

# **Ligands and Modifiers in Vitreous Materials**

**Spectroscopy of Condensed Systems**

**Alfred A. Margaryan**

**World Scientific**

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**Dedicated to my sons  
Ashot and Ara**

## Introduction

Development of modern optics, photonics, fiber optics, quantum electronics and opto-electronics are related to the creation of specific properties in optical materials; such as glass, crystals and polymers.

For instance, in the area of glass lasing materials the presence of specific dopants affects the laser performance. In materials used for creating fiber optics cables the presence of dopants affects the absorption, or loss characteristics of the cable.

The evaluation of spectroscopic and spectrochemical parameters of doped (activated) glass forming materials from the point of view of the nature of the chemical bond is very important.

The main purpose of this book is to collect and present theoretical and experimental results on the nature of chemical bonds created by ligands, modifiers and dopants on the vitreous phase, and their influence on the spectral properties of inorganic optical glasses.

It is well known that in crystalline materials, especially in monocrystals, ligands define the strength of the crystalline fields surrounding transition elements ( $d^n$  and  $f^n$  elements).

This book has for the first time combined data into one reference several measurement methods, i.e., luminescence, absorption, and electron paramagnetic resonance (EPR). This data leads to the conclusion that in solid materials in the vitreous state the modifiers determine predominantly the spectroscopy of activators.

Spectroscopic characteristics of inorganic compounds of transition elements and their solutions is well developed theoretically in the spectrochemistry of complexes, but developments for vitreous materials in this condition are absent. This book fills this gap by presenting a new spectrochemical approach in the research of structure and spectroscopy of doped (activated) inorganic vitreous materials.

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Alfred Margaryan

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## **Chapter 1**

### **CHEMICAL BONDS IN VITREOUS MATERIALS**

All materials in nature exist in three states of aggregation: gas, liquid and solid. Gases can exist as the usually familiar gas or as plasma (ionized gas); liquids can exist in the form commonly known as liquid or as liquid crystals; and solids can be amorphous or have different crystalline forms.

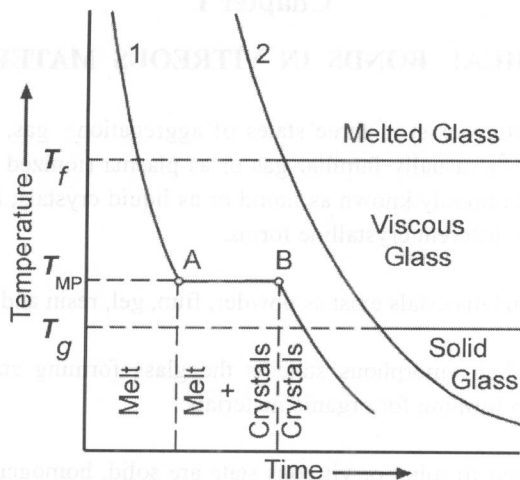
The solid amorphous materials exist as powder, film, gel, resin and glass form.

The basic form of an amorphous state is the glass forming state for inorganic materials, and resin forming for organic materials.

Materials in the glass forming or vitreous state are solid, homogeneous, fragile and transparent matter. The glass forming state is located between the crystalline and liquid state.

All materials in the glass forming state have some general physico-chemical characteristics. Typical glass forming subjects are:

1. Isotrop; which means that all properties are same on all sides of matter.
2. Glasses during heat process do not melt as crystals, but gradually soften and pass from fragile to a high viscosity and liquid state (Figure 1.1). In this process all physico-chemical properties are changed uninterrupted.



**Figure 1.1:** Nature of cooling of the melts crystalline (curve 1), and glass forming (curve 2) materials.

3. Glasses melts and solidify in reverse (Figure 1.1), which means that repeated process of melting and cooling of glass takes the same temperature regime.

Reverse process of properties indicates, that glass forming melts and solid glasses are true liquids, therefore the solid glass state is supercooled liquid.

Special scientific interest must be presented for evaluation of the glass forming process by from point the perspective of view of the nature of the chemical bonds, which are formed between individual elements of the structure.

The nature of the chemical bonds is one of the dominant factors in the glass forming process. However, in scientific literature there are few publications on this subject.

