MAGNETIC SUSCEPTIBILITY of SODIUM DISILICATE GLASSES CONTAINING PuO_2

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ABSTRACT

A solubility limit of ∿6 mol % PuO_2 in sodium disilicate ($Na_2O \cdot 2SiO_2$) glass has been determined. Magnetic susceptibility measurements on these glasses yield approximate Curie-Weiss behavior, in contrast to the temperature-independent susceptibility of crystalline PuO_2. This result is interpreted to indicate that the local site symmetry around the Pu ion in the sodium disilicate glass is much different than in crystalline PuO_2. The effective paramagnetic moments determined from the temperature dependence of the susceptibility are found to be consistent with calculated free-ion values based on the most likely 5f electron configurations.

INTRODUCTION

The potential use of oxide glasses as a storage medium for radioactive waste products makes a study of the bonding of actinide ions in such glasses a topic of major importance [1]. Very few basic studies of glasses containing actinide ions have been made. Uranium dioxide is known to dissolve in silicate glasses, and was used as a coloring agent in the 1930's. Glasses melted under different oxidizing/reducing conditions and containing different amounts of U^{6+} and U^{4+} ions have characteristic colors, and detailed absorption spectra have been determined [2]. A recent investigation [3] has shown that at least 30 mol % of UO_2 (or higher oxides) can be dissolved into sodium disilicate ($Na_2O \cdot 2SiO_2$) glass. The major conclusion of this study, which motivated the present work, was that x-ray photoelectron spectroscopy (XPS) results indicated that the electron configuration and local symmetry around a uranium ion (either 4+, $5f^2$ or 6+, $5f^0$) was the same as in crystalline UO_2 or UO_3. On the other hand, there was no optical evidence of any macroscopic phase separation. This puzzling observation stimulated the present investigation of the analagous PuO_2-containing sodium silicate glasses. Bulk magnetic susceptibility measurements have been made on samples containing up to 6 mole % PuO_2 as an initial part of a study to obtain information about the electron configuration and bonding of the Pu ion.

EXPERIMENTAL

A master batch of sodium disilicate glass was prepared by mixing appropriate amounts of Na_2CO_3 and SiO_2 in an argon atmosphere glovebox and then melting the subsequent mixture in air in a platinum crucible at 1125°C. After powdering, the master batch was mixed with the necessary amount of PuO_2 and then slowly heated in a platinum crucible in vacuum over a period of approximately 2 days to 1150°C, held at this temperature for about 8 hours, and then cooled. Previous observations [3] had indicated that melting under vacuum was necessary to maintain a single electron configuration (U^{4+}) and also that vaporization took place if the melt was held above 1200°C. Optical inspection showed that samples containing up to 6 mol % PuO_2 were uniform in color (green) and x-ray powder patterns showed no evidence of crystalline phases. Samples containing more than 6 mol % PuO_2 were found to be phase separated. After initial susceptibility measurements had indicated a lack of complete homogeneity, two compositions were powdered and remelted, with a subsequent improvement in properties.

Small pieces of glass were broken from the platinum crucible in an argon atmosphere glovebox and approximately 300 mg was inserted into a cylindrical aluminum capsule. After an aluminum lid was welded onto the capsule, the sample could be brought into an open laboratory.

Magnetic susceptibility measurements were made between 4 and 300 K by the Faraday method with a system consisting of a Varian electromagnet with shaped pole caps to produce a field gradient, and a Cahn electronic microbalance to measure the force on the specimen in the presence of this field gradient [4]. The aluminum sample capsule was inserted in a brass sample holder. The temperature was monitored by an Au(Fe) vs Cu thermocouple in intimate contact with the sample holder, and the thermocouple wires formed the suspension which was used to hang the sample from the balance and between the magnet pole caps. At each temperature, the magnetization was measured at ten different magnetic fields between 2 and 15 kOe. The magnetization M was found to vary linearly with field H within experimental error, for all samples and temperatures, and the magnetic susceptibility was determined from the slope of this plot ($\chi = \partial M/\partial H$). Corrections for the susceptibility of the suspension system and the aluminum capsule were determined in separate experiments; they were of the same magnitude as the forces arising from the susceptibility of the sample itself.

RESULTS AND DISCUSSION

An initial result of this study is the determination of the solubility limit of $\sim$6 mol % PuO_2 in sodium disilicate glass. By contrast, previous work [3] has suggested a solubility $\sim$30 mol % UO_2 in the same composition glass. It is difficult to attach any particular significance to this result until the relevant phase diagrams have been obtained in more detail.

