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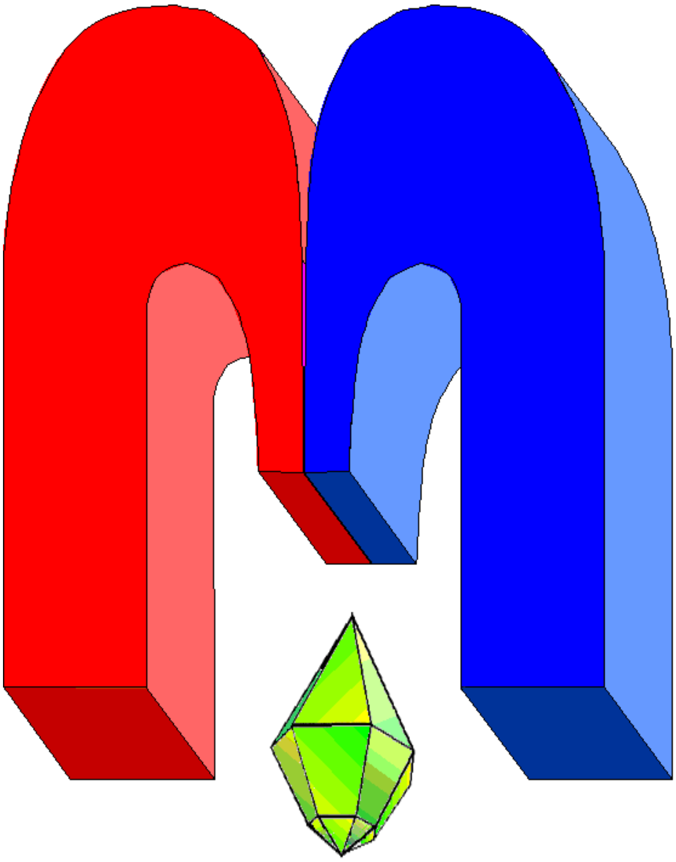

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

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Electron paramagnetic resonance study on phosphosilicate glasses

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The phospho-silicate glass containing 10 mol% CrF_2 was studied by electron paramagnetic resonance (EPR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) equipped with electron diffraction apparatus which is specified for measuring the electron diffraction pattern (EDP). EPR spectroscopy offers information about oxidation states of Cr ions and their coordination symmetry in the vitreous network. The EPR spectra of Cr^{3+} of glass containing 10 mol% CrF_2 have revealed two essential resonance signals with effective g values at $g_{\mathrm{eff}} = 4.93$ and $g_{\mathrm{eff}} = 2.14$. Presence of the two resonances is considered as a good evidence for the presence of trivalent chromium ions of octahedral coordination in glass containing 10 mol.% CrF_2. X-ray and electron diffraction measurements on sample containing 10 mol% CrF_2 have confirmed that there are some crystalline phases distributed in the main glass network. TEM micrograph has revealed a heavy accumulation of crystalline species. The glass which was exposed to irradiation process has showed different EPR signal when it compared with that of unirradiated sample.

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Keywords: magnetic resonance, g_{eff}-factors, CrF_2 based glass, irradiation effects.

1. Introduction

A special attention has been recently paid to explore the structural role of transition metal ions (TMI) in presenting stable magnetic responses in different materials [1-5]. TMI can be used to probe the glass structure since their outer d-electron orbital functions have a broad radial distribution. Among TMI, chromium ion can be involved as one of the most important category [6-9]. This is because Cr^{3+} is a paramagnetic probe which can be worked as magnetic ions in the glass matrix [10, 11].

Many special glass systems have been studied in terms of influence of unpaired spin electrons on physical and structure properties of the investigated material. These different systems have been ranged from enzymes that function via transient radical intermediates to those involving stable unpaired electron spins and transition metals. Since the electrons being observed often participate intimately in transition metal systems, EPR technique can be considered as a good powerful method for revealing pertinent structural information for these systems [10, 11].