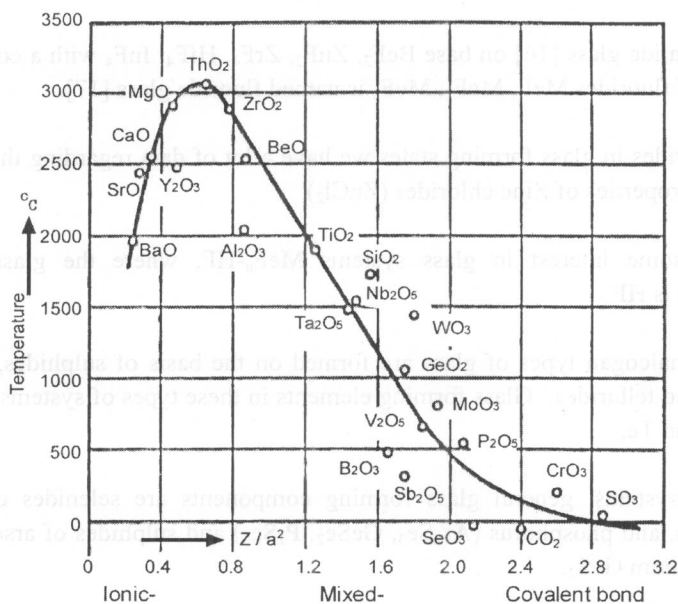
The investigation of chemical bonds in glass forming melt and in the solid glass are one of the general problems of the material sciences, especially for glass forming materials [1-9].

Winter-Klein [10-12] recommended the replace conception about glass forming elements by the conception of the glass forming bonds, accomplished by P-electrons.

Britton [13] and Rawson [14] established that for glass formation the first factor is the nature of the chemical bonds between particles of existing cells. Glass forming is made possible by the presence of a variety of mixed bonds ionic-covalency.

Dietzel [15] determined the position of glass forming oxides in the group of existing oxides and showed dependence of the melting points of some oxides at strength of the fields as  $Z/a^2$  ( $Z$ -charge,  $a$ -distance of center between both ions). This dependence is presented on Figure 1.2. It shows the curve passed through fields of oxides, which have high melting point (2000-3000°C). These types of oxides have a predominantly ionic bond.

After the curve passes through the field of glass forming oxides ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ) the end of the curve lies down in the field of oxides having very low melting point (0-400°C) which is characterized with covalence bonds. In glass forming oxides there are intermediate types of ionic-covalent bonds.



**Figure 1.2:** Melting points of some oxides function at strength of cations fields  $Z/a^2$  (after ref. [15]).

In the glass forming or vitreous state there is a large quantities of inorganic materials, from individual elements to complicated multicomponent systems.

Inorganic glasses are classified by several types:

1. Elementary or monoatomic glass, which consists of one base element (S, Se, As, P).
2. Oxide glass where typical glass forming components are  $B_2O_3$ ,  $SiO_2$ ,  $GeO_2$ ,  $P_2O_5$ . Other oxides become to glassy state in small quantities under fast cooling conditions ( $As_2O_3$ ,  $Sb_2O_3$ ,  $TeO_2$ ,  $V_2O_5$ ). Some oxides cannot become to vitreous form independently ( $Al_2O_3$ ,  $Ga_2O_3$ ,  $Bi_2O_3$ ,  $TiO_2$ ,  $MoO_3$ ,  $WO_3$ ), however in combination with different components in binary and multicomponent systems develop glass-forming abilities.

Finally we have the types of silicate, borax, phosphate, germanate, tellurate, aluminate and other oxide glasses.

3. Halide glass [16] on base  $BeF_2$ ,  $ZnF_2$ ,  $ZrF_4$ ,  $HfF_4$ ,  $InF_4$  with a combination of fluorides  $MeF$ ,  $MeF_2$ ,  $MeF_3$  is named fluoride glass [17].

From chlorides in glass forming states we have a lot of data regarding the physico-chemical properties of Zinc chlorides ( $ZnCl_2$ ).

There is some interest in glass systems  $MeF_n$ -HF, where the glass forming component is HF.

4. Chalcogan types of glass are formed on the basis of sulphides, selenides and tellurides. Glass forming elements in these types of systems are S, Se, and Te.

In binary systems, general glass forming components are selenides of arsenic, germanium, and phosphorus ( $As_2Se_3$ ,  $GeSe_2$ ,  $P_2Se_3$ ) and sulphides of arsenic  $As_2S_3$  and germanium  $GeS_2$ .

In general, chalcogan glass is very complex and different in composition.

5. Special types of glass, such as groups of nitrate, acetate and sulphate glasses have low melting points. These types of glass are chemically unstable.
6. A mixed type of glass formed by using a mix of previously glass formed components: oxides and Halides, oxides and chalcogens, chalcogens and halides.

