EPR Studies of Cu\textsuperscript{2+} and V\textsuperscript{4+} Ions in Phosphate Glasses\textsuperscript{*}

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Abstract. Two lead-phosphate glass systems doped with both copper and vanadium ions in different ratios were studied by EPR (electron paramagnetic resonance) method. EPR spectra and parameters \((g_\parallel = 2.44, g_\perp = 2.08\) and \(A_\parallel = 117.6 \cdot 10^{-4} \text{ cm}^{-1}\)) obtained for \(x(\text{CuO} \cdot \text{V}_2\text{O}_5)(1-x)[\text{2P}_2\text{O}_7 \cdot \text{PbO}]\) glasses with \(x \leq 10\) mol\% suggest a tetrahedral (Td) coordination of Cu\textsuperscript{2+} ions and not a tetragonally elongated octahedron as has been assumed in previous works. The ground state of the paramagnetic electron is the \(d_{zy}\) copper orbital with a 4p, contribution of 6\%. For \(20 \leq x \leq 40\) mol\% a broad line \((\Delta B = 307\) G) characteristic for clustered ions appears at \(g = 2.18\). The V\textsuperscript{4+} ions are evidenced only in the spectra of \(x(\text{CuO} \cdot 2\text{V}_2\text{O}_5)(1-x)[\text{2P}_2\text{O}_7 \cdot \text{PbO}]\) glasses and the resonance parameters suggest a pentacoordinated \(C_4v\) local symmetry for these ions. The hyperfine structures characteristic for Cu\textsuperscript{2+} and V\textsuperscript{4+} ions disappear for \(10 \leq x \leq 40\) mol\% due to the mixed exchange Cu\textsuperscript{2+}-V\textsuperscript{4+} pair formation in these glasses.

1 Introduction

EPR studies of Cu\textsuperscript{2+} ions in phosphate [1–3] and fluoride [4] glasses have attracted much attention because of the unusual values obtained for \(g\) and \(A\) parameters. It has been shown that the characteristic parameters of Cu\textsuperscript{2+} ions in these glasses are the following: \(g_\parallel = 2.4-2.50, g_\perp = 2.05-2.08, A_\parallel < 120 \cdot 10^{-4} \text{ cm}^{-1}\) and \(A_\perp \leq 20 \cdot 10^{-4} \text{ cm}^{-1}\).

We remark that in contrast to these values of EPR parameters, for Cu\textsuperscript{2+} ions in silicate or borate glasses it were generally obtained \(g_\parallel \leq 2.36\) and \(A_\parallel \geq 140 \cdot 10^{-4} \text{ cm}^{-1}\) [5–11]. The local symmetry assumed for Cu\textsuperscript{2+} ions in these cases was tetragonally elongated octahedron (\(D_{4h}\)) in a six-coordinated form.

EPR parameters for V\textsuperscript{4+} ions in phosphate glasses \((g_\parallel \leq 1.93, g_\perp \geq 1.98, A_\parallel \geq 176 \cdot 10^{-4} \text{ cm}^{-1}\) and \(A_\perp \leq 67 \cdot 10^{-4} \text{ cm}^{-1}\)) [12, 13] are different from those

obtained in other oxide glasses where $g_{ij} \geq 1.935$ and $A_{\parallel} \geq 170 \cdot 10^{-4} \text{ cm}^{-1}$ [15–18]. The supposed symmetry of coordination polyhedra is $C_{4v}$ (square-pyramidal) and distorted octahedral, respectively. A similar coordination by oxygen ligands in a $C_{4v}$ symmetry with a Mo=O double bond was also evidenced for Mo$^{5+}$ ions in $P_2O_5$-$Na_2O$ glasses [19].

The interest in oxide glasses containing mixed transition metal (TM) oxides has grown because in these glasses the presence of mixed exchange pairs has been detected [7, 20, 21]. The effects of the formation of mixed exchange Cu$^{2+}$-V$^{4+}$ pairs on some electrical properties of phosphate glasses are reported in papers [20, 21].

In order to obtain further information on the local structure and interaction between copper and vanadium ions in phosphate glasses, the $x$($CuO$·$V_2O_5$$(1-x)$×

![EPR spectra of $x$($CuO$·$V_2O_5$$(1-x)$×$[2P_2O_5$·$PbO]$ glasses.](image)

Fig. 1. EPR spectra of $x$($CuO$·$V_2O_5$$(1-x)$×$[2P_2O_5$·$PbO]$ glasses.