RAMAN STUDY OF B₂O₃-SrO-CuO GLASSES

D. Maniu^{1*}, T. Iliescu¹, I. Ardelean¹ and W. Kiefer²

¹Babes-Bolyai University, Physics Faculty, Kogalniceanu 1, 400088, Cluj-Napoca, Romania; E-mail: dmaniu@phys.ubbcluj.ro ²Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany; E-Mail: wolfgang.kiefer@mail.uni-wuerzburg.de

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Abstract: The influence of vanadium oxide on the structure of $3B_2O_3$ ·SrO glasses was investigated by Raman spectroscopy. The addition of V_2O_5 in strontium borate glasses determines the formation of orthoborate groups.

Raman spectroscopy is an effective tool for resolving the structure of local arrangement in glasses. The samples were prepared by melting the admixtures of H_3BO_3 , SrCO₃ and V_2O_5 (in suitable proportions) at 1523 K. Vitrification was achieved by rapid cooling of the melts at room temperature and atmospheric pressure. In order to obtain Raman spectra, the 514.4 nm line of an Ar⁺ laser (Spectra Physics 2016) was used. An Olympus microscope objective (Olympus ULWD 80, NA 0.75) was used to focus the laser beam as well as to collect the backscattered light. The laser power was 400 mW at the sample. A Dilor XY Raman triple monochromator with a Peltier cooled CCD camera and a spectral slit width of 2 cm⁻¹ was used.

The Raman spectra of $xV_2O_5 \cdot (1-x)[3B_2O_3 \cdot SrO]$ glass samples with various contents of vanadium oxide ($0 \le x \le 0.1$) are shown in Fig. 1. The following bands are present in these spectra: 475, 670, 770, 800, 935, 970 and 1300 cm⁻¹. In the spectra with low V₂O₅ content a broad and intense band situated at high wavenumbers occurs. We presume that this band is due to fluorescence from strontium. The addition of vanadium oxide decreases this fluorescence.

The Raman spectra of pure B_2O_3 glass is dominated by the ~806 cm⁻¹ band. This band was assigned to boroxol rings [1]. The addition of a modifier oxide determines the appearance of a strong band at ~770 cm⁻¹ and induces a shift of the 806 cm⁻¹ band to lower wavenumber values (~800 cm⁻¹). Brill [2] assigned the ~770 cm⁻¹ Raman band to the symmetric breathing vibration of six membered rings with one BO₄ tetrahedron (i.e. triborate, tetraborate or pentaborate). Because the Raman spectra of the 3B₂O₃·SrO glass (x = 0) reveal the ~770 cm⁻¹ band together with the ~925 cm⁻¹ band [3], we consider that in the studied glass pentaborate groups are present.

For the Raman spectra with V_2O_5 ($0 \le x \le 0.01$), the 770 and 800 cm⁻¹ bands rise above the other Raman bands, the intensity of the 770 cm⁻¹ band being higher than that of the 800 cm⁻¹ band. Hence, we conclude that pentaborate groups and boroxol rings dominate the structure of the mentioned glasses and the number of pentaborate groups is higher than the number of boroxol rings (the cross section of these two borate groups are very similar). The introduction of the third element in $3B_2O_3$ ·SrO glass leads to the changes in the glass structure, clearly evidenced by the Raman spectra from Fig. 1. High content of vanadium oxide determines the growing of the 935 cm⁻¹ band and the appearance of the 970 cm⁻¹ band. Crystalline lithium and magnesium orthoborate exhibit a strong peak around 950 cm⁻¹ [4]. Therefore the ~935 and ~970 cm⁻¹ bands can be attributed to orthoborate groups.

The increase in intensity of the 970 cm⁻¹ band compared with that of the 770 and 800 cm⁻¹ bands indicates that the number of non-bridging oxygen (involved in orthoborate groups) increases with vanadium oxide concentration and the glass structure becomes more randomized. The very large band at \sim 1300 cm⁻¹ indicates the presence of pyroborate groups [5] for high content of vanadium

oxide. For all spectra the ~475 and ~670 cm⁻¹ bands also appear. The ~670 cm⁻¹ band is assigned to the metaborate groups [5] and the 475 cm⁻¹ band to a ring angle bending (B-O-B) [1], which is observed at 470 cm⁻¹ for pure B_2O_3 [6].



Fig. 1. Raman spectra of $xV_2O_5(1-x)[3B_2O_3SrO]$ glasses with $0 \le x \le 0.1$.

Raman spectra reveal bands specific to borate groups such as boroxol rings, pentaborate groups, orthoborate groups, pyroborate groups and metaborate groups. The main bands in the observed spectra are characteristic to boroxol rings and pentaborate groups. When the V_2O_5 content increases the number of pentaborate groups decreases and orthoborate groups are formed. Therefore, we conclude that the vanadium ions act as network modifier in the studied glasses.

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