 15 mm o.d. cylindrical quartz furnace equipped with 3 mm diameter chromel heating element regulated by a Bruker B-VT temperature controller. The radio-frequency coil was made from copper capillary cooled by a thermostated water flow. A small volume of the molten sample (ca. one-third of

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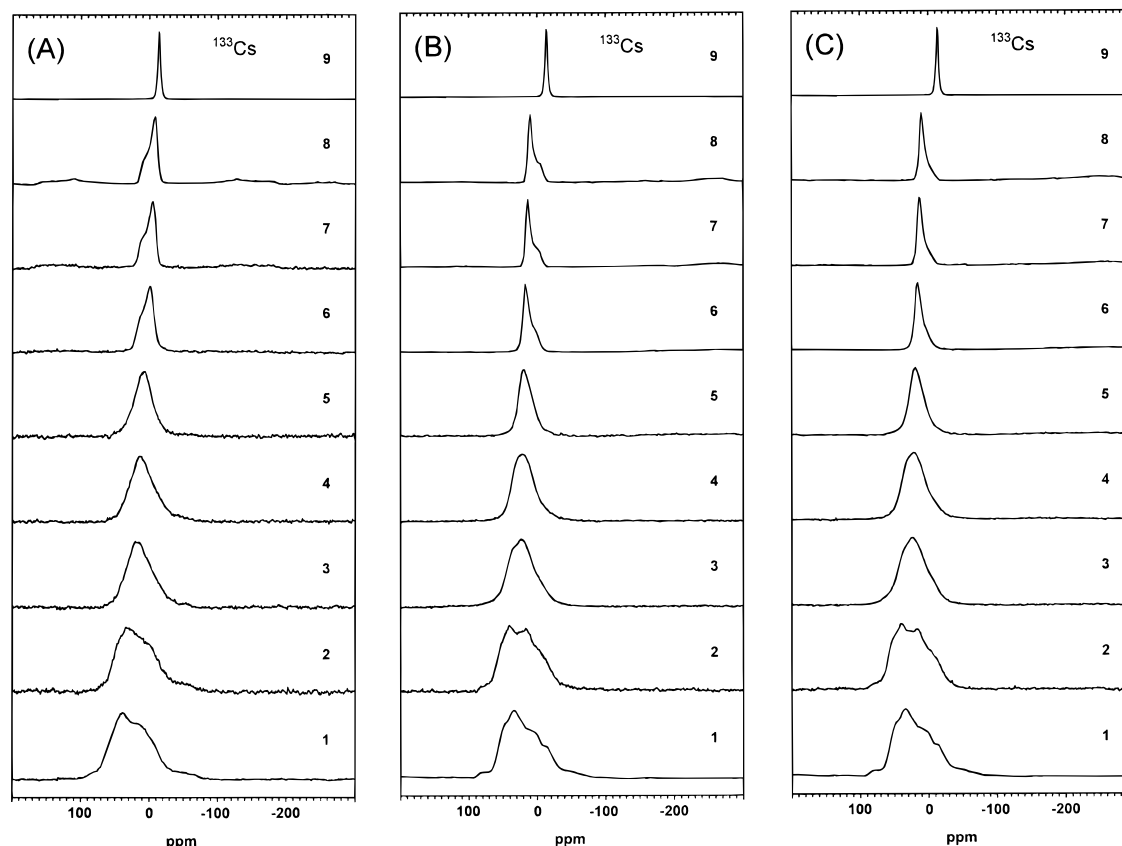


Figure 1. ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ at different temperatures. (A) Increase of the temperature for powdered $\text{Cs}_2\text{S}_2\text{O}_7$: 1, 22 °C; 2, 100 °C (spectra 1 and 2 comprise superposition of four lines from unequivalent Cs sites); 3, 150 °C; 4, 200 °C; 5, 250 °C (spectra 3–5 are symmetric lines with a position that is close to the position of the most populated Cs sites); 6, 300 °C; 7, 350 °C; 8, 400 °C (spectra 6–8 are typical for axial anisotropy of the shielding tensor with first-order quadrupole satellite transitions); 9, 480 °C (9, spectrum of the melt). (B) Decrease of the temperature of the $\text{Cs}_2\text{S}_2\text{O}_7$ melt from 480 °C (spectrum 9) to 22 °C (spectrum 1): 1, 22 °C; 2, 100 °C; 3, 150 °C; 4, 200 °C; 5, 250 °C; 6, 300 °C; 7, 350 °C; 8, 400 °C; 9, 480 °C. (C) Increase of the temperature of the crystalline sample $\text{Cs}_2\text{S}_2\text{O}_7$ obtained after melting (spectra A) and slow cooling (spectra B): 1, 22 °C; 2, 100 °C; 3, 150 °C; 4, 200 °C; 5, 250 °C; 6, 300 °C; 7, 350 °C; 8, 400 °C; 9, 480 °C.

the volume of the sample tube) ensured minimal temperature gradient over the sample, which did not exceed 5 °C at 450 °C.

