Letter to the Editor

Magneto-induced microwave conductivity in Mn²⁺-doped silicate glass

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Abstract

A non-resonant microwave absorption induced by low magnetic field (magneto-induced microwave conductivity) was observed in Na_2O–CaO–MgO–SiO_2 glasses doped with Mn in addition to the usual EPR signal of Mn^{2+}. The non-resonant response increases with the increase of Mn^{2+} concentration in glasses. In contrast to the EPR signal, the magnitude of non-resonant absorption does not show saturation at high microwave power and grows much faster as the temperature decreases. The magneto-induced microwave conductivity in the glass dielectric is explained by the magnetic field-dependent electron tunneling between non-bridging oxygen ions adjacent to paramagnetic Mn^{2+} ions. The high probability of tunneling is provided by aligning the electron spins in Mn^{2+} and adjacent non-bridging oxygen ions in the external magnetic field. © 2000 Elsevier Science B.V. All rights reserved.

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Magneto-induced changes in electron transport characteristics of different materials are under intense study because of a growing industrial interest in spin electronics based on magneto-induced spin orientation. The externally applied magnetic field dramatically changes properties of the materials from insulator to conductor (magneto-conductance), e.g., in perovskite manganites [1–3]. The magneto-conductance effect in perovskite manganites is explained by the enhanced electron hopping migration occurring via a double-exchange mechanism in mixed valence Mn^{3+}–O–Mn^{4+} structures and additional magnetic coupling ener-gy that provides ferromagnetism [3]. Charge migration leads not only to changes in the dc conductivity but can also cause a microwave response with the applied magnetic field. This phenomenon is known as microwave magneto-resistance that was observed in manganites [4,5] and in amorphous Fe–Co–Si–B ribbon [6]. A similar phenomenon (non-resonant microwave absorption with minimum centered at zero magnetic field) was observed in the superconducting state of high-temperature superconductor ceramics as a result of charge migration [7–11]. Similar signals were detected [12] at low temperatures in dielectric borosilicate glasses doped with Cu, Ni, Co, and Fe in high concentrations >10%, and were interpreted in terms of local superconductivity.

Thus, microwave magneto-conductance effects were observed in materials containing high

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concentrations of transition metals, and were explained as a result of coupling between metal ions in different valence states [1–6]. In this Letter we report magneto-induced microwave absorption observed in a diluted paramagnetic system – manganese-doped (doping level below 1%) insulating $Na_2O–CaO–MgO–SiO_2$ glass, and describe the effect as the result of electron tunneling in the vicinity of Mn^{2+} ions caused by a reduction in potential barrier due to spin orientation in the magnetic field.

The glass composition in mol% is $13Na_2O–10CaO–6MgO–71SiO_2$. Purified raw materials with the sum of transition and heavy metals in chemicals in the range of units of ppm were used to melt high-purity glasses by the method described in Ref. [13]. Glasses were melted in fused silica crucibles in an electric furnace. Silica and carbonates of sodium, magnesium, and calcium were used to produce a neutral glass. To produce oxidizing melting conditions, part of the sodium oxide was introduced as sodium nitrate. To obtain reduced glasses, carbon was added to the batch. Manganese concentration in the glasses ranged from 0.001 to 1 wt% MnO_2. The glass samples prepared for EPR studies were in the form of parallelepipeds $2 \times 2 \times 10$ mm^3 with a mass of approximately 0.1 g each. EPR spectra were measured using a Bruker EMX spectrometer operating at 9.5 GHz. Polished samples with thickness ranged from 0.015 to 0.5 cm were used for optical absorption measurements from 200 to 2500 nm using a double beam spectrophotometer.

No EPR signal exceeding the level of noise was observed in undoped glasses. Microwave absorption spectra of all glasses doped with manganese had a similar response (Fig. 1). It is known that manganese in silicate glasses exists in the forms of Mn^{3+} and Mn^{2+} [14] but only Mn^{2+} is usually seen in EPR spectra [15]. The EPR spectrum of Mn^{2+} contains three sets of lines with effective values of the g-factor of approximately $g \approx 4$, 3 and 2. Six hyperfine components due to ^{55}Mn are usually well observed for the $g \approx 2$ signal. All these lines with $g \approx 4$, 3 and 2 are seen in Fig. 1 at magnetic field values of about 1350, 2250, and 3400 G, respectively. The magnitude of all EPR bands is linearly proportional to manganese concentration in the
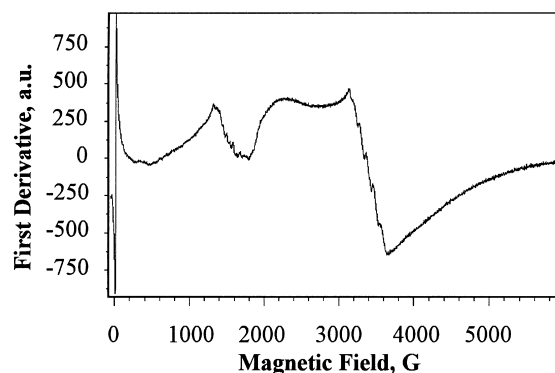