Particular types of glass are nitride and oxide-nitride glasses on the base  $\text{Si}_3\text{N}_4$  (MP-1900°C),  $\text{AlN}$  (MP-2200°C),  $\text{BN}$  (MP-3000°C),  $\text{Be}_3\text{N}_2$  (MP-2200°C) [19]. These types of glasses are absolutely new. They have a very high chemical resistance and a high melting point.

In recent years we are finding in scientific literature some results about metallic glass (Fe, Pd, Zr, Ni, Cu) [20-22].

Petrovski [23,34] after conclusion of all presentations on glass forming states showed on the sample of beryllium fluorine glasses that covalence bonds favorable for glass forming, but ionic bonds for crystallization.

Generally the glass forming state of materials depend on the existence of mixed types of bonds ionic-covalence characters between elements of structure.

Spectroscopic investigation of transition elements in glass forming and crystalline materials are giving us the opportunity to evaluate the change of degree of covalency and strength of ligands field in above matrices.

In fundamental works Bethe [25] and Van Vleck [26-29] successfully developed the theory of crystalline field regarding crystalline materials.

The second period development of theory on crystalline field begins with the progress of spectrophotometry and electron paramagnetic resonance [30-35].

During this period the theory of fields of ligands was formed, it combined the theory of crystalline fields with the Mulliken [36] method of molecular orbitals.

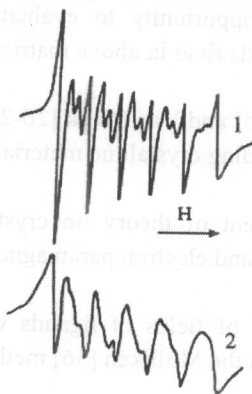
Consequently, positive results of the theory of chemical bonding and the theory of crystalline fields were included in theory field of ligands.

One of the successful results of theory field of ligands are energetic diagram types of Tanabe-Sugano [37,83]. These diagram types are presenting the influence of the nature of ligands on the parameters of crystalline fields (spectrochemical and nephelauxetic lines) [39-43]. Margaryan et al. [44-47] showed that in vitreous materials the following chemical bonds exist between D-L-G-L-M, where D-dopant (ions of transition elements  $d^n$ ,  $f^n$ ), L-ligand, G-glass forming atom near coordination sphere, M-modifier.

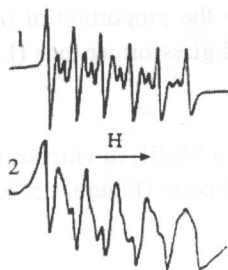
In the degree of covalency of L-G is higher (O-Si, O-Ge, O-B, O-P or F-Be) the degree of covalency between D-L ( $L-d^n$  or  $L-f^n$ ) will be lower. The differences in covalency are described by the changes in the polarization of the ligands.

In glass forming (vitreous), the material elements of structure (L-G) have to be predominantly in covalent bonding, owing to  $sp^n$ -hybridization of electron orbitals between the glass forming atom (G) and ligand (L). The opposite occurs in the crystalline form of matter.

Allen and Nebert [48,49] discovered that the EPR spectra of transition metals, in particular Mn(II), within organic and inorganic solvents show finer structures when the sample is in the glass forming phase rather than a polycrystalline phase. Figures 1.3 and 1.4 show the EPR spectra of Mn(II) in methanol ( $CH_3OH$ ) and 12N HCl. The hyperfine structure becomes quite different when the sample changes from a transparent glass phase (curve 1) to a polycrystalline phase (curve 2).



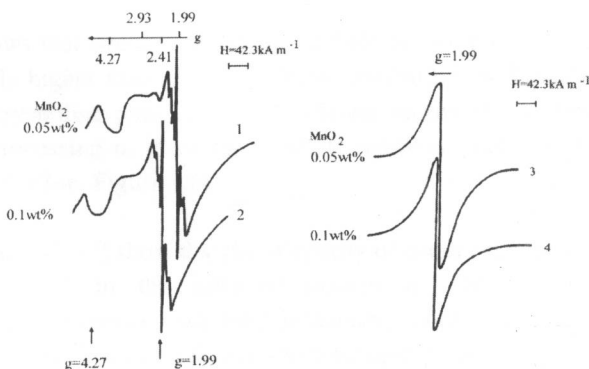
**Figure 1.3:** EPR spectra of Mn(II) in vitreous (curve 1) and polycrystalline (curve 2) methanol (after ref. [48]).