^{51}V NMR spectra were recorded in a frequency range of 250 kHz with a pulse width of 10 ms and a delay between pulses of 0.1 s. A frequency range from 100 to 500 kHz and 10 μs pulse width and 0.1 s delays between pulses were used for ^{133}Cs nuclei. The chemical shifts of ^{51}V and ^{133}Cs were measured relative to liquid VOCl_3 and 0.1 M solution of CsNO_3 in water at room temperature.

To study the slow dynamic exchange in the solids, 2D-EXSY (exchange spectroscopy) NMR spectroscopy was used.^{16,17} The standard pulse sequence consists of three equal 90° pulses ($\pi/2$) and three time delays t_1 , t_2 , and t_m ($\pi/2 - t_1 - \pi/2 - t_m - \pi/2 - t_2$). The chemical exchange occurring during mixing time t_m can be monitored by the 2D-EXSY NMR. The presence of chemical exchange within the mixing time should appear in the 2D-EXSY spectrum as off-diagonal cross-peaks between the resonance of the sites in exchange. ^{133}Cs 2D-EXSY NMR spectra were acquired at room temperature on a Bruker probe with a mixing time of 1 s. A total of 64 and 256 points were acquired in the t_1 and t_2 domains, respectively, with a 12 μs $\pi/2$ pulse and a repetition time of 30 s.

Results and Discussion

^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ and ^{51}V and ^{133}Cs NMR spectra of three different $\text{Cs}_2\text{S}_2\text{O}_7$ – V_2O_5 mixtures with molar ratios Cs/V = 4, Cs/V = 2, and Cs/V = 1, respectively, have been recorded in the temperature range from 20 to 550 °C.

The ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ (mp 461 °C¹⁵) at different temperatures are illustrated in Figure 1A. In accordance with previous data,¹⁴ the static spectrum of $\text{Cs}_2\text{S}_2\text{O}_7$ consists of a broadened (about 5 kHz) line which is a superposition of four lines from unequivalent Cs atoms in the structure of this compound (Figure 1A, spectrum 1). The latter is clearly demonstrated by the MAS spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ reported earlier.¹⁴ Figure 2 shows the 2D-EXSY ^{133}Cs NMR spectrum of $\text{Cs}_2\text{S}_2\text{O}_7$. The complete absence of the off-diagonal cross-peaks at a mixing time of 1 s indicates that no significant exchange between the different Cs sites occurs during this period at room temperature. This exchange takes place only at elevated temperature.

The progressive increase of the temperature results in narrowing of the line (Figure 1A) due to increase of the mobility of the Cs cations in the crystal lattice. In the temperature range from 200 to 300 °C a symmetric line, with a position that is close to the average position of the most populated Cs sites, is observed (spectra 3–5). This may indicate that the cation mobility occurs as jumps between Cs sites and begins at this temperature. Further increase of the temperature transforms this spectrum to that typical for axial anisotropy of the chemical shielding tensor, at the same time the first-order quadrupole transitions appeared in the spectra (spectra 6–8). These satellite transitions are broadened at 300 °C and become well resolved at 400 °C. Above the melting point of $\text{Cs}_2\text{S}_2\text{O}_7$ a single narrow line typical for liquids appears in the spectra (spectrum 9). The chemical shift slightly decreases by increase of temperature.

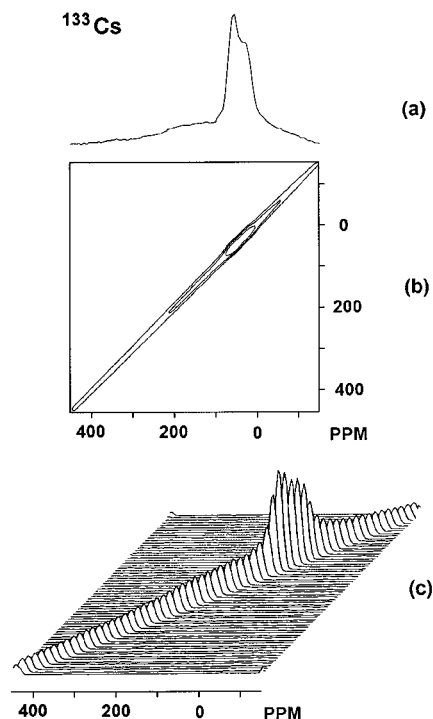


Figure 2. 2D-EXSY ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$: (a) 1D projection; (b) contour-plot spectrum; (c) stack-plot spectrum.

