Absorption Studies on Some Silicate and Cabal Glasses Containing NiO or Fe_2O_3 or Mixed NiO + Fe_2O_3

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Ultraviolet and visible absorption of some sodium and potassium silicate and cabal glasses containing nickel oxide, ferric oxide or both nickel and ferric oxides together have been investigated. In alkali silicate glasses, nickel ions reveal no ultraviolet absorption bands but they show characteristic visible absorption bands due to octahedral and tetrahedral coordinations while iron ions show weak visible absorption bands which are related to ferric ions mostly in tetrahedral state, especially at high alkali oxide content; also iron ions reveal charge transfer ultraviolet absorption bands which are assigned mostly to ferric ions with few ferrous contributions. The proportion of tetrahedral state increases with the increase in the alkali oxide content for the two transition metal oxides. In cabal glasses, nickel ions tend to exist mostly in octahedral state, while ferric ions exist mostly in octahedral and some in tetrahedral form, all the absorption obtained are attributed to their respective energy levels. The ratio of the different coordinations states are discussed in relation to the glass composition.

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1. Introduction

The spectroscopy of transition metal and rare earth ions in glass has been of widely ranging importance in the optical glass industry for many years for a variety of reasons [1]. In highly transparent materials it represents a source of energy loss because of the numerous absorptions they introduce throughput the ultraviolet, visible and near infrared spectral regions.

In other cases, they are used to produce color or active devices such as optical amplifiers, optical cooler, or solarenergy converters based on fluorescence or scintillation. In all cases, their behavior related to the local environment and detailed optical studies have proved fruitful in structural analysis. Changes in the surrounding legends cause significant peak shifts, while changes in matrix composition can alter the coordination number of the metal ions or shift the redox balance.

Previously, some of the authors from our laboratory had studied a single or mixed transition nickel oxides, especially nickel oxide [2–5] and ferric oxide [6, 7] in various glass hosts. They arrived to the conclusion that the states of the transition metal ions depend on the type and composition of glass, melting condition and concentration of the transition metal content.

Iron species have unique optical absorption in the ultraviolet, visible and near infrared spectral regions, which make them well suited to solar control. Well-documented Fe^{2+} ions absorption bands occur in the near infrared at 2222, 1000 nm and 10,000 cm⁻¹, and Fe³⁺ ions reveal absorption bands in the visible and near UV range in many different glass compositions [8–13]. The coordination of Fe²⁺ and Fe³⁺ ions has been debated for many years; the general consensus is that iron is present in silicate glasses as Fe²⁺ and Fe³⁺ ions, both of which can exist in tetrahedral and octahedral sites. Each redox and coordination state produces its own set of characteristic optical absorption bands. The majority of Fe³⁺ ions are believed by many authors to occupy tetrahedral network-forming sites in silicate glasses [10, 11, 14], although this has been disputed. Conversely, the majority of Fe²⁺ ions are thought to occupy octahedral network--modifying sites [15–17].

Earlier spectral studies on nickel by Moore and Winkelmann [18], Weyl [19], Bamford [20] had indicated that nickel exists as divalent Ni^{2+} ions in all glasses with octahedral and tetrahedral coordinations but few postulated the presence of square planar [21] or cubic [22] systems. However, recent investigations [5, 23, 24] demonstrate that divalent nickel ions exist in glasses, in both octahedral and tetrahedral coordination, and the ratio of them depends on the type and the composition of the host glass.

Although studies on iron in glass have attracted the attention of the majority of scientists interested in transition metal behavior in various glasses, yet much recent work by Sreekanth Chakradhar et al. [16, 17] have postulated that Fe^{3+} ions exhibit an octahedral symmetry in contradiction with most previous published works. It is

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evident, therefore, that further studies are still needed by different recent techniques to justify the exact coordination of both iron states in various glasses. The objective of this work is to study the UV-visible absorption spectra of some prepared Ni-doped, Fe-doped or mixed Ni + Fe doped some alkali silicate and cabal glasses in order to investigate the effect of the glass composition and the states of these specific transition metals of the glasses.

2. Experimental

2.1. Preparation of glasses

The studied glasses were prepared from chemically pure materials, in amounts sufficient to produce 50 g glass. Silica was introduced in the form of pulverized pure quartz. Alkali oxides and lime were added in the form of their respective anhydrous carbonates. Boric oxide was introduced as orthoboric acid. Alumina, nickel oxide and ferric oxide were introduced as such.

