

SPECTROSCOPIC INVESTIGATIONS ON SOME VANADIUM-CALCIUM-PHOSPHATE GLASSES

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IR and EPR investigations on $xV_2O_5 \cdot (1-x)[P_2O_5 \cdot CaF_2]$ glasses with $0.005 \leq x \leq 0.4$ are reported. Both methods give information about the structural effect of the V_2O_5 oxide component on the glass matrix.

IR spectra contain the absorption bands characteristic for both P_2O_5 and V_2O_5 oxides. The IR spectra for $0.005 \leq x \leq 0.1$ show the characteristic bands of phosphate glasses because of the small content of V_2O_5 oxide. These bands are: O-P-O and O=P-O bending vibrations at 518 cm^{-1} and P-O-P stretching vibrations at 760 cm^{-1} . Between $920\text{-}1280 \text{ cm}^{-1}$ a very large band with three distinct peaks dominates the spectra. These peaks are due to the P-O-P stretching vibration, ionic groups $P-O^{(-)}$ stretching vibration and P=O stretching vibration respectively (DAYANAND et al., 1996). At high concentration of V_2O_5 ($x \geq 0.1$) the bands specific for P_2O_5 become weaker and at $x = 0.4$ the spectrum shows clearly all the typical bands belonging to V_2O_5 oxide. Thus at 595 cm^{-1} is present the V-O-V bending vibration, at 980 cm^{-1} the V-O stretching vibration and at 1080 cm^{-1} the V=O stretching vibration appears (BRATU et al., 1999). It can be concluded that with the increase of V_2O_5 content in the studied glasses the peaks attributed to P_2O_5 are partially covered by those attributed to V_2O_5 oxide; in consequence, the V_2O_5 oxide plays the role of a network modifier at low concentrations and network former at high concentrations.

The shape of the EPR spectra is also changed with the increase of the vanadium content, this consisting in a progressive disappearance of the hyperfine structure characteristic to the V^{4+} ions. This fact may be explained by the superposition of two EPR signals, one with a well-resolved hyperfine structure typical for isolated V^{4+} ions in a C_{4v} symmetry and the other one consisting in a broad line without hyperfine structure characteristic for clustered V^{4+} ions (RAMESH KUMAR et al., 2003). These EPR data are in agreement with those obtained from IR spectra and show that at low concentration V^{4+} ions destroy the phosphate matrix structure imposing their own coordination polyhedra in an isolated scattered manner. At high concentration ($x > 0.1$) the broad line typical for clustered ions shows that the magnetic interactions prevail between paramagnetic centers.

References

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