The ^{133}Cs NMR spectra measured during slow cooling of the $\text{Cs}_2\text{S}_2\text{O}_7$ melt are shown in the Figure 1B. In general, these spectra are very similar to those obtained by heating of the powdered $\text{Cs}_2\text{S}_2\text{O}_7$ sample (compare parts A and B of Figure 1); nevertheless, some features should be mentioned. In the temperature range from 400 to 300 °C the axial anisotropy of the line in Figure 1B (spectra 6–8) differs from that in Figure 1A (spectra 6–8) by the sign of anisotropy of the magnetic shielding tensor and the position of the quadrupole satellite transitions (Figure 3, A and B). In the temperature range from 300 to 22 °C the position of the central quadrupole transition slightly shifts compared to the previous ones (compare spectra 5, 4, and 3 in Figure 1A,B). The room-temperature ^{133}Cs NMR spectrum of the $\text{Cs}_2\text{S}_2\text{O}_7$ crystalline sample obtained from the melt (Figure 1B, spectrum 1) is also different from that of the powdered $\text{Cs}_2\text{S}_2\text{O}_7$ sample obtained by thermal decomposition of $\text{Cs}_2\text{S}_2\text{O}_8$ (Figure 1A, spectrum 1).

The ^{133}Cs NMR spectra measured during the second heating of the $\text{Cs}_2\text{S}_2\text{O}_7$ sample are shown in Figure 1C. These spectra coincide well with the spectra of Figure 1B recorded at the same temperatures.

The behavior of the system under repetitive heating and cooling becomes reproducible with the ^{133}Cs spectra being quite similar to those presented in Figure 1B,C.

Thus, the data presented show significant decrease in the total width of the ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ by elevation of the temperature from 22 to 400 °C (Figure 1A–C). Further, it is important to note that the spectra at 400 °C may be perfectly described by NMR signals with $e^2Qq/h = 225$ kHz, $\eta = 0.18$, $\sigma_{\perp} = 13$ ppm, and $\sigma_{\parallel} = -12$ ppm (Figure 3A) and with $e^2Qq/h = 430$ kHz, $\eta = 0$, and $\sigma_{\text{iso}} = -11.3$ ppm (Figure 3B). The most likely reason for this behavior is a fast cesium cation mobility at higher temperatures, resulting in fast exchange between four low-temperature (22 °C) cation sites. The NMR spectrum in the fast-exchange region is described by quadrupole coupling and magnetic shielding tensors averaged among the exchangeable sites. The relative orientations of principal axes of these tensors between four low-temperature NMR signals

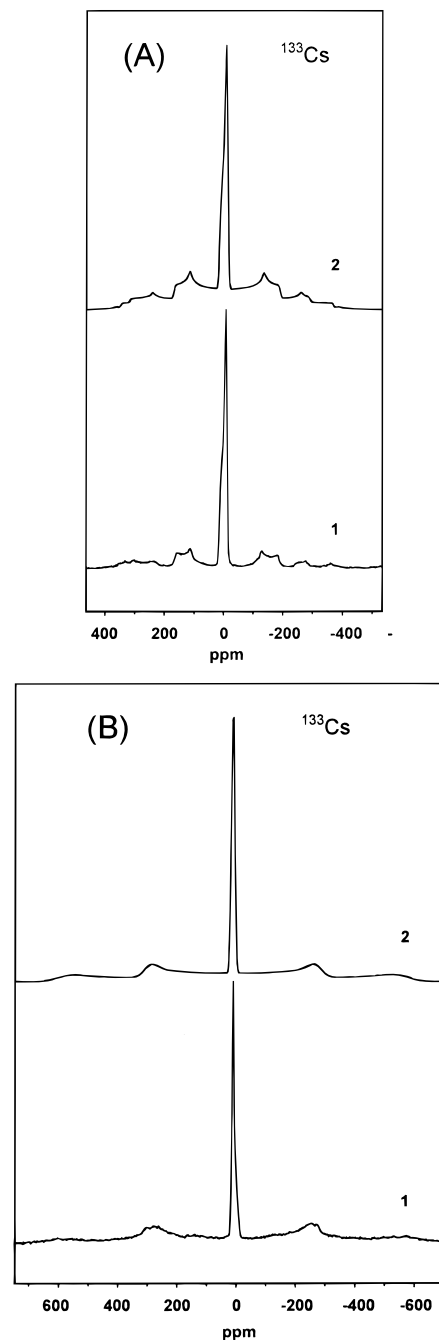


Figure 3. ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7$ measured at 400 °C. (A) Powdered sample of $\text{Cs}_2\text{S}_2\text{O}_7$ (spectrum is typical for axial anisotropy of the shielding tensor, with first-order quadrupole satellite transitions): 1, experimental spectrum; 2, simulated spectrum with the parameters $e^2Qq/h = 225$ kHz, $\eta = 0.18$, $\sigma_{\perp} = 13$ ppm, and $\sigma_{\parallel} = -12$ ppm. (B) Crystalline sample of $\text{Cs}_2\text{S}_2\text{O}_7$ obtained by slow cooling of $\text{Cs}_2\text{S}_2\text{O}_7$ melt (spectrum is typical for small axial anisotropy of shielding tensor with the opposite sign of anisotropy compared with spectrum A). The satellite transitions also differ from those of (A): 1, experimental spectrum; 2, simulated spectrum with $\sigma_{\text{iso}} = -11.3$ ppm, axial quadrupole tensor $\eta = 0$, and quadrupole constant e^2qQ/h slightly distributed around 430 kHz in a Gaussian-like fashion, $g(x) = [1/\Delta(2\pi)^{1/2}] \exp(-x^2/2\Delta^2)$ with the distribution parameter $\Delta = 30$ kHz.

