

High Resolution Electron Microscopy Studies of SbCl_5 -GIC

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Introduction

Both electron¹⁻⁴ and x-ray⁵ diffraction studies have shown that SbCl_5 forms several in-plane structures such as the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ and $(\sqrt{39} \times \sqrt{39})\text{R}16.1^\circ$ structures that are commensurate with the graphite lattice and often coexist in the same sample. Along the c-axis direction, the intercalate forms a three layered sandwich with two layers of Cl^- ions, one above and one below each layer of Sb ions.^{3,6} Mössbauer experiments have shown that there is a disproportionation of sites into SbCl_5 , SbCl_6^- , SbCl_3 and SbCl_4^- molecular species in SbCl_5 -GICs.⁷ Several models for the molecular arrangements of these species in the commensurate phases have been suggested.⁸⁻¹⁰ In this work, models for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure are proposed based on high resolution transmission electron microscopy (TEM) and computer image simulation. Based on one of these structural models a mechanism is suggested for the radiolysis process responsible for the commensurate $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ to glass (C-G) transformation observed using the TEM.¹⁻⁴ The C-G transformation is the result of atomic displacements induced by electron beam irradiation through the creation of an electronic excited state (radiolysis).¹⁰ The energy of the excited state in the radiolysis process is transformed into kinetic energy of the atoms by an energy-momentum conversion mechanism.¹¹

Experimental Details

Stage 2 SbCl_5 -GIC samples were prepared using the two-zone method¹² and characterized for stage using (002) x-ray diffraction techniques. The samples for electron microscopy were prepared by repeated cleavage of the SbCl_5 -GIC samples. The TEM observation was carried out using a JEOL 200CX top entry transmission electron microscope ($C_s = 1.2$ mm) with a liquid He cooled specimen stage.¹³ The high resolution images were taken under axial illumination by placing an objective aperture that encompassed reflections up to the (100) ($1.108 \text{ \AA}^{-1}$) $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ superlattice reflections. The image simulation was carried out using the multi-slice method¹⁴ for several molecular structures for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ superlattice in the SbCl_5 system. The in-plane (electron beam parallel to c-axis) simulated images were obtained by dividing the unit cell along the c-axis into five slices of equal thickness ($2.55 \text{ \AA}$), each slice containing one atomic species. The calculations were carried out for several graphite and intercalate stacking sequences.

Results and Discussion

An in-plane lattice image for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure obtained using the TEM is shown in Fig. 1. During the TEM observation, the intensity of the high resolution $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ image changes (giving the appearance of sample bending). Thus, the intensity in the image shown in Fig. 1 corresponds to the average intensity over the period of time when the picture was taken (~ 2 sec). Consequently, some of the fine detail of the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure may be lost in Fig. 1. Figs. 2a) and 2b) show in-plane images for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure obtained by computer image simulation. The models used for the positions of the Sb and Cl atoms in the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ superlattice are schematically shown as insets to Figs. 2a) (SbCl_6^-), and 2b) (SbCl_5 and SbCl_3). Both models preserve the three layer structure of the intercalate along the c-axis. The stacking sequences used in the multi-slice calculations were $\dots\text{A}\alpha\text{AB}\beta\text{BC}\gamma\text{CA}\alpha\text{A}\dots$ (Fig. 2a)) and $\dots\text{A}\alpha\text{AB}\beta\text{BC}\gamma\text{CA}\delta\text{AB}\eta\text{BC}\theta\text{CA}\alpha\text{A}\dots$ (Fig. 2b)), in which the Greek (Roman) letters are used to denote the intercalate (graphite) layers. In the model shown in Fig. 2b) the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ sites are occupied by alternating Sb^{5+} and Sb^{3+} ions. Thus, for this structure the area of the unit cell is four times that for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ unit cell. This periodic arrangement of Sb^{5+} and Sb^{3+} ions requires spots in the electron diffraction pattern at $\sim 0.55 \text{ \AA}^{-1}$ which are not observed experimentally. We have evidence for this structure from in-plane lattice fringes ($11.62 \pm 0.08 \text{ \AA}$ spacing) observed in small regions of the SbCl_5 -GICs. On the other hand, a non periodic arrangement of the SbCl_6^- and SbCl_3 molecular species at the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ sites would not require the extra spots at $\sim 0.55 \text{ \AA}^{-1}$ in the electron diffraction pattern.