Weighed batches were melted in platinum crucibles in electrically heated SiC furnaces, at temperature of 1400°C for three hours after the last traces of batches had disappeared. The melts were rotated several times every 30 min to produce satisfactory homogeneity. The melts were cast as rectangular slabs of the dimensions $(l \times l \times 4 \text{ cm}^3)$ for the optical absorption measurements and the prepared specimens were transferred to a muffle furnace regulated at 480°C. After one hour, the muffle was left to cool down to room temperature at a rate of 30° C/h. The annealed specimens were ground and highly polished. Tables I–V give the chemical compositions of the glasses studied.

2.2. Optical absorption measurements

UV-visible absorption in the range 190–900 nm was measured using a recording Shimadzu spectrophotometer (Japan) at room temperature.

3. Results

3.1. Alkali silicate glasses

The effect of introducing one of the monovalent alkali oxides soda or potash on the absorption spectra of the glasses containing 0.2 g NiO, 1.0 g Fe₂O₃, or both 0.2 g NiO and 1.0 g Fe₂O₃ together/100 g glass, was studied and are presented in Figs. (1-4).

- 1. Four absorption bands at 450, 560, 650 and 850 nm were observed in the absorption spectrum given by the glass of the composition SiO_2 70%, Na_2O 30%, NiO 0.2 g.
- 2. Five absorption bands at 210, 230, 340, 380 and 440 nm were observed in the absorption spectrum given by the glass of the composition SiO_2 70%, Na_2O 30%, Fe_2O 1.0 g.

- 3. Eight absorption bands at 205, 230, 330, 380, 450, 565, 630 and 860 nm were observed in the absorption spectrum given by the glass of composition SiO₂ 85%, Na₂O 15%, NiO 0.2 g, Fe₂O₃ 1.0 g, while nine absorption bands at 205, 230, 335, 380, 450, 510, 570, 640 and 750 nm were observed in the absorption spectrum given by the glass of the composition SiO₂ 75%, K₂O 25%, NiO 0.2 g and Fe₂O₃ 1.0 g.
- 4. The progressive increase in the soda or potash content caused the following changes:
 - (i) The position of the absorption bands at 205, 230, 330, 380, 450, 565, 630 and 860 nm in the glass of the composition SiO₂ 85%, Na₂O 25%, NiO 0.2 g, Fe₂O₃ 1.0 g changed to 210, 238, 338, 390, 460, 580, 650 and 890 nm, respectively, in the glass of the composition SiO₂ 65%, Na₂O 35%, NiO 0.2 g, Fe₂O₃ 1.0 g; while the position of the absorption bands at 205, 230, 335, 380, 450, 510, 570, 640 and 750 nm in the glass of the composition SiO₂ 75%, K₂O 25%, NiO 0.2 g, Fe₂O₃ 1.0 g changed to 210, 240, 360, 390, 460, 520, 580, 647 and 760 nm, respectively, in the glass of the composition SiO₂ 65%, K₂O 35%, NiO 0.2 g, NiO 0.2 g, Fe₂O₃ 1.0 g changed to 210, 240, 360, 390, 460, 520, 580, 647 and 760 nm, respectively, in the glass of the composition SiO₂ 65%, K₂O 35%, NiO 0.2 g, NiO 0.2 g, Fe₂O₃ 1.0 g.
 - (ii) The intensity of the absorption bands generally increased with the gradual progressive increase in the alkali oxide content.
 - (iii) The visual color of the glasses studied was pale yellowish brown.

3.2. Cabal glass

The absorption spectra of some cabal glasses containing 0.2 g NiO, 1.0 g Fe_2O_3 or both 0.2 g NiO and 1.0 g Fe_2O_3 , together/100 g glass were studied and are shown in Figs. (5–7).

- 1. Two absorption bands at 430 and 830 nm were observed in the absorption spectra given by the glass of the composition CaO 30%, B₂O₃ 40%, Al₂O₃ 30%, NiO 0.2 g.
- 2. Four absorption bands at 205, 230, 310 and 470 nm were observed in the absorption spectra given by the glass of the composition CaO 30%, B_2O_3 40%, Al_2O_3 30%, Fe_2O_3 1.0 g.
- 3. Six absorption bands at 205, 230, 390, 410, 425, 540 and 840 nm were observed in the absorption spectra given by the glass of the composition CaO 30%, B_2O_3 40%, Al_2O_3 30%, NiO 0.2 g, Fe₂O₃ 1.0 g. The position of the above absorption bands changed to 210, 235, 400, 420, 430, 560 and 860 nm, respectively, in the glass of the composition CaO 30%, B_2O_3 40%, Al_2O_3 40%, NiO 0.2 g, Fe₂O₃ 1.0 g.

