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Magnetic and magnetoelectric properties of nickel ferrite–lead iron niobate relaxor composites

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Abstract

Magnetoelectric effect in bulk ceramic and multilayer (laminated) structures consisting of 6 nickel ferrite and 7 lead iron niobate relaxor (PFN) layers was investigated. This paper describes the synthesis and tape-casting process for ferrimagnetic $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ ferrite and multiferroic relaxor $Pb(Fe_{0.5}Nb_{0.5})O_3$. X-ray analysis and studies of the electrical and magnetic properties were performed for bulk and layered composites. Complex impedance and dielectric permittivity of bulk and layered composites were studied in a temperature range from −40 to 300 °C and a frequency range of 10 Hz to 2 MHz. Magnetic hysteresis, ZFC–FC curves and dependencies of magnetization versus temperature for nickel ferrite, PFN relaxor and magnetoelectric composites were measured with a vibrating sample magnetometer (VSM) in an applied magnetic field up to 85 kOe at −269 °C. Magnetoelectric effect at room temperature was investigated as a function of static magnetic field (0.3–6.5 kOe).

Keywords: Tape casting; X-ray methods; Magnetic properties; Magnetoelectric properties; Ferrites; Perovskites

1. Introduction

Magnetoelectric effect (ME) in multiferroic materials has been studied at great length for its fundamental usefulness and practical applications.[1–10] Defined as an induced dielectric polarization under an applied magnetic field, ME is generally characterized by the magnetoelectric voltage coefficient[2]:

$$\alpha_{ME} = \frac{V}{H_{AC} \cdot d} \tag{1}$$

where V is the voltage generated due to magnetoelectric effect, H_{AC} is the amplitude of the sinusoidal magnetic field and d is the thickness of the sample. The magnitude of magnetoelectric effect in multiferroics is determined by magnetostrictive deformation and piezoelectric effect in the material. The magnetoelectric effect obtained for multiferroics is directly proportional to the piezomagnetic coefficient $d\lambda/dH$, where λ is the magnetostriction. The stress generated in the piezoelectric subsystem directly corresponds to the stiffness in the subsystem, which results in effective mechanical coupling.[2] The stress causes an increase in the polarization of the domains oriented in the direction of tension and a decrease in the polarization of those oriented in the direction of compression. The change in polarization causes a bound electric charge to appear at the domain wall. These bound charges induce an electric field in the grains.[2] The ME effect observed for single phase materials like Cr_2O_3, $BiFeO_3$ and $Pb(Fe_{0.5}Nb_{0.5})O_3$ is usually small. Much larger ME effects can be obtained in composites consisting of two functional phases: magnetostrictive phase, in which a strain is produced by applying a magnetic field, and piezoelectric phase, in which a change in electric polarization is produced by an applied stress. The reported values for ferrite/relaxor composites are 10–100 times higher than the magnetoelectric coefficient for single-phase multiferroics.[7–10]

From a practical point of view cobalt and nickel ferrites are frequently used as giant magnetostrictive materials, because they possesses good dielectric and magnetic properties and high magnetostriction.[7,11,12] As a piezoelectric phase, the ferroelectric relaxor has often been employed in several applications because it has good ferroelectric properties.[7,11,12]

In the present work we report on our investigation of new magnetoelectric composites based on $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ ferrite as a magnetostrictive phase and $Pb(Fe_{0.5}Nb_{0.5})O_3$ relaxor as a ferroelectric phase. The composites were prepared as bulk

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ceramic samples and multilayer tape cast and cosintered laminates. The dielectric, magnetic and magnetoelectric properties of both types of composites are compared.

2. Materials and methods

The $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ ferrite was prepared by the standard solid-state reaction method. High-purity Fe_2O_3, NiO, ZnO and CuO powders were weighed in stoichiometric proportions, ball-milled in isopropyl alcohol, dried, pelletized and calcined at 900 °C for 4 h. The synthesis of $Pb(Fe_{0.5}Nb_{0.5})O_3$ was carried out by the two-step "wolframite" method. The wolframite $FeNbO_4$ was prepared by ball-milling Fe_2O_3 and Nb_2O_5 in stoichiometric proportions in isopropyl alcohol for 8 h. After drying, the powder was pressed into pellets and calcined at 1000 °C for 4 h. The reaction product was then mixed by ball milling with PbO, dried, pelletized and calcined at 800 °C for 4 h in a covered crucible, 1 mol.% MnO_2 was introduced to the batch in order to improve its resistivity. Crystal structures of the synthesized powders were tested by standard X-ray powder diffraction procedure using CuK_α radiation (TUR-M61 diffractometer). The good quality X-ray diffractograms obtained for these materials were analysed using a Rietveld-type method.[13,14] X-ray diffraction analysis of the synthesized powders confirmed their single phase compositions.

Bulk composites were prepared by ball-milling ceramic constituents for 8 h in stoichiometric proportions corresponding to $0.5Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$–$0.5Pb(Fe_{0.5}Nb_{0.5})O_3$, then pressed into pellets and sintered at 900 °C for 2 h.

