

The Effect of Silicate Network Modifiers on Colour and Electron Spectra of Transition Metal Ions

A. Terczynska, K. Cholewa-Kowalska, M. Laczka

*AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
Department of Glass Technology and Amorphous Coatings Technology
Ave. Mickiewicza 30, Cracow, Poland*

Glass colour is a very essential factor both in glass making technology and glass state science. Compounds of transition metals and rare earths, where electron mechanism of colouring occurs, are the most often used as a glass dyes. The colour depends both on electron structure of the transition metal ions and chemical composition and structure of base glass, determining the local site of these elements. Knowledge of the influence of the glass matrix on glass colour has both technological and scientific aspect. The UV/VIS spectroscopy is the most often used method allowing to determine the local state of the transition metals in glasses. We use this method to determine influence of the glass matrix on the character of the local state of chosen transition metal ions.

Silicate glasses from oxide systems: R_2O-SiO_2 , (R – K, Na, Li) are used in our examinations as a glass matrix. In order to obtain the colour glass, the compounds of cobalt (Co), nickel (Ni), manganese (Mn) and chromium (Cr) introduced into glass batch in various concentrations. The aim of these examinations was to determine the influence of modifiers (K_2O , Na_2O , Li_2O) of silicate network on the valency and local state of chosen transition metal ions. We also try to confirm UV/VIS spectroscopic results by EPR spectroscopy.

On the base of these examinations complex conclusions are proposed with respect to the influence of inorganic matrix on the coordination state of Ni, Co, Mn, Cr ions in silicate glasses. Particularly, it has been found that Co and Ni ions occur in examined glasses in four and six coordination while Cr occurs only in octahedral coordination.

Conclusions of our research about complexes forming by transition metal ions in glasses and about oxidation state of transition metals were as follows:

- 1) Kind of modifiers of silicate network (Li_2O , Na_2O , K_2O) effects on both the colour of glasses caused to presence of transition metal ions (Ni, Co, Cr, Mn) and the character of electron spectra in visible range.
- 2) Nickel and cobalt occurs in examined silicate glasses as divalent ions in both tetrahedral (LK-4) and octahedral (LK-6) coordination. Coordination equilibrium (LK4/LK6) shifts in direction tetrahedral complex with decreasing of ion potential of modifiers ($Li \rightarrow Na \rightarrow K$).
- 3) Chromium occurs in examined glasses as trivalent ions in octahedral coordination with oxygen but other oxidation state of chromium is also possible. Proportion of Cr(III) ions in K_2O-SiO_2 glasses is lower in comparison with Na_2O-SiO_2 and Li_2O-SiO_2 probably as a result of oxidation of chromium part to higher valence (Cr(VI)).
- 4) Manganese ions occur in examined glasses as trivalent (Mn(III)) but the presence of divalent manganese ions is also possible. Proportion of Mn(III) increases with decreasing of ion potential of silicate network modifiers ($Li \rightarrow Na \rightarrow K$).
- 5) Decrease of ion potential of silicate network modifiers corresponding to increasing of basicity of anion surroundings in glasses. Thus, increasing of oxygen ions basicity favours of both the tetrahedral coordination and higher oxidation state of transition metal ions.