Both simulated images shown in Fig. 2 are in good agreement with the image shown in Fig. 1. On the other hand, our previous calculation of the average $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ intercalate domain size of $\sim 650 \text{ \AA}$,¹⁰ suggests that islands of intercalate containing only SbCl_6^- molecular species are not likely to exist, since this would imply that the charge is concentrated in these islands, rather than being homogeneously distributed in the intercalate layer. Simulated images obtained with the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ phase formed by SbCl_3 molecular species only do not show good agreement with the TEM image shown in Fig. 1. This is because for this structure the distribution of the Cl^- ions in the intercalate layer is not homogeneous. We therefore consider the

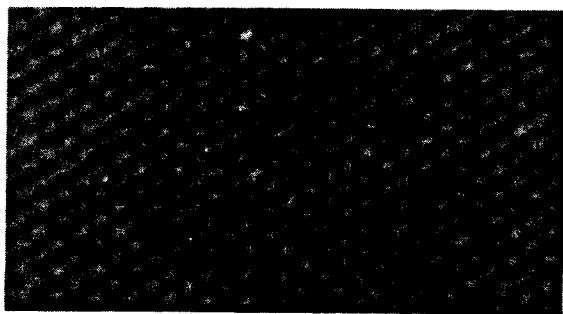


Figure 1. High resolution lattice image of a stage 2 SbCl_5 -GIC sample showing the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure.

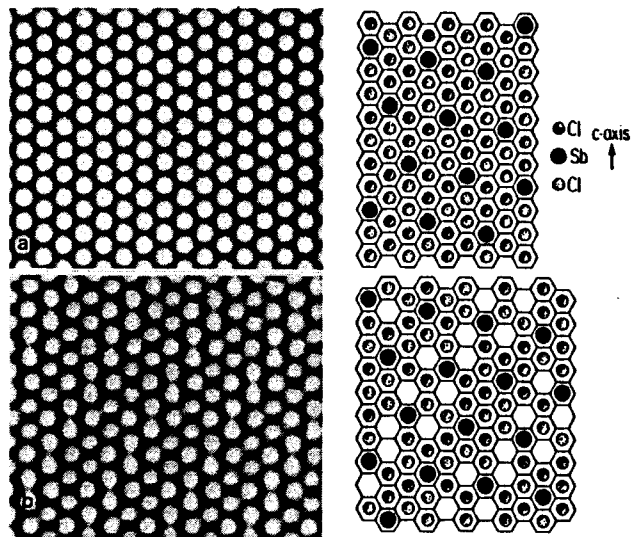


Figure 2. Multi-slice simulation of the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure for a) SbCl_5 and b) a mixture of SbCl_5 and SbCl_3 molecules. The insets are schematic representations of the molecular arrangements for each model.

$(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ islands more likely to be formed by a mixture of SbCl_5 and SbCl_3 molecules with no Sb^{5+} to Sb^{3+} long range order, and the background by a mixture of SbCl_5 and SbCl_3 molecules. We have obtained simulated images for the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure using the models shown in Fig. 2 for several sample thicknesses and defocusing values. Our results show that the dependence of the image intensity on these parameters is very different for the two models. Therefore, a more detailed study taking thru-focus series of images of the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ structure on samples of different thicknesses is necessary to help decide which is the right model for this structure.

In the following, the structural model of Fig. 2b) is used to explain a possible mechanism for the radiolysis process responsible for the electron beam induced commensurate-glass transition observed using the TEM.¹⁰ This model is based on similar observations in electron irradiated NaCl ¹⁵ and sketched in Fig. 3. Under electron beam irradiation a Cl^- ion of the SbCl_5 molecule is ionized leaving a hole behind. This hole becomes localized between two Cl^- ions of the SbCl_5 molecule and a Cl_2^- molecule is formed at a single lattice site (see Fig. 3b)). The latter is unstable and produces a displacement of one of the Cl^- ions (leaving behind an SbCl_5 molecule) to a site next to an SbCl_3 molecule, and an SbCl_4^- molecule is formed (see Fig. 3c)). The new molec-

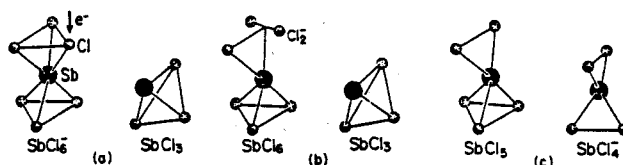


Figure 3. a)-c) Model for the radiolysis mechanism responsible for the electron beam-induced C-G transformation in SbCl_5 -GICs.

ular species have a different arrangement relative to the graphite lattice, and a glass phase is obtained.

Conclusions

From this study we suggest that the $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ phase is formed by a mixture of SbCl_5 and SbCl_3 molecular species. This model is consistent with a model proposed to explain the mechanism for the C-G transition observed using the TEM. Higher resolution such as that obtained with the atomic resolution microscope (ARM) would be necessary to obtain more detailed information about the structure of these compounds.

Acknowledgments

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