are unknown. We may only expect significant reduction of the effective quadrupole interaction at high temperatures in the case of different orientations of quadrupole tensors for the four cesium cations positions. This is in agreement with the experiment. Additional evidence for the presence of cesium cation exchange and mobility may be found from the analysis of satellite transitions for ^{133}Cs nuclei at intermediate

temperatures. It is evident from the magnified spectra that satellite transitions at 300 or 350 °C are significantly more broadened than at 400 °C, as expected for the intermediate rate of chemical exchange.

Thus, ¹³³Cs spectra demonstrate a high cation mobility in the temperature range below the melting point. These data need to be correlated with details of the crystal structure of this compound in order to describe the detailed mechanism of Cs mobility in Cs₂S₂O₇. Attempts to grow single crystals suitable for X-ray investigations are in progress.

The introduction of vanadium pentoxide to the cesium pyrosulfate leads to a marked change in the NMR spectra of the Cs₂S₂O₇–V₂O₅ system. ⁵¹V NMR spectra of the sample with Cs/V = 4 (Figure 4A) demonstrate an interesting behavior by change of temperature. At room temperature the spectrum of the melt-quenched glassy sample of this composition consists of a broadened line with an axial anisotropy corresponding to V atoms in distorted octahedral oxygen environment with one short V=O bond. Elevation of the temperature above 100 °C greatly changes the line shape in a way that usually takes place for rapid isotropic motion of the molecular fragments and completely averages the chemical shift anisotropy at 220 °C (Figure 4A, spectrum 4)—probably due to rapid changes in the vanadium environment taking place at these temperatures. It is remarkable, however, that keeping the sample at this temperature slows the rate of this process, as it follows from the line broadening at 220 °C (Figure 5, spectrum 2). Moreover, leaving the sample at this temperature results in the appearance of a highly broadened line (Figure 5, spectrum 3) and then an anisotropic line ($\delta_{\perp} = -355$ ppm) typical for V in crystalline Cs₄(VO)₂O(SO₄)₄¹⁴ (Figure 5, spectra 4 and 5). Increase of the temperature above 220 °C does not affect the spectra, and the anisotropic line still remains (Figure 4A, spectra 6 and 7) until 400 °C when a fully averaged spectrum caused by fusion of the sample appears with $\delta = \text{ca. } -660$ ppm (Figure 4A, spectrum 8).

The ¹³³Cs NMR spectrum of the same melt-quenched glassy sample at ambient temperature shows a broad line (Figure 4B, spectrum 1) that does not narrow under MAS conditions. The latter is possible if (i) there is a random distribution of different Cs sites and the ¹³³Cs NMR central line is composed of a large number of individual transition frequencies overlapping in a broad unresolved line or (ii) exchange of cesium cations between the unequivalent positions takes place in this glass whereby the line observed is broadened by the exchange.

2D-EXSY ¹³³Cs NMR experiments permit to eliminate the latter assumption: A priori, a circular pattern of 2D-EXSY spectrum should indicate that cesium ions essentially occupy all the local positions during the mixing time. Figure 6 shows the 2D-EXSY ¹³³Cs NMR spectra of this sample. The observed diagonal shape of the spectrum indicates that there is apparently no significant exchange of cesium ions between regions with different environment during the mixing time of 1 s at room temperature.

A progressive increase of the temperature up to 220 °C is accompanied by a narrowing of the ¹³³Cs line (Figure 4B, spectra 2 and 3) until the minimum line width is achieved at 220 °C (Figure 4B, spectrum 4). Keeping the sample at this temperature leads again to increase of the line width (Figure 4B, spectrum 5). Moreover, this line comprises the superposition of two anisotropic lines typical for equilibrium mixture of Cs₂S₂O₇ and Cs₄(VO)₂O(SO₄)₄. It is remarkable that, under these conditions, ⁵¹V NMR spectra are characterized by an axial anisotropic line typical for crystalline Cs₄(VO)₂O(SO₄)₄ (Figure 4A, spectra 4 and 5). By increase of temperature, the ¹³³Cs