The results of the magnetic measurements are shown in Fig. 1, where the molar susceptibility is plotted vs temperature for a nominally pure sodium disilicate glass and for glasses containing 3, 5 and 6 mol % PuO_2. Several features of interest in this plot should be pointed out. First, although the susceptibility of the pure sodium disilicate glass is diamagnetic over most of the temperature range, there is an increase in paramagnetic behavior at low temperatures characteristic of a magnetic impurity. The data for the base glass can be well fit over the entire temperature range as the sum of a Curie-Weiss paramagnetic term $\chi_p = C/(T-\theta)$ and a temperature independent diamagnetic term. Least squares analysis yields a diamagnetic susceptibility of -0.66×10^{-4} emu/mol which, given the experimental uncertainties, is close to the calculated diamagnetic core susceptibility of one mole of $Na_2O \cdot 2SiO_2$ (-0.76×10^{-4} emu/mol [5]). The paramagnetic term yields $\theta = -3$ K and an effective paramagnetic moment μ_{eff} calculated from C ($\mu_{eff} = 2.839\ C^{1/2}$) of $\sim 0.1\ \mu_B$/mol, and probably arises from impurities incorporated in the glass during the preparation procedure.

A second feature of Fig. 1 is the monotonic increase in both the the susceptibility and the temperature dependence at low temperatures with an increase in the concentration of PuO_2. Third, the 5 mol % PuO_2 sample shows a susceptibility maximum at ~ 6 K (more data than are plotted in Fig. 1 were taken to define this maximum). This sample was made prior to the other samples with a different batch of master glass, and a susceptibility maximum in the same temperature range was found for a separate 6 mol % PuO_2 sample made from this same master batch. It was this result which suggested that the samples were not homogeneous, and led to the refinement of the sample preparation procedures to include an additional crushing and remelting step. Despite this likelihood of the lack of complete homogeneity, the data from the 5 mol % PuO_2 sample have been included in the analysis.

To attempt a more quantitative analysis of the data, the susceptibilities of the PuO_2 glasses were corrected by a point-by-point subtraction (as a function of temperature) of the susceptibility of the base sodium disilicate glass. Rather large systematic errors are likely in the results above 50 K where the susceptibilities are all small. Therefore corrected susceptibilities χ_M(corr) are shown in the inverse form only for $T \leq 50$ K in Fig. 2. The pronounced temperature dependence seen in Fig. 2 is in contrast to the behavior of crystalline PuO_2, which has a susceptibility of 4.8×10^{-4} emu/mol that is independent of temperature between 4 and 1000 K [6]. Raphael and Lallement attribute this lack of a Curie-Weiss susceptibility from the Pu^{4+}, f^4 ion as arising from the influence of the strong crystalline electric field produced by the eight nearest-neighbor oxygen ions surrounding a Pu^{4+} ion in the cubic fluorite structure. It appears therefore that the local site symmetry around the Pu ion in sodium disilicate glass is much different from that in the crystalline fluorite structure, and thus the behavior of Pu ions in this glass is quite different from that of U ions [3].

Even for the temperature range of Fig. 2, the data do not precisely fit the simple Curie-Weiss expression. This is additional evidence for systematic errors in the corrections applied. However, from the initial slope of the χ^{-1} vs T plot at low temperatures, reasonably accurate determinations of θ and C can be made. This value of C is then used to determine the effective paramagnetic moment. The results of this procedure are given in columns 3 and 4 of Table I. Because of the susceptibility maximum at ~6 K in the 5 mol % sample, only data above 8 K were used in the analysis. This is reflected in the apparently more negative θ value (compared to the 3 and 6 mol % samples) which, in turn, implies that C and therefore μ_{eff} obtained in the analysis is too high. The possible clustering indicated by the susceptibility maximum and noted earlier would also lead to too high an effective moment for the 5 mol % PuO_2 sample. Again, because of possible systematic errors it is difficult to estimate the uncertainties in the effective moments. However, the value for the most concentrated sample, which has the highest measured susceptibility, should be the most precise. For comparison, the free-ion effective moments based on the Hund's rule ground state with intermediate coupling g-values are listed for several probable 5f configurations in the right-hand side of Table I. From the data at hand, it is obviously not possible to decide if a single ground-state configuration exists. However, it is apparent that the results obtained are consistent with the most reasonable configurations ($5f^2$ - $5f^4$). A more detailed understanding of the electronic properties of Pu ions in sodium disilicate glasses will await both improved preparation and measurement procedures to enhance the accuracy of the susceptibility results and also investigations by microscopic probe techniques.