**Figure 1.4:** EPR spectra of Mn(II) in vitreous (curve 1) and polycrystalline (curve 2) 12N HCl (after ref. [48]).

Margaryan et al. [50-58] investigated the EPR spectra of the paramagnetic Mn(II) ion in glass forming and crystalline (hexagonal form) germanium dioxide. The compositions of glass forming-dopant and crystal-dopant have a significant importance in determining the structure and character of bonds in vitreous-glassy (isotropic) and crystalline (anisotropic) systems. The important parameters are: the degree of covalency in  $\text{GeO}_2$  of the electron orbitals of Mn(II) and ligands, the field intensity of the ligands, the coordination position of Mn(II), regularity of the structure of  $\text{GeO}_2$  in the vitreous and crystalline states.

Figure 1.5 shows EPR spectra Mn(II) in vitreous (curves 1 and 2) and crystalline (curves 3 and 4)  $\text{GeO}_2$ . Any change in the solvate cloud will lead to some difference in the EPR spectra of Mn(II) (see Figure 1.5).



**Figure 1.5:** EPR spectra of Mn(II) in vitreous (curves 1 and 2) and crystalline (hexagonal forms) (curves 3 and 4)  $\text{GeO}_2$  (after refs. [50,51]).

An important role is played by the proportion of one or another type of bonding existing between the ligand and glassformer ions (L-G), and the ligand and dopant ions (L-D) in the structures.

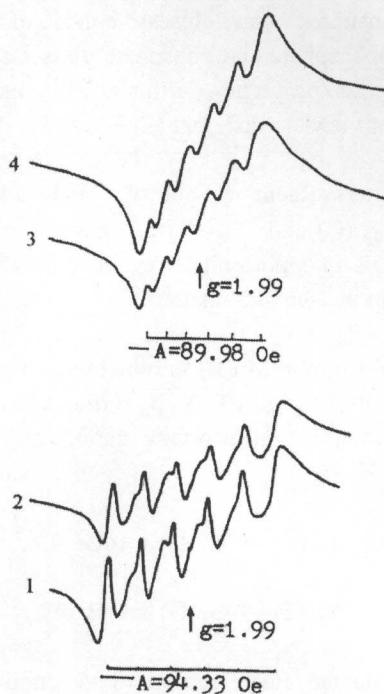
A comparison of the EPR spectra Mn(II) in vitreous (curves 1 and 2) and crystalline (curves 3 and 4) germanium dioxide (Figure 1.5) shows identical data in [48,49] (Figures 1.3 and 1.4).

From the EPR data for Mn(II), we can conclude that the degree of hyperfine splitting (*hfs*) in a covalent ligand-dopant interaction is lower than that in an ionic bond. The hyperfine splitting for Mn(II) is directly proportional to the degree of ionic bonding in the ligand-dopant bond [50-52].

Previous interpretations received their confirmation for vitreous and crystalline form of fluorophosphates type of  $45\text{P}_2\text{O}_5.55\text{BaF}_2$  (in mol%), when investigated EPR spectra of Mn(II) respectively [54].

Figure 1.6 illustrates EPR spectra of Mn(II) in vitreous (curves 1 and 2) and crystalline (curves 3 and 4) form of fluorophosphates. It shows significant difference in spectra EPR and means of hyperfine splitting (*hfs*). Constant of hyperfine splitting for vitreous fluorophosphate (curves 1 and 2) equals to 94.33oe in crystalline form of the same composition (curves 3 and 4)  $A=89.98\text{oe}$  (Figure 1.6)





**Figure 1.6:** EPR spectra of Mn(II) in glasses of composition (mol%): 45P<sub>2</sub>O<sub>5</sub>.55BaF<sub>2</sub>; Mn(II) 0.05 wt% (curve 1), 0.1 wt% (curve 2), and in their crystalline forms; Mn(II) 0.05 wt% (curve 3), 0.1 wt% (curve 4) (after ref. [54]).

Figure 1.6 shows that strength of the ligand field on Mn(II) in crystallized samples are significantly higher than in glass. These types of bonds, ligand-Mn(II) in glass forming and crystalline phases, have a different means of covalency. Under the crystallizing processing of glass the bond of covalency between ligand-Mn(II) is increases ( $A=89.98\text{oe}$ , Figure 1.6).

Margaryan et al. [44-47] show that the similarity of chemical bonds between ligands and dopants (L-D) in the different natures of glasses (berylliumfluorine, fluorophosphate, phosphate, silicate, germanate, borax and others) causes an analogy in their spectrochemical and spectroscopic parameters; even though they have the crystallochemist similarities of some other glass-formers (BeF<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>).