The structural role of CrF_2 as an effective agent for cluster and crystal formation in silicate network was clearly evidenced by XRD technique [12]. The structure and size of well-formed chromium separated clusters have a great effect on the structure and magnetization of glasses [8, 9, 12, 13]. Presence of even a small concentration was found to enhance the crystallization process of the phospho-silicate glasses. In addition, aggregation processes of small clusters enriched with Cr^{3+} ions were documented to be formed in different range ordered structures. Intermediate and long range orders are the most structures in which chromium phases are involved. The formation of nano-sized crystallized species can play the role of improving magnetization of material.

The structure of glasses containing chromium ions has been recently studied via different spectroscopic tools [7, 11, 12, 13]. The measured and calculated nuclear magnetic resonance (NMR) of both silicate and phosphate structural species in glasses as a function of chromium fluoride concentration have been recently discussed [12]. Results based on NMR spectroscopy are consistent with those obtained from the experiments FTIR (Fourier transform infra-red), SEM (scanning electron microscopy), TEM and XRD investigations. It has been found that the contribution of the chemical bond between the central activated Si and Cr ions increases gradually with the increase of CrF_2 concentration [12]. This was confirmed from NMR spectroscopy, since the corresponding peak positions of ^{29}Si NMR spectra undergone clear more lower values of chemical shift. These results support that some of CrF_2 can enter the glass network as a strong glass former species. Increasing of Cr as a former may lead to enhance the distribution of silicate structural species which contain Cr ions. As a result more ordered structural units have constructed in the glass network. This was evidenced, since sharper XRD patterns assigned to chromium phosphate crystalline phases are documented to be present in rich CrF_2 glasses [12].

Several studies on glasses containing metal oxide such as Ag_2O [13-15] or transition metal ions have been reported [1-6, 13-15]. But a limited work has been done for exploring magnetic behavior of Cr^{3+} ions in glasses. Materials containing Cr^{3+}cations can posses spin-allowed transitions corresponding to transition for octahedral and tetrahedral coordinated Cr^{3+} sites [4, 5, 10, 11]. This property makes the glass to be available martial in an extended field of applications such as in white light emitting diodes, field emission displays, and as spin glasses [4, 9, 14]. The information on phospho-silicate glasses of high spin-allowed transitions may be limited, therefore it is our aim in this study is to shed more light on the magnetic behaviors of CrF_2 in phosphor-silicate glass. In this work glasses containing specific concentration of CrF_2 (10 mol%) has been prepared and studied. Spectroscopic studies are carried out to determine the state of Cr ions in the glass. It is our additional aim is to use the advantage of EPR, XRD, TEM and EDP-spectroscopy, for first time, to shed light on effect of Cr^{3+} on magnetic properties of phospho-silicate glasses. In addition, effect of irradiation on EPR parameters will be considered.

2. Experimental

2.1 Sample preparation

Glass ceramics based on the system ($SiO_2 – Na_2O – CaO – P_2O_5 – CrF_2$) has been prepared from reagent grade SiO_2, Na_2CO_3, $CaCO_3$, NH_4H_2PO, and CrF_2. All of high reagent grade purity (sigma-Aldrich). The samples were melted at 1350°C. The melt was swirled severally to attain homogeneity. The glass samples were obtained by pouring the melt between two flat plates. The glass samples were kept in a desiccator until required.

2.2 Experimental techniques

XRD measurements were carried out on a Brucker AXS-D8 spectrometer. Emitting source of type (λCuKα) has been utilized. The numerical data was steeply accumulated with small scanning steps, 2θ range of 4°-60° and a dwell time of 0.4 seconds have been applied. The obtained X-ray diffraction spectra were revised to reference samples related to standards which were gathered by technique of powder diffraction and standards (JCDPS).

EPR measurements have been carried out on a Bruker E-580 FT/CW X-band spectrometer of applied frequency of 9.48 GHz. The measurements were applied on powdered samples. The results were collected before and after irradiation with the dose of 10 M rad.

TEM is a well-known technique applied usually to analyze the shape, size, and morphology of the bulk material. TEM measurements were performed on a JEOL–JEM–2100 apparatus. An acceleration voltage of 200 kV is applied. An electron diffraction apparatus is connected with TEM to obtain a diffraction patterns characterized the bulk samples.