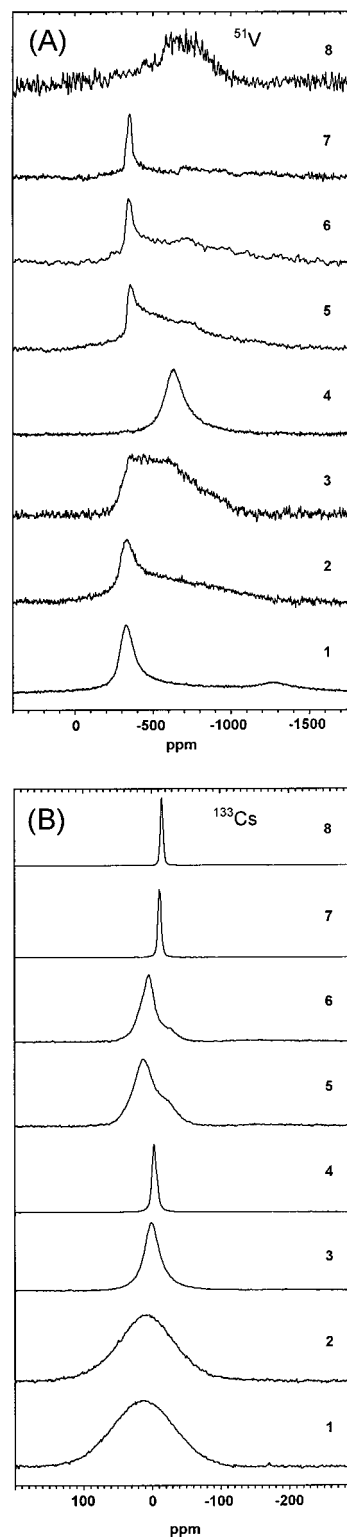


Figure 4. (A) ⁵¹V NMR spectra of Cs₂S₂O₇–V₂O₅ (Cs/V = 4) measured at different temperatures: 1, melt-quenched glassy sample at 22 °C; 2, 100 °C; 3, 200 °C (spectra 1–3 represent an axial anisotropic line with $\delta_{\perp} = -325$ ppm and $\delta_{\parallel} = -1280$ ppm of vanadium in distorted octahedral oxide coordination of the glassy sample); 4, 5, 220 °C (spectrum 4 is typical for liquid samples); 6, 250 °C; 7, 350 °C (5–7, spectra of crystalline Cs₄(VO)₂O(SO₄)₂ with $\delta_{\perp} = -355$ ppm); 8, 400 °C (liquid spectrum as earlier obtained¹⁴). (B) ¹³³Cs NMR spectra of Cs₂S₂O₇–V₂O₅ (Cs/V = 4) at different temperatures: 1, 22 °C; 2, 100 °C; 3, 200 °C; 4, 5, 220 °C; 6, 250 °C; 7, 350 °C; 8, 400 °C (7, partly liquid, and 8, liquid spectra as earlier observed¹⁴).

NMR line width again decreases in accordance with the model of activated diffusion of Cs cations (Figure 4B, spectrum 6). The

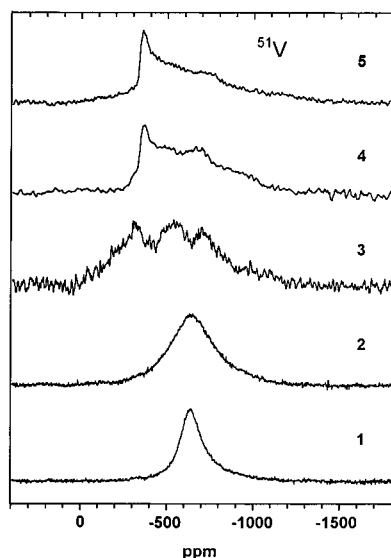


Figure 5. ^{51}V NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{-V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 4$) exposed at 220 °C and measured with a time delay of 30 min between each spectrum. Spectra 1 and 2 are typical for the liquid (subcooled) phase, and spectrum 5 is typical for crystalline $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ with superposition of features from the residual subcooled phase.

line position also depends upon the temperature (Figure 4B, spectrum 7, partly, and 8, completely, molten sample).

The NMR data permit us to describe the mechanism of the glass-crystal transition of the sample $4\text{Cs}_2\text{S}_2\text{O}_7\text{-V}_2\text{O}_5$ in the following way: At room temperature the melt-quenched glassy sample represents a three-dimensional network of vanadium-oxo-sulfate and/or -pyrosulfate complexes connected by sulfate and/or pyrosulfate ligands. Cs cations are distributed randomly within this network. By heating, the Cs cations become able to jump between different Cs sites. Simultaneously, cooperative motion of the network caused by bond breaking and bond formation takes place. Increase of the temperature increases the number of broken bonds. This results in a drastic decrease of the viscosity and transition of the solid sample into a subcooled liquid state. This occurs around 220 °C, which is assumed to be the glass-transition temperature, T_g .

