LETTERS
TO THE EDITOR

Novel Method of Glasses SiO₂–GeO₂ Preparation Monitoring

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Kinetic spectrophotometric analysis of germanium and silicon in aqueous alcohol without their separation or concentration is an important analytical issue, as such systems have been widely applied in the sol–gel synthesis of SiO₂–GeO₂ glasses, the technology to introduce varied concentrations of germanium to the silicon matrix. Of extreme interest is the initial stage of copolycondensation of germanium and silicon compounds; to a great extent, it determines the properties of the final product. The proposed method can be applied to other Si- and Ge-containing systems [1].

The method proposed here is based on the reactions of Si and Ge compounds with ammonium molybdate with formation of the corresponding heteropoly anions [2].

In the formal kinetics, such reactions are considered as the pseudo-first order reactions [3] as they are performed in the excess of the molybdate reagent and solvent.

The kinetics of silicomolybdate polyanion formation was described in detail in [4]. We showed as well that at the conditions of silicomolybdate formation, the β-form of germanomolybdate polyanion was unstable, and the isomerization into the α-form was observed independently of the medium pH in the range of 0.4–2. It was demonstrated that the absorbance profiles of silicomolybdate and of isomeric germanomolybdate polyanions were additive, allowing determination of each of the components from the difference of the

molybdate reaction kinetic parameters. In order to develop the kinetic model for quantitative Ge and Si determination in the mixture, we determined the molar absorptivity of the β and α forms of germanomolybdate polyanion and the rate constant of isomerization ($k_{\beta \rightarrow \alpha} = 0.06 \text{ min}^{-1}$) from the dynamic experiment data. From the model, the rate constant of the β-polyanion formation was determined ($k_{\beta} = 2.45 \text{ min}^{-1}$). The basics of the model have been described in [5].

From the elucidated kinetic parameters, the β-polyanion formation and its β→α isomerization were strictly consecutive reactions.

The relative error of the components determination in the model mixtures using the proposed kinetic method was of 2.3% (SiO₂) and 3.1% (GeO₂).

To conclude, the proposed analysis method is a promising approach for monitoring of the SiO₂–GeO₂ glasses sol–gel preparation.

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