3. Results and discussion

Figure 1a represents EPR spectra of glasses containing 10 mol% CrF_2. The features of EPR resonance are affected by material structure as presented by XRD spectra, figure 1b. Figure 2 clarifies the distribution of Cr ions in cases of clusters or isolated species. Crystalline species was also evidenced in the studied glass as presented by TEM micrograph, figure 3. Figure 4 reveals several major absorption lines at X-band microwave frequency which are the features of the obtained spectra under the effect of irradiation. Details of the several line resonances have been found to depend on the irradiation only, since the concentration of CrF_2 has limited effect on the irradiated glasses.

3.1 EPR spectroscopy

Both crystalline and polycrystalline phases containing Cr^{3+} species can simply possess narrow and sharp EPR signals. It can be seen from figure 1a that a glass of 10 mol% CrF_2 offers a good resolved signal with two more intense EPR resonance lines shape. The formation of the well resolved signals in the glass of 10 mol% CrF_2 can be correlated to the well-formed ordered polycrystalline (figure 1b) species containing unpaired magnetic spins. In the matrix of this glass (10 mol% CrF_2), there are two resolved intense EPR signals as is presented in figure 1a. The first resonance peak was appeared at an extremely low magnetic field with g_{eff} value of ~4.93 and the second one is a broad asymmetric line in a higher magnetic field with an effective g value of ~2.14. For both low and high magnetic field regions, the intensity of the EPR signals is simply resolved (figure 1a).

The low field value of $g_{\mathrm{eff}} = 4.93$ is attributed to isolated metal cations in distorted octahedral sites [13-17]. The distorted glass network is considered due to the high content of the modifier oxide (49 mol%) which is involved in the glass sample. The modifier oxide in such a case plays the role of forming non bridging oxygen atoms (NBO) which create some distorted sites around silicate and phosphate structural units. On the other hand, the higher field g value ($g_{\mathrm{eff}} = 2.14$) is related to Cr^{3+} and Cr^{2+} ions which have electron configuration d^3 and d^4 with $S = 3/2$ and $S = 2$, respectively, that are similar to the ions of Mn^{4+} and Mn^{3+} in manganite with charge-spin dynamics in concentrated substances. This means that the contribution of both Cr^{2+} and Cr^{3+} coupled pairs in the crystalline matrix has the main effect on the magnetic behavior of the investigated material [14-17]. Then there are two types of chromium cations in the sample of 10 mol% CrF_2. The first type is individually and randomly distributed as six-fold coordinated units. The second is the clustered chromium ions distributed as axially-distorted octahedral sites [14-17]. These arguments agree well with that reported previously [18], since the obtained g_{eff} values are in agreement with other EPR studies on metal phosphate glasses.

It was known that a free electron has an g value of 2.00231930436153, which is one of the most precisely known values in physics [19]. The shifts from this value occur due to spin orbit coupling within the molecule or clustered metallic chromium cations. The most to be noticed from figure 1a is that the values of both intensity and area of the EPR resonance at a high magnetic field of $g_{\mathrm{eff}} = 2.14$ are more higher than that of low field strength. This difference leads that the concentration of the clustered chromium ions is more higher than that of isolated octahedral cations. Also the concentration of Cr^{3+}– Cr^{2+} unpaired magnetic pairs increases in the crystalline species containing 10 mol% CrF_2 which in turns results in increasing the signal amplitude in the high field region.

For the separated chromium ions in octahedral sites, the present data is fitted to a great extend with the structural model which was considered by Landry et al [16]. It was evidenced from NMR studies [20] that both SiO_4 and PO_4 tetrahedral units contain three nonbridging oxygens (non ligands oxygen, NLO) for