4. Discussion

4.1. Alkali silicate glasses

Generally, there are several conflicting theories on the structure of vitreous silica [25–28]. Each of these theories accepts that the basic structural unit is SiO_4 tetrahedra with a silicon atom at its center and four oxygen atoms at the vertices and it is generally agreed that the tetrahedral units are linked together via the common or "bridging" oxygen atoms. However, the theories differ in proposing the types of geometrical configuration which occur in the structure. The most accepted theory, the so-called random network theory due originally to Zachariasen [25], states that the SiO_4 tetrahedra form a connected three-dimensional random network, the mechanism of randomness is the relative orientation of adjacent tetrahedral. The Si-O-Si angle takes any value in a range from approximately 120° to 180° ; there is some recent evidence that the mean value is about 150° . The Si–O–Si angle, on the other hand, does not differ appreciably from the ideal tetrahedral angle. In a completely connected structure of this type, each oxygen atom is connected with two silicon atoms.

It is thought [26] however, that in real samples of vitreous silica, a small proportion of oxygen atoms may constitute the so-called non-bridging oxygen atoms which are linked to one silicon atom.

The other theories of the structure of vitreous silica include the vitron theory proposed by Tilton [27] which has been developed by Robinson [28] and the crystallite theory of the Russian school [29]. The true structure may be somewhere between a connected random network and a crystallite system, i.e., it may be a connected network with small regions almost crystalline in character and other region essentially of a random structure. The tetrahedral coordination of silicon was supported by X-ray [29, 30] and neutron diffraction studies [31].

Another study [32] of the structure of vitreous silica has been made under improved X-ray techniques, the interpretation of which leads to the familiar random network model.

4.2. Effect of alkali oxides

The introduction of alkali oxide such as soda in sodasilica glasses results in the formation of single-bonded or nonbridging oxygen atoms, i.e., oxygen atoms linked to only one silicon atom [33]. Sodium ions are linked to the surrounding oxygen by bonds which are much more ionic and also much weaker than the silicon-oxygen bonds. Thus, the structure of the sodium silicate glass is weaker than that of vitreous silica. As the soda content is increased, more and more non-bridging oxygen are formed until eventually the material consists of isolated SiO₄ tetrahedra linked together by ionic Na–O bonds. It has been also stated that the range of the glass formation in soda-silica system is continuous from pure SiO to a limiting composition close to that of the metasilicate Na₂O·SiO₂ [33]. Douglas [34] suggested that the structure of the sodium metasilicate may be probably represented by the position of sodium ions which are distributed much more at random throughout the structure than can be the case with the thread or ring structures.

According to Abou El-Azm [35], all the interstices in the silicate glass structure are occupied by sodium ions when SiO₂:Na₂O ratio approached 1:0.85. From the point of view of the polarizability of oxygen ions [36], the oxygen ions in silica have low polarizability. Each oxygen ion is exposed to two Si⁴⁺ ions in close proximity. The presence of an alkali oxide in a silica glass provide possibility of better screening of silicon ions, by increasing the alkali oxygen distances, a change which increases the polarizability, and with it, the screening power of some oxygen ions without rousing the energy excessively.

Recently, it was stated that [37] the addition of any alkali oxide to silica to form a binary glass results in major reductions in the viscosity of the melt. The densities and refractive indices and the thermal expansion coefficients of the glasses increase with increasing alkali oxide concentration, also the electrical conductivity increases with the increase in the alkali oxide content. These trends in properties are due to the formation of non-bridging oxygen, which decrease the conductivity of the melt. Each non-bridging oxygen must be associated with a nearby alkali ion to maintain local charge neutrality. These alkali ions occupy the interstices in the network, reducing the unoccupied free volume of the structure. The concentration of the non-bridging oxygen increases directly in proportion to the alkali oxide content, until a network can no longer be maintained and glass formation cannot be reached.



Fig. 1. Absorption curve for a sodium silicate glass of the composition SiO₂ 70%, Na₂O 30% containing 0.2 g NiO/100 g glass (101).