The transverse relaxation times, T_2 , of cesium and vanadium nuclei permit us to estimate the size of vanadium-containing fragments in the subcooled liquid. It can be assumed that they are approximately vanadium-sulfate spheres with a hydraulic radius r , placed in the liquid with the viscosity η . Assuming that in the molten state, as well as in the subcooled liquid, the Cs cation has the same radius, the value of the viscosity of the subcooled liquid, η , has been calculated from the cesium relaxation data. As discussed for example by Vashman and Pronin,¹⁸ knowing the viscosity η and the transverse relaxation time T_2 of vanadium nuclei, the radius r of the vanadium fragments has been estimated to be less than 10 Å. This is comparable with the characteristic size¹⁹ of the $(\text{VO})_2\text{O}(\text{SO}_4)_4^{4-}$ anion.

Near the glass-transition temperature T_g , the crystallization process becomes more effective. This process leads to bonds and lattice structures characteristic for the crystalline compound $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ as follows from the X-ray diffraction data obtained on a monocrystalline sample.¹⁹ Sulfate and pyrosulfate anions released in this process form a frame of pyrosulfate with certain positions for Cs cations. This is why ^{133}Cs NMR spectra of this system in equilibrium at T_g represent superposition of the lines of the compounds $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ and $\text{Cs}_2\text{S}_2\text{O}_7$.

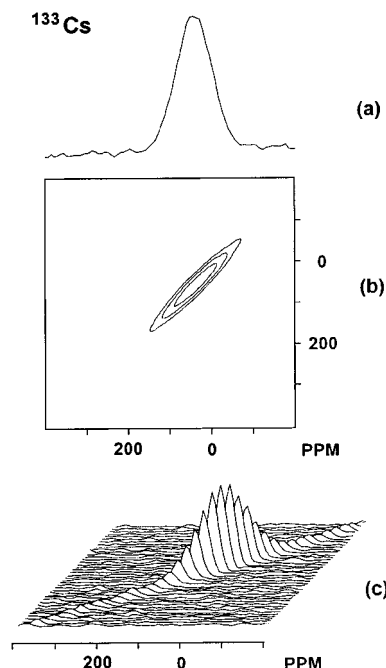


Figure 6. 2D-EXSY ^{133}Cs NMR spectra of glassy $\text{Cs}_2\text{S}_2\text{O}_7\text{-V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 4$): (a) 1D projection; (b) contour-plot spectrum; (c) stack-plot spectrum.

Increase of the temperature above T_g increases the cations' mobility whereas anion frames remain immobile until the sample melts.

The ^{51}V NMR spectra of the melt-quenched glassy sample with $\text{Cs}/\text{V} = 2$ are shown in Figure 7A. Up to 200 °C the spectra have an axial anisotropy of the magnetic shielding tensor, typical for a glassy sample (Figure 7A, spectra 1–3). At about 220 °C some transformation of the spectrum near δ_{\perp} takes place, and by keeping the sample at this temperature, the axial anisotropy lines typical for crystalline $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ appears (Figure 7A, spectra 4 and 5). This line does not change up to 400 °C (spectra 6–8). All attempts to obtain ^{51}V NMR spectra above 400 °C, i.e., above the temperature of fusion¹⁵ around 412 °C, failed.

The ^{133}Cs NMR spectra of the sample with $\text{Cs}/\text{V} = 2$ are presented in Figure 7B. The features of the spectra by increase of the temperature is very similar to the previous case for the sample with $\text{Cs}/\text{V} = 4$. The progressive increase of the temperature up to 220 °C leads to a decrease of the line width (Figure 7B, spectra 1–3). At 220 °C the minimum line width is observed (Figure 7B, spectrum 3). After prolonged exposure at this temperature a broadened line, consisting of the superposition of four lines, appears in the spectra (Figure 7B, spectra 4 and 5). The increase of the temperature from 220 to 300 °C is accompanied by narrowing of this composed line (Figure 7B, spectra 6 and 7). Near the temperature of fusion only one narrow line is observed in the spectra (Figure 7B, spectrum 8).

Thus, for the sample with the composition corresponding to the crystalline compound $\text{Cs}_4(\text{VO})_2\text{O}(\text{SO}_4)_4$ ($\text{Cs}/\text{V} = 2$) the glass-crystal transition also takes place. The temperature of the transition is close to that observed for the previous sample ($\text{Cs}/\text{V} = 4$). In this case the glass-crystal transition takes place via the solid state, according to the ^{51}V NMR data. The new crystalline phase appears in the glassy sample without formation of a metastable liquid phase (Figure 7A, spectra 4 and 5). Nevertheless, an increased mobility of the Cs cations at T_g follows from the ^{133}Cs NMR spectra (Figure 7B, spectrum 3). Increase of the temperature up to the melting point of the sample