Fig. 1. Dependence of the first derivative of microwave absorption of the $Na_2O–CaO–MgO–SiO_2$ glass doped with 0.1 wt% MnO_2 at 77 K on external magnetic field. Microwave power is 200 mW.

series of glasses melted under the same redox conditions (Fig. 2). This means that valence distribution of manganese is stable at different concentrations of such series. Small deviations from linearity at low concentrations are probably caused by the noise impact because of low signal levels.

Absorption spectra of glasses melted in oxidized and neutral conditions show the well-known absorption band of Mn^{3+} with a maximum at 485 nm
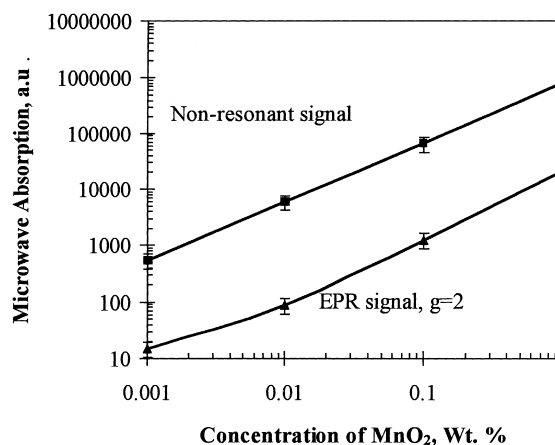

Fig. 2. Dependence of the microwave absorption at 77 K on manganese concentration in the oxidized $Na_2O–CaO–MgO–SiO_2$ glasses. Non-resonant signal corresponds to zero magnetic field, EPR signal with $g = 2$ corresponds to the magnetic field ≈ 3500 G.

[14]. This absorption is proportional to the total manganese content in a series of glasses with the same redox conditions. The linear relation of both Mn^{2+} EPR absorption and Mn^{3+} optical absorption with total manganese content in glass shows that the valence distribution of manganese is stable. Melting of glass under reduced conditions results in the strong decrease of absorption in the visible region, because the specific absorption of Mn^{2+} is significantly less than that of Mn^{3+}. A small absorption band of Mn^{2+} at 420 nm is observed in strongly reduced glasses [14]. We found that the EPR signal of Mn^{2+} in these reduced glasses increased along with the increase in optical absorption of Mn^{2+} and the decrease of Mn^{3+}.

In addition to the well-known Mn^{2+} EPR spectrum, we have observed a line centered at zero magnetic field (Fig. 1) in all Mn-doped Na_2O–CaO–MgO–SiO_2 glasses. This line has opposite phase relative to the normal EPR absorption due to Mn^{2+}. This means that the microwave absorption has a dip at zero magnetic field and it increases with applied magnetic field (Fig. 3). In other words, this is a non-resonant microwave absorption induced by the magnetic field. We found that this microwave response, as well as the normal EPR signal from Mn^{2+}, is linearly correlated with the amount of Mn in the glass series with variable Mn concentration (Fig. 2). This proves that the non-resonant absorption is caused by the introduction of manganese in the glass network. Moreover, it was found that the non-resonant signal increases in the reduced glasses
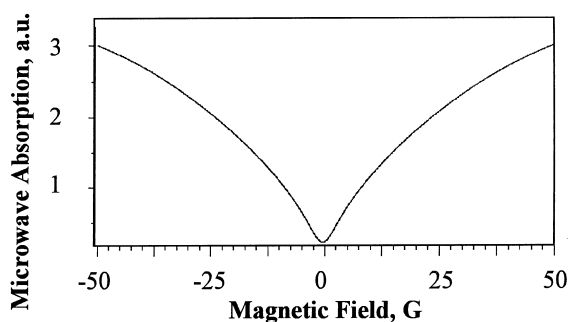
compared to oxidized ones being proportional to the EPR signal of Mn^{2+}. Thus, we can conclude that the magneto-induced non-resonant microwave absorption in Na_2O–CaO–MgO–SiO_2 glasses is generated by Mn^{2+}.