Accordingly, the experimental and results obtained from spectrophotometer measurements of the alkali silicate glasses studied can be explained and discussed as follows:

1. In the sodium silicate glass of the composition SiO_2 70%, Na_2O 30%, NiO 0.2 g, it would be expected that the absorption bands at 450 and



Fig. 2. Absorption curve for sodium silicate glass of the composition SiO₂ 70%, Na₂O₃ 30% containing 1.0 g $Fe_2O_3/100$ g glass (102).



Fig. 3. Absorption curves for a number of sodium silicate glasses containing both 0.2 g NiO and 1.0 g Fe₂O₃ together /100 g glass. 105: SiO₂ 85%, Na₂O 15%, NiO 0.2 g, Fe₂O₃ 1.0 g; 106: SiO₂ 80%, Na₂O 20%, NiO 0.2 g, Fe₂O₃ 1.0 g; 107: SiO₂ 75%, Na₂O 25%, NiO 0.2 g, Fe₂O₃ 1.0 g; 108: SiO₂ 70%, Na₂O 30%, NiO 0.2 g, Fe₂O₃ 1.0 g; 109: SiO₂ 65%, Na₂O 35%, NiO 0.2 g, Fe₂O₃ 1.0 g.



Fig. 4. Absorption curves for a number of potassium silicate glasses containing both 0.2 g NiO and 1.0 g Fe_2O_3 together /100 g glass. 111: SiO_2 75%, Na_2O 25%, NiO 0.2 g, Fe_2O_3 1.0 g; 112: SiO_2 70%, Na_2O 30%, NiO 0.2 g, Fe_2O_3 1.0 g; 113: SiO_2 65%, Na_2O 35%, NiO 0.2 g, Fe_2O_3 1.0 g.



Fig. 5. Absorption curve for a cabal glass of the composition CaO 30%, B₂O₃ 40%, Al₂O₃ 30% containing 0.2 g NiO/100 g glass (121).



Fig. 6. Absorption curves for a cabal glass of the composition CaO 30%, B_2O_3 40%, Al_2O_3 30% containing 1.0 g Fe₂O₃/100 g glass. 122: CaO 30%, B_2O_3 40%, Al_2O_3 30%, Fe₂O₃ 1.0 g.



Fig. 7. Absorption curve for a number of cabal glasses containing both 0.2 g NiO and 1.0 g Fe_2O_3 together/100 g glass. 123: CaO 30%, B_2O_3 40%, Al_2O_3 30%, NiO 0.2 g, Fe_2O_3 1.0 g; 124: CaO 30%, B_2O_3 35%, Al_2O_3 35%, NiO 0.2 g, Fe_2O_3 1.0 g; 125: CaO 30%, B_2O_3 35%, Al_2O_3 35%, Al_2O_3 40%, NiO 0.2 g, Fe_2O_3 1.0 g; Fe_2O_3 1.0 g.

850 nm, of the transitions ${}^{3}F_{2} \rightarrow {}^{3}P_{4}$ and ${}^{3}F_{2} \rightarrow {}^{3}F_{4}$ respectively, can be attributed to the presence of octahedral coordination of nickel ion while the double absorption band at 560 and 650 nm, of the transition ${}^{3}F_{4} \rightarrow {}^{3}P_{4}$ is attributed to the presence of tetrahedral coordinations of nickel ion. Therefore, it would be expected that nickel ion exists in both octahedral and tetrahedral coordinations in the glass studied [9].