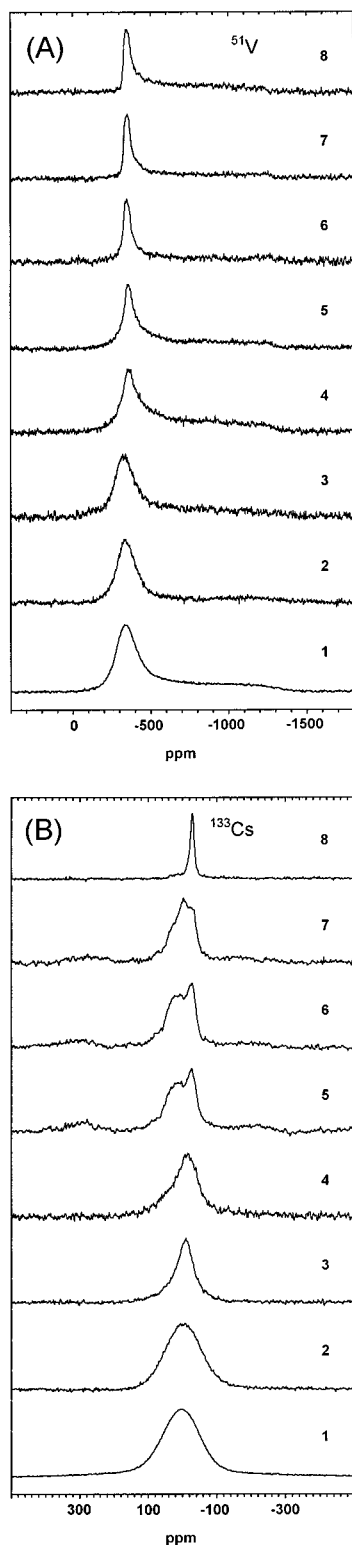


Figure 7. (A) ^{51}V NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 2$) measured at different temperatures: 1, 22 °C; 2, 100 °C; 3–5, 220 °C; 6, 250 °C; 7, 300 °C; 8, 400 °C. (B) ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 2$) measured at different temperatures: 1, 22 °C; 2, 100 °C; 3–5, 220 °C; 6, 250 °C; 7, 300 °C; 8, 400 °C.

does not influence the mobility of the anion frames, whereas some mobility of cesium cations similar to that in pure $\text{Cs}_2\text{S}_2\text{O}_7$ takes place.

Figure 8A illustrates the ^{51}V spectra obtained for the melt-quenched glassy sample with $\text{Cs}/\text{V} = 1$. At room temperature (Figure 8A, spectrum 1) the spectrum demonstrates an axial anisotropy of the chemical shift tensor, typical for glassy V-containing compounds in distorted octahedral oxide environ-

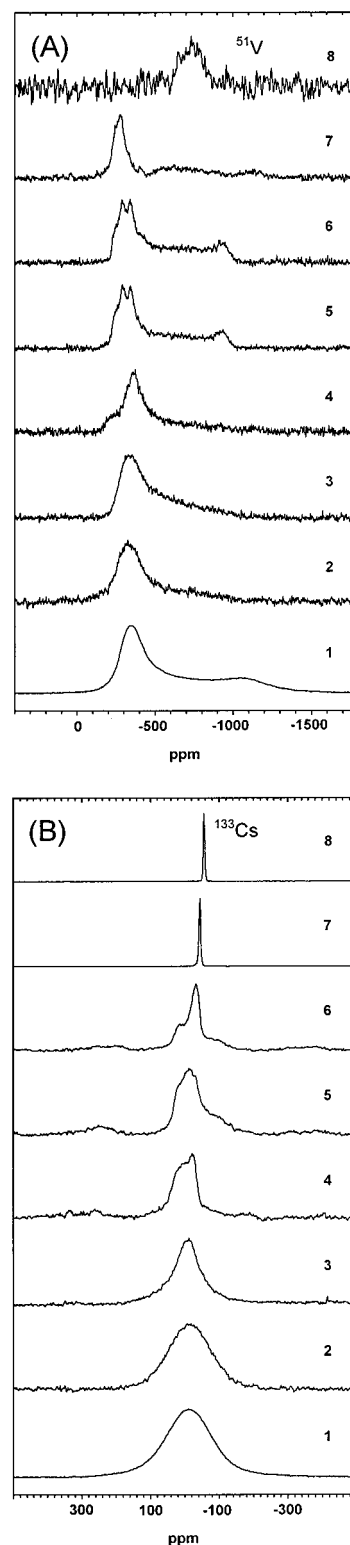


Figure 8. (A) ^{51}V NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 1$) measured at different temperatures: 1, 20 °C; 2, 100 °C; 3, 200 °C; 4, 250 °C (low temperature not completely crystallized phase of $\text{CsVO}_2\text{--SO}_4$); 5, 300 °C; 6, 350 °C (spectra 5 and 6 correspond to completely crystallized phase of CsVO_2SO_4); 7, 400 °C; 8, 550 °C. (B) ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ ($\text{Cs}/\text{V} = 1$) measured at different temperatures: 1, 20 °C; 2, 100 °C; 3, 200 °C; 4, 250 °C; 5, 300 °C; 6, 350 °C; 7, 400 °C; 8, 550 °C.