SUMMARY

The magnetic susceptibility of sodium disilicate glasses containing 0, 3, 5 and 6 mol % PuO_2 has been measured between 4 and 300 K. After subtraction of the susceptibility of the pure sodium disilicate glass, the corrected susceptibility of the PuO_2 - containing samples was found to have an approximately Curie-Weiss temperature dependence. This result is in contrast to the susceptibility of crystalline PuO_2 which is temperature independent, and thus it is suggested that the local site symmetry around the Pu ion in the glass is much different than in crystalline PuO_2. On the other hand, it has been found previously [3] that UO_2 dissolved in sodium disilicate glass closely resembles crystalline UO_2 both in terms of electron configuration and site symmetry. The effective moment per Pu ion determined from the temperature dependence of the corrected susceptibility is found to be consistent with any of the three most likely 5f configurations.

ACKNOWLEDGEMENT

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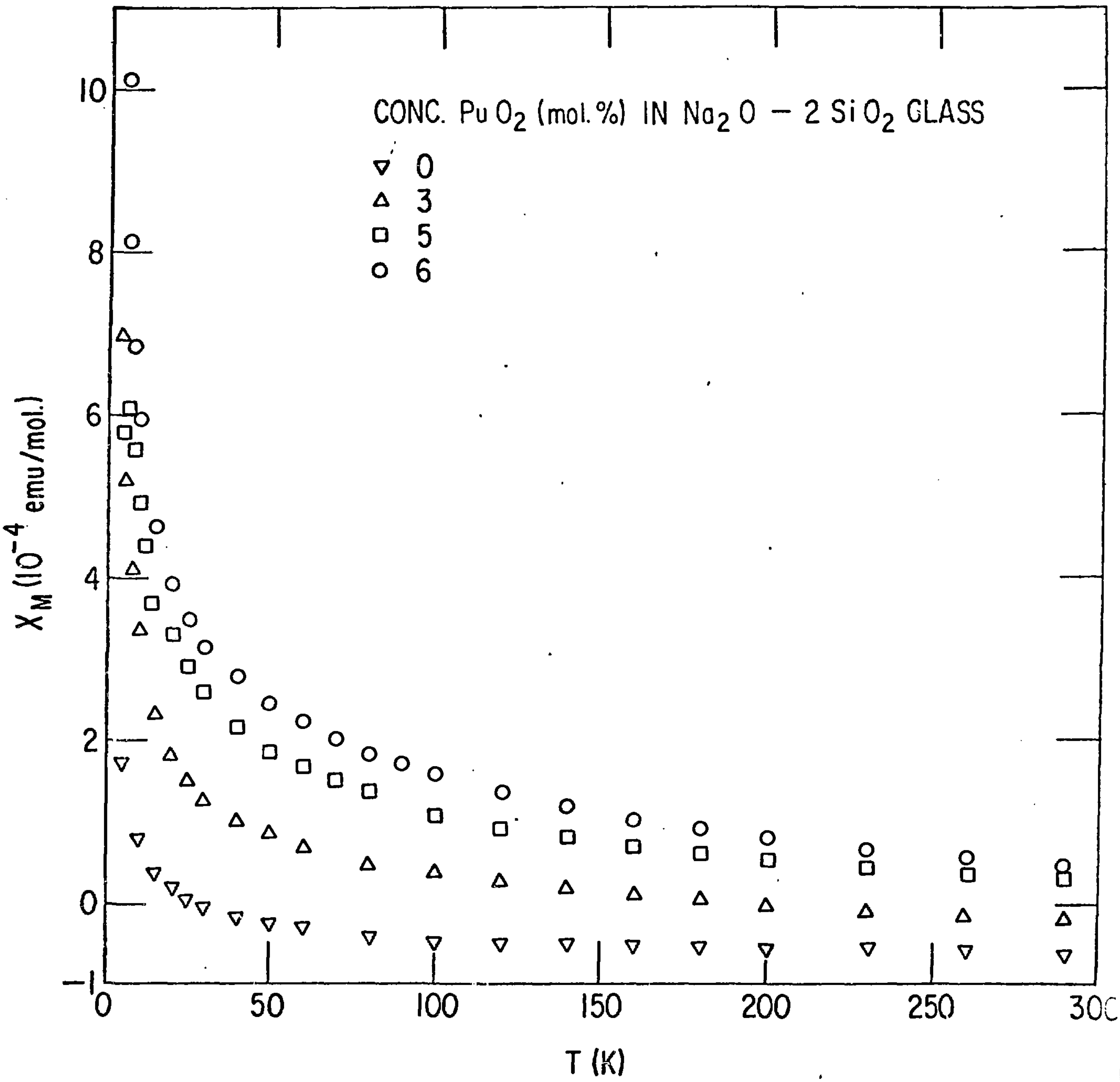
Table 1. Magnetic properties of sodium disilicate glasses contianing PuO_2

Conc. PuO_2 (mol%)	θ (K)	μ_{eff} (μ_B/mol)	μ_{eff} (μ_B/Pu ion)	Ionization State	5f Configuration	Ground State	μ_{eff} (μ_B/Pu ion)
3	-1	0.13	4.3	6+	2	$^3H_4$	3.7
5	-9	0.21	4.2	5+	3	$^4I_{9/2}$	3.8
6	-3	0.18	3.0	4+	4	$^5I_4$	2.9
				3+	5	$^6H_{5/2}$	1.2

Figure Captions

Fig. 1 Molar susceptibility versus temperature for sodium disilicate glasses containing the indicated amounts of PuO_2.