- 2. In the sodium silicate glass of the composition SiO_2 70%, Na_2O 30%, Fe_2O_3 1.0 g, it would be expected that the two ultraviolet absorption bands at 210 and 230 nm may be considered as charge transfer bands for ferrous and ferric ions, respectively. Also, these absorption bands may be attributed to the combined action of raw materials impurities [12]. The double absorption band at 340 and 380 nm may be attributed to 4D_5 for ferric ion in tetrahedral state while the absorption band at 440 nm may be due to 4G_5 for ferric ion mostly in tetrahedral form [7, 9–12].
- 3. In alkali silicate studied, for sodium silicate and potassium silicate glasses, respectively, the two ultraviolet absorption bands at 205-210 nm and 230–240 nm may be considered as charge transfer bands for ferrous and ferric ions, respectively, also these absorption bands may be attributed to be due to raw materials impurities [12]. The double absorption band at 330-340 and 380-390 nm may be attributed to ${}^{4}D_{5}$ for ferric ion in tetrahedral state [10]. The absorption band at 450–460 nm of the transition ${}^{3}F_{2} \rightarrow {}^{3}P_{4}$ may be due to octahedral coordination of nickel ion and it may be also attributed to ${}^{4}G_{5}$ for ferric ion mostly in tetrahedral form [7, 9–12]. The double absorption band at 560-580 nm and 630-650 nm, of the transition ${}^3\!F_4 \rightarrow {}^3\!P_4$, can be attributed to the presence of tetrahedral coordination of nickel ion [9], in addition to that the absorption band at 560–580 nm may be due to the presence of ferric ion in octahedral state [7, 9-12]. The absorption band at 750-890 nm, of the transition ${}^{3}F_{2} \rightarrow {}^{3}F_{4}$, was attributed to octahedral form of nickel ion [9]. The absorption band at 510-520 nm in potassium silicate glasses may be due to ${}^{3}G_{4}$ for ferric ion mostly in tetrahedral state. Therefore, it would be expected that nickel ions exist in low alkali silicate glasses mostly in octahedral state while they exist in high alkali silicate glasses mostly in tetrahedral state, while ferric ions exist mostly in tetrahedral state in the glass studied [7, 9–12]. The proportion of the tetrahedral form increases with the gradual increase in the alkali oxide content [7–13]. The increase in the intensity of absorption bands with the increase in the alkali oxide content may arise generally from increased d-p orbital mixing [13], related to the lower legend field strength as indicated by

the shift of absorption bands towards longer wavelengths.

4.3. Cabal glasses

The name cabal glass was firstly given by Sir Herbert Jackson [18] to non-alkali, non-silicon glasses with lime, boric oxide and alumina as their basic constituent.

The structure of these glasses is very different from that of silicate glasses. However, this ternary glass system may be treated as a binary system, with lime as the modifier oxide and boric oxide and alumina serving jointly as network silicate formers [38].

The limiting composition of cabal glasses was assumed to be influenced by the following factors [39].

- 1. One molecule of lime must be present, at least, to provide the oxygen required for each molecule of alumina to form tetrahedron.
- 2. Two AlO₄ tetrahedra can be linked together and one BO₃ or BO₄ group, at least, should be present between two AlO₄ tetrahedra, then the ratio of alumina to boric oxide tetrahedra, should not be greater than unity, but alumina in amounts greater than this ratio can be introduced in the presence of 2.3 mol lime, probably because calcium ion can form bridges between the adjacent AlO₄ tetrahedra.
- 3. By considering cabal glasses as alumino-borate glasses, the number of the interstices within the glass structure will be much higher than the number of calcium ions present. Accordingly, the calcium ions would all be housed in the interstices in which they will be surrounded with eight oxygen which represent a preferable state than one in which the calcium ions are present as bridges between the adjacent AlO_4 tetrahedra. With more lime greater than is required for the four coordination of alumina, part of borons become four coordinated till one fifth of boron ions have formed BO_4 tetrahedra groups. The excess lime will occupy bridging positions in the glass network.

Owen [40] assumed that all aluminum and only one fifth of borons might be four coordinated by oxygens, but with greater amounts of lime than are necessary for this, BO_3 groups with non-bridging oxygens were formed and the proportion of the non-bridging oxygen increased with the increase of the lime content.

Bray and Keefe [41], from nuclear magnetic resonance, suggested that Abe hypothesis [42] should be an oversimplification of the structure and that more than one fifth of the boron atoms could be four coordinated and that not all the aluminum was four coordinated. However, the proportion of non-bridging oxygen ions would be expected to increase with the increase of the lime content. Ghoneim et al. [43] assumed that the tetrahedrally coordinated boron in cabal glasses is energetically more stable than the non-bridging oxygen. It is also assumed that aluminium cannot be bridged through oxygen to another aluminium or to a tetrahedrally coordinated boron, thus it is expected that the concentration of alumina will influence the coordination of boron. With more lime introduced than is required for fourfold coordination of aluminium ions and part for boron ions, the excess lime will create non-bridging oxygens which would certainly be expected to increase with the increase of the lime content, whereas BO_4 groups increase the coherence of the network, while non-bridging oxygen ions are thought to have an opposite effect.

De Waal [44] previously suggested that the replacement of boric oxide by alumina was not entirely without consequences. It appears that the concentration of non--bridging oxygen ions increases with the introduction of alumina. It was further assumed that not all aluminium ions in alumino-borate glasses were in fourfold coordination with bridging oxygen ions.