The following observations show that the non-resonant response has more features that distinguish it from the regular EPR signal. First, we could not saturate the non-resonant signal using applied microwave power up to 200 mW, while the saturation of the $g \approx 4$, 3 and 2 EPR signals was clearly seen. It should be noted that the absence of saturation means that the shape of the non-resonant response does not change with the increase of microwave power. This signifies that the magneto-induced microwave absorption is a linear one, since all non-linearities must result in the power dependent response. Comparison of the temperature dependencies of the non-resonant and EPR signals shows that the EPR signal increases by about 30% when the temperature drops from 250 to 80 K. By contrast, the non-resonant signal in the same conditions increases by four times. The study of all features of a non-resonant microwave absorption and development of the detailed physical model of this phenomenon will be the subject of future investigations. However, the results observed allow formulating of a model that explains the experimental data.

The presence of the non-resonant absorption in glasses with the concentration of Mn as low as 0.001% does not allow any assumptions about ferromagnetic or exchange coupling between manganese ions with different charge states, that were used for explanation of magneto-resistance in perovskite manganites [3]. Therefore, the observed effect cannot be related to changes in dc conductivity of the glass, but should be considered as the enhancement of dielectric loss by the external magnetic field, or magneto-induced microwave conductivity provided by individual manganous ions.

It is well known (see e.g., [16], p. 40) that chemical bonding in silicate glasses is partially covalent. This means that the coordination sphere of the Mn^{2+} ion may exhibit a non-zero electric dipole moment due to the partially covalent bonds between the manganous ion and one of the oxygen

Fig. 3. Non-resonant microwave absorption near-zero magnetic field for the Na_2O–CaO–MgO–SiO_2 glasses doped with 0.1 wt% MnO_2.

ions $Mn^{+2-\delta}$–$O^{-2+\delta}$. One of the five unpaired electrons from the d-shell of Mn^{2+} will pair with that of the two electrons from the p-orbital of oxygen to provide covalent bonding, so that electron spin density will be partially delocalized in favor of the oxygen ion. In any case, the total electron spin of the system remains unchanged ($S = 5/2$). We suppose that the bonding $Mn^{+2-\delta}$–$O^{-2+\delta}$ may switch between different oxygen ions in the vicinity of Mn^{2+}

$$O^{-2} \ldots Mn^{+2-\delta}\text{–}O^{-2+\delta} \rightarrow O^{-2+\delta}\text{–}Mn^{+2-\delta} \ldots O^{-2}. \tag{1}$$
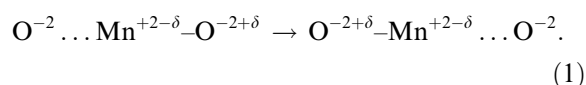
In the absence of the magnetic field, a spontaneous hopping migration of the charge $+\delta$ between oxygen ions in the manganous environment contributes to regular dielectric losses caused by hopping migration of different charges in the glass network [15].

If the external magnetic field is applied, it reduces fluctuations of unpaired electron spins and aligns them in one direction, so that electrons can tunnel from one oxygen atom to another without a change of the total spin of the system

$$O^{-2}(\uparrow\downarrow) \ldots Mn^{+2-\delta}(\uparrow\uparrow\uparrow\uparrow \ldots \uparrow\downarrow \ldots \uparrow)O^{-2+\delta}$$
$$\rightarrow O^{-2+\delta}(\uparrow \ldots \uparrow\downarrow \ldots \uparrow\uparrow\uparrow\uparrow)Mn^{+2-\delta} \ldots O^{-2}(\uparrow\downarrow). \tag{2}$$
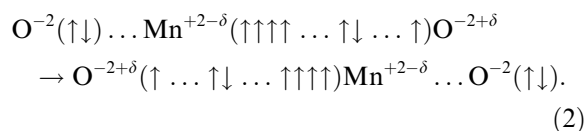
In this case, the dielectric loss will increase due to the additional tunneling migration of the electron stimulated by manganous spin alignment. This means that magneto-induced microwave conductivity in Mn-doped dielectric glass is localized to the volume that contains a few spin-coupled O^{-2} and Mn^{2+} ions.

In summary, we have observed magneto-induced non-resonant microwave absorption (magneto-induced microwave conductivity) caused by paramagnetic Mn^{2+} ions in insulating silicate glass. This phenomenon is explained by spin orientation of Mn^{2+} in an external magnetic field followed by electron tunneling between oxygen ions in the vicinity of manganous ion. The spin-dependent tunneling described in the present work results in an easily detectable microwave response in low magnetic fields below 100 G, which makes manganese-doped glasses potential magneto-sensitive materials.

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