Fig. 2 Reciprocal corrected (see text) molar susceptibility versus temperature ($\leq$ 50 K) for sodium disilicate glasses containing the indicated amounts of PuO_2.



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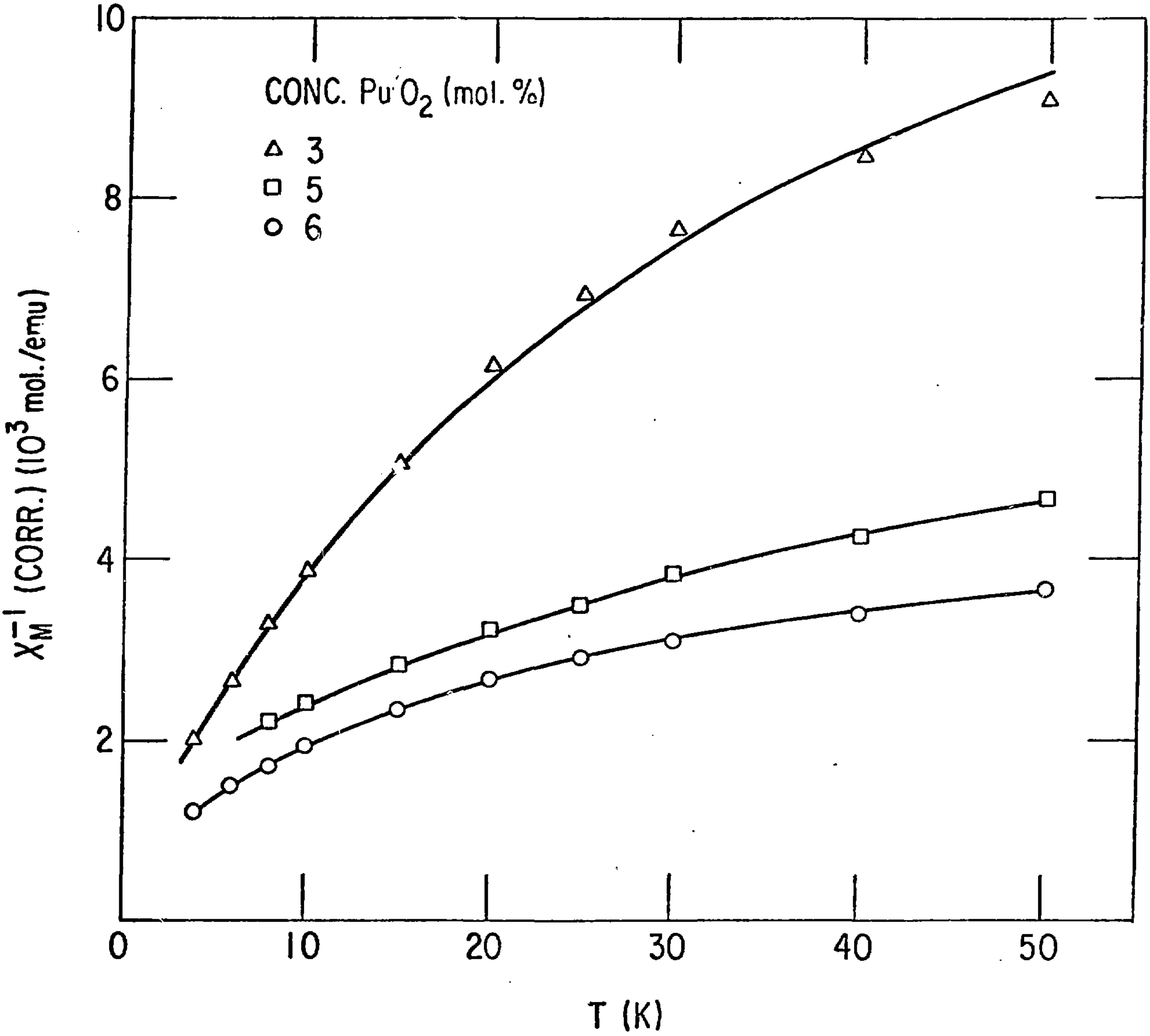

Fig. 2 Reciprocal corrected (see text) molar susceptibility versus temperature (≤ 50 K) for sodium disilicate glasses containing the indicated amounts of PuO_2.