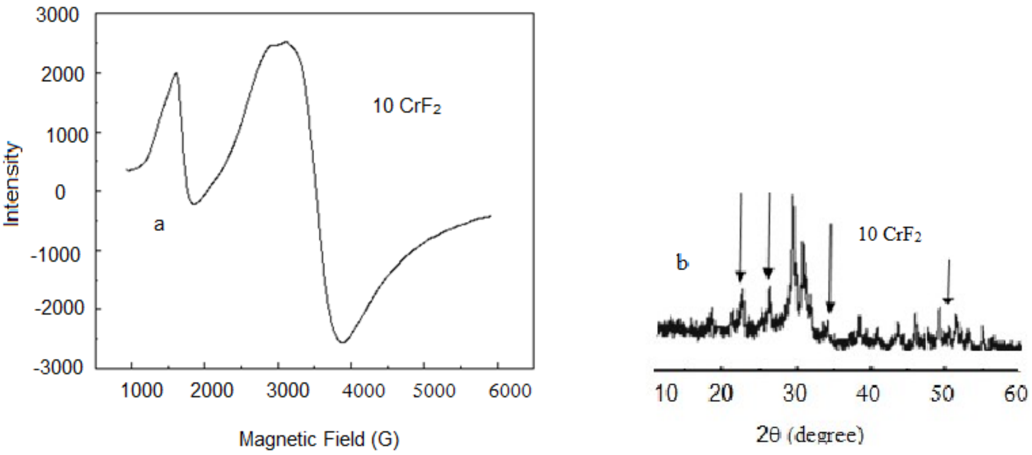

Figure 1. (a) EPR and (b) XRD pattern of sample containing 10 mol% CrF_2.

each tetrahedron. Some of these NBO atoms can form bonds with metallic oxides, Cr, Ca or Na. Therefore the most suitable configuration of chromium cation is considered as a trivalent ion with octahedral sites coordinated by non-ligand O_2. This leads that, in such case, six oxygens are required to continue the glass structure (called ligand oxygen, LO) that forms P-O-Si or P-O-P or Si-O-Cr bonds. But different attributions are considered in the case of the clustered Cr^{3+} pairs as proposed by Founier et al. [20]. They proposed that two chromium ions are distributed in the six-fold coordination but with non-ligand O^{2-} ions and are sited on the sides of a triangle of O^{2-} ions. The representations of the Cr^{3+} in the glass structure with octahedral isolated and clustered Cr^{3+} ion pairs are presented by figure 2.

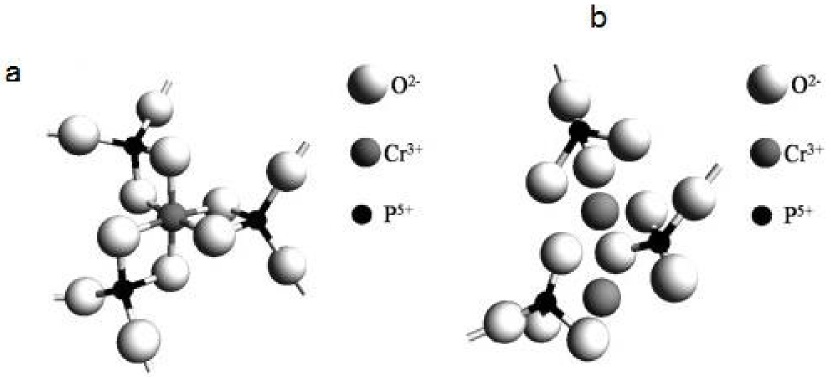

Figure 2. (a) Isolated Cr^{3+} ions in the form of octahedral with O_2 ions in the PO_4 tetrahedra. (b) Cr^{3+} antiferromagnetic pair, each Cr^{3+} ion is six-fold coordinated by O_2 ions [16] and [20].

3.2 TEM-EDP analysis

The above arguments are in well agreements with results obtained from TEM and EDP, see figure 3. CrF_2 was mainly magnetite and usually crystallizes as large accumulation of crystallized species.

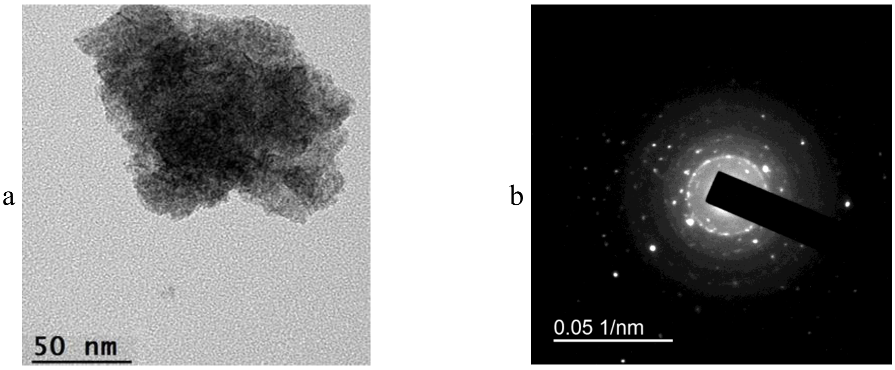

Figure 3. (a) TEM and (b) EDP of glass containing 10 mol% CrF_2 showed regular distribution of clustered chromium species.