The dilemma about the "lodging" of alumina in the glass could be solved by assuming the occurrences of triclusters proposed by Lacy [45], who pointed out that in the glasses with low number of non-bridging ions, some of aluminium ions might be surrounded by three three-bridging oxygen ions and one "tripod" or "inactive" oxygen ion, touching three network forming cations instead of two. The excess oxygen ions, resulting from these structural units may be used partly to form BO_4 groups and partly to raise the number of non-bridging oxygen ions.

The results of Bishop and Bray [38] showed that both Al(4) and B(4) were present at all modifiers contents, contradicting the idea of Owen [41] which stated that borate network strongly preferred Al(4) to B(4). Although Bishop and Bray model [39] predicts that modifier addition can form both B(4) and Al(4), the model predicted that all aluminium should be Al(4) at high modifier contents.

Bunker et al. [46] from magic angle NMR studies advanced a significant different model for alkalineearth boroaluminate glasses based on crystal chemical concepts, structural predictions and comparisons to known crystal structures. The model allowed for significant Al(5) concentrations, large concentrations of three-coordinate oxygen in neutral sites such as B(3)-Al(6) and B(4)-B(4)-Al(4) and anionic sites such as B(3)-Al(6) which are not associated with B(4), Al(4)or non-bridging oxygens. They indicate that the ionic potential of the modifier cation should also affect the distribution of anionic oxygen sites in the boroaluminates.

Bunker et al. [46] also assumed that favored oxygen units in boroaluminate glasses tended to contain bonds to both aluminum and boron indicating that the glasses should not phase-separate into aluminate and borate-rich volumes and that there is no evidence of phase separation. Bunker et al. [46] further showed that at high modifier contents, B(4) should be converted back to B(3) and the relative amounts of Al(4), Al(5) and Al(6) should not be changed with modifier content.

Khedr et al. [47] stated that in cabal glasses, the oxygen ions donated by lime will be largely claimed by Al^{3+} and B^{3+} ions. Most or all of alumina present was previously assumed to be present as AlO_4 tetrahedral coordinated till one fifth of boron ions have formed tetrahedral groups with the rest of boron in threefold coordination. The excess lime, if present, will occupy bridging positions in the network.

Accordingly, the experimental results obtained from spectrophotometric studies of cabal glasses can be explained and discussed as follows. From the results obtained, it would be expected that the two absorption bands at 205–210 and 230–235 nm may be considered as charge transfer bands for ferrous and ferric ions respectively, also these absorption bands may be due to raw materials impurities [12]. The absorption band at 395–400 nm may be due to ${}^{4}D_{5}$ for ferric ion in tetrahedral or octahedral form according to the glass composition. The absorption band at 410–420 nm of transition ${}^{3}F_{2} \rightarrow {}^{3}P_{4}$, can be related to nickel ion in octahedral form and also it may be due to ferric ion in octahedral symmetry [6, 9–12]. The absorption band at 425–430 nm of transition ${}^{3}F_{2} \rightarrow {}^{3}P_{4}$, can be related to nickel ion in octahedral state and also it may be due to ${}^{4}D_{5}$ for ferric ion in tetrahedral symmetry [6, 9–12]. The absorption bands at 540–560 nm, of transition ${}^{3}F_{4} \rightarrow {}^{3}P_{4}$ would be due to nickel ion in tetrahedral state [6, 9–12, 14], in addition it may be attributed to the presence of ${}^{4}\Gamma_{5}(D)$ for ferric ion mostly in tetrahedral state [6, 9–12]. The absorption band at 840–860 nm of transition ${}^{3}F_{2} \rightarrow {}^{3}F_{4}$, can be related to nickel ion in octahedral form [6, 9–12, 25].

Thus, it can be assumed that nickel ions in cabal glasses mostly exist in octahedral state, while ferric ions tend to exist in these glasses in the two states of coordination, namely octahedral and tetrahedral. The above conclusion can be understood by taking into consideration the structure of cabal glasses and the role of alumina in it.

5. Conclusion

UV-visible spectroscopic measurements of NiO or Fe_2O_3 doped alkali silicate and cabal glasses were carried out together with the same glasses containing mixed NiO + Fe₂O₃. Spectral results indicate the presence of characteristic absorption bands due to Ni²⁺ in octahedral and tetrahedral states and iron ions in both Fe³⁺ and Fe²⁺ ions. The tetrahedral state is observed to be predominant with the increase of modifier content for the two transition metal ions. In mixed doped NiO + Fe₂O₃ glasses, the absorption bands for both TM ions are identified. All the absorption spectra are attributed to their respective energy levels.

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