ment of V, in the absence of the rapid (on a NMR time scale) dynamic processes. The increase of temperature up to 200 °C does not change the spectra significantly (Figure 8A, spectra 2 and 3). A prolonged exposure of this sample at 250 °C leads to a spectrum (Figure 8A, spectrum 4) of the partly crystallized

sample. The subsequent increase of the temperature results in the spectrum (Figure 8A, spectrum 5), after complete transformation to the crystalline compound CsVO_2SO_4 ($\delta_1 = -200$ ppm, $\delta_2 = -370$ ppm, $\delta_3 = -1200$ ppm) as earlier obtained¹⁴ for the $\text{Cs/V} = 1$ sample. The latter spectrum of CsVO_2SO_4 is observed until 400 °C where some changes in the spectrum, probably caused by the transformation of CsVO_2SO_4 to another crystalline modification of this compound, take place (Figure 8A, spectrum 7). At 550 °C, well above the temperature of fusion,¹⁵ only a single line with $\delta = -720$ ppm has been detected in the spectrum (Figure 8A, spectrum 8). This means that all V sites in the melt undergo rapid exchange (on a NMR time scale), resulting in a chemical shift that is averaged over all possible states of V atoms. Note that the value $\delta = -720$ ppm differs considerably from the average value $\delta_{\text{iso}} = 1/3(\delta_1 + \delta_2 + \delta_3) = -590$ ppm. This suggests a transformation of the local environment of the V nuclei when going from solid to molten state of this sample, possibly to tetrahedral coordination, i.e., by bidentate SO_4^{2-} coordination to the cis oxo VO_2^+ unit of the VO_2SO_4^- complex ion or by bridging SO_4^{2-} groups in a $(\text{VO}_2\text{SO}_4)_n^{n-}$ polymeric species.

The ^{133}Cs NMR spectra of the same melt-quenched glassy sample $\text{V}_2\text{O}_5\text{--Cs}_2\text{S}_2\text{O}_7$ ($\text{Cs/V} = 1$) obtained at different temperatures are presented in Figure 8B. At room temperature a broad line characteristic of glassy samples is observed (Figure 8B, spectrum 1). The progressive increase of the temperature up to 200 °C as previously for the samples with compositions of $\text{Cs/V} = 4$ and 2 is accompanied by a narrowing of the ^{133}Cs NMR line (Figure 8B, spectra 2 and 3). Likewise, the ^{51}V NMR spectra indicated the presence of partly and fully crystalline phases of CsVO_2SO_4 ; also, the ^{133}Cs spectra have line shapes characteristic of the same transformation process (Figure 8B, spectra 4–6). Increase of the temperature up to 400 °C results in the appearance of a narrow isotropic line (Figure 8B, spectrum 7). The chemical shift of the single line changes with the increase of temperature (spectra 7 and 8) and is different from that for $\text{Cs}_2\text{S}_2\text{O}_7$, indicating the participation of Cs cations in a rapid exchange between different anionic sites which probably includes vanadium–oxo–sulfate anions. The spectrum is very similar to that obtained previously¹⁴ on the molten $\text{Cs/V} = 1$ sample at 470 °C.

These data indicate that the mechanism of the glass–crystal transition of the sample with $\text{Cs/V} = 1$ is close to that for the sample with $\text{Cs/V} = 2$ with nearly the same T_g temperature of 220 °C, but probably with a slower kinetic of transformation. Thus, heating of the melt-quenched glassy sample up to a certain temperature permits one to obtain a homogeneous polycrystalline compound. This is a fast and convenient way to obtain pure polycrystalline samples in the $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ system. A similar experience was obtained¹⁵ in connection with the outline of the phase diagram of the $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ system.

Conclusion

This investigation shows that ^{51}V and ^{133}Cs NMR spectra of $\text{Cs}_2\text{S}_2\text{O}_7\text{--V}_2\text{O}_5$ mixtures at elevated temperatures provide essential information on the glass–crystal transition in these systems.

The mechanism of the transition seems to be the same for all the samples investigated. At room temperature the melt-quenched glassy samples represent a three-dimensional network of vanadium–oxo–sulfate and/or –pyrosulfate complexes connected by probably sulfate ligands. Cs cations are distributed randomly within this frame. During heating, Cs cations obtain high mobility and jumps between different Cs sites. Simultaneously, the cooperative motion of the anion networks, caused by bond breaking and bond formation, takes place. Increase of the temperature increases the number of broken bonds, resulting in a decrease of the viscosity and subsequent transformation of the glassy sample into a crystalline one. The relative number of broken bonds for the sample $\text{Cs/V} = 4$ is higher than for the samples $\text{Cs/V} = 2$ and 1. This permits the registration of the metastable liquid in the first case, whereas in the latter cases, the polymeric network mobility is slow on the NMR time scale. Above the T_g temperature the anion frame of the crystalline samples formed is stable until the melting point is reached, while the mobility of the cesium cations continuously increases with the temperature.

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