3.3 Effect of irradiation

From the above discussion, it was considered that presence of Cr^{3+} ion pairs leads to resolving the EPR spectra and consequently the magnetic properties of the investigating material should also be improved. Based on figure 2, the mechanism of transforming octahedral separated chromium species (figure 2a) to chromium units containing non-ligand oxygen, figure 2b plays the role of enhancing both crystallinity and magnetization of the tested sample. There is another a more effective route which can lead to more (than that of effect of composition) enhancement in magnetic properties. In this regard, more transformations to clustered Cr^{3+} pairs could be done by exposing the sample to any type of ionizing radiation. The irradiation process can simply break several bonds in the glass network [20]. As a consequence, enhanced and very resolved EPR signals are simply obtained in the network of the irradiated glass, see figure 4. As can be seen from figure 4, several major resonance lines at X-band microwave frequency are the features of the obtained spectra under the effect of irradiation. The EPR spectra of the irradiated sample exhibited more line resonances in comparison with that of unirradiated sample.

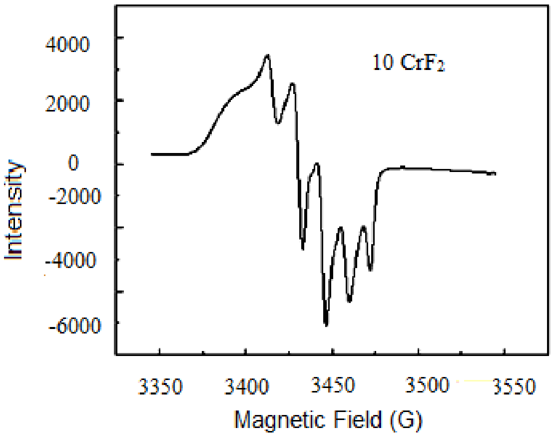

Figure 4. EPR spectra of irradiated glass and containing 10 mol% CrF_2.

The differences occurring in the EPR spectra before and after irradiation have been referred to irradiation induced structural defects and compositional changes [13]. An isotropic signal has all the signal intensity spread over a very small field region causing the signal to have a very large amplitude, while a broad axial or rhombic signal is spread over a larger field region causing the observed amplitude to decrease significantly. Therefore, it can conclude that the several-line structures arise from an isotropic hyperfine interaction of a hole and electron centers formed by effect of irradiation is the dominant, regardless the effect of glass composition [21-23]. The electron centers are assigned to E′(Si) centers with different local environments. EPR spectrum of hole centers is ascribed to O^- centers, localized on non-bridging oxygen of the glass network. The E′(Si) and O^- centers show stability in the glass network. The obtained EPR spectra are described by spin Hamiltonian with g-factor of axial and rhombic symmetry for the E′(Si) and O^- centers, respectively. The nature, electron structure and some formation peculiarities of the radiation defects in glasses play the role of splitting in EPR spectra of irradiated glasses.

In summary, the radiation creates more electrons and holes whose density notably via their interaction with defects. Irradiation-induced photoelectrons which are trapped within the glass matrix. Irradiation promotes metal atom diffusion, which, in turn, leads to cluster nuclei formation with enhanced magnetic properties. Our results and findings indicate that, the investigated samples may be seemed to be a good candidate for radiation processing purposes

4. Summary

EPR, XRD, TEM and EDP measurements on glass containing 10 mol% CrF_2 have been carried out. EPR measurements have been applied on the glass sample before and after gamma irradiation. By comparing the spectra of glasses before and after irradiation, it can be considered that the concentration of magnetic chromium ions increased in the irradiated glasses. It is found that, the EPR intensity is higher in the irradiated samples. This may be considered as a result of the accumulation of paramagnetic centers due to radiation effects. However, there is an additional influence in the irradiated glass which may be considered due to spin conversion of magnetic centers created by the effect of γ-irradiation. There are sets of signals for which the position of the g-factor is determined by the distribution of the energy parameters of the well formed magnetic centers.

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