The following describes the fabricating process of the ferrite and relaxor tape: ferrite and relaxor powder was mixed with binder solutions and solvent to make slurry for tape casting. Slurries destined for tape casting of the tapes were prepared by ball-milling for 4 h inorganic (powders) and organic components mixed in carefully chosen proportions. The following composition for the organic part was chosen as optimal: fish oil – 2.1%, polyvinyl butyral – 16.7%, polyethylene glycol – 4.2%, dibutyl phthalate – 4.2%, toluene – 35.4%, isopropyl alcohol – 37.5%. Polyvinyl butyral (PVB) was used as a binder, fish oil as a dispersant, polyethylene glycol and dibutyl phthalate as plasticizers, and toluene and isopropyl alcohol as solvents. Tape casting was done with a table top tape caster (TTC-1200, Richard E. Mistler, Morrisville, US) with a 20 cm wide doctor blade on moving polyester carrier film. The doctor blade was conducted with a blade gap of 500 μm to fabricate the tapes, which has a dry thickness of 110–150 μm after tape casting and drying. The fabricating process of the ferrite $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ tape has been described in detail elsewhere.[15] The next step was to stack and laminate the composite. Three basic parameters in lamination (temperature, pressure and dwell time) must be controlled. In our study, eleven alternate layers of the ferrite and the relaxor were used to form a multilayer composite, which was laminated at temperature 40 °C under 10–15 MPa of pressure. Following the stacking and lamination, the multilayer composite was sintered at 950 °C for 2 h and then allowed to cool down along with the furnace at approximately 200 °C/h.

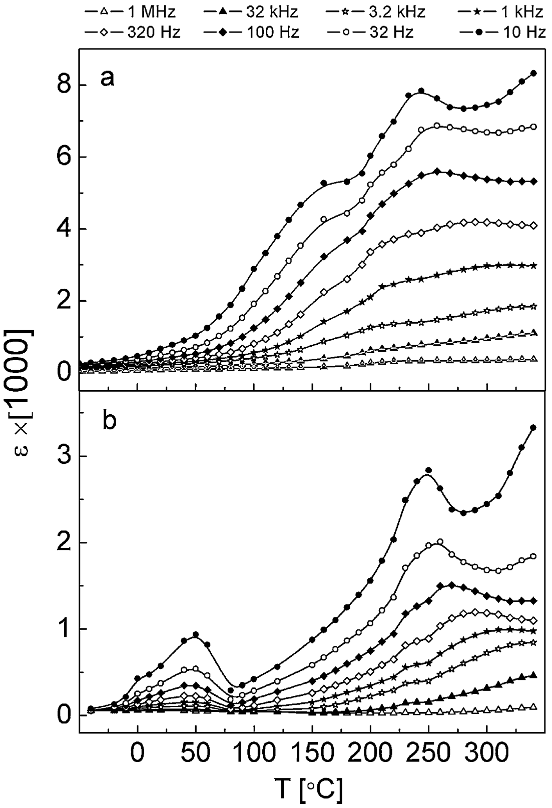

Fig. 1. Dielectric permittivity for the bulk ceramic (a) and laminated composite (b) versus temperature at frequencies 10 Hz to 1000 kHz.

Bulk magnetization measurements performed using a vibrating sample magnetometer from a Quantum Design PPMS6000 system were taken in the external magnetic field up to 85 kOe in the temperature range 10–400 K. A magnetic field of $H = 50$ Oe was applied for the zero-field (ZFC) and field-cooled (FC) magnetization profiles, both of which were acquired at increasing temperature. The same field value was to cool the sample prior to FC measurements. Remanence magnetization (M_r) and coercive field (H_c) were determined from hysteresis curves ($M(H)$), which were measured at 10 K, 100 K, 223 K, 293 K, 343 K, and 393 K. In the case of the laminated sample, the direction of the applied magnetic field was parallel to the layers. The samples dielectric properties were investigated using an LCR QuadTech meter in the temperature range −50 to 350°C and in a frequency range 10 Hz to 2 MHz. The magnetoelectric effect was evaluated at room temperature by dynamic lock-in method, which has been described previously in the literature.[16] The induced voltage between sample surfaces was measured with a lock-in amplifier (Stanford Research System, model SR 830) with input resistance of 100 MΩ and a capacitance of 25 pF. The lock-in amplifier was used in differential mode. To measure the DC and AC magnetic field, a Hall probe SM 102 was employed.

3. Results and discussion

Fig. 1 depicts the dielectric permittivity of a bulk composite (a) and laminated composite (b) as a function of temperature for various frequencies. As can be seen from Fig. 1a, the bulk composite exhibits broad and high maxima of dielectric permittivity in the frequency range 10 Hz to 1 MHz, decreasing and shifting to higher temperatures with increasing frequency. The positions of these maxima (transition temperatures) are closer to ferrite $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ transition temperature rather than ferroelectric transition temperature of $Pb(Fe_{0.5}Nb_{0.5})O_3$ relaxor (112 °C at 1 kHz[17]). The transition temperature of $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrite equals 344 °C[18] and slightly, nonlinearly decreases with *Ni*/*Cu* substitution.[19]

Two peaks are observed in the plots of laminated composite (Fig. 1b). The first is near the ferroelectric Curie temperature of $Pb(Fe_{0.5}Nb_{0.5})O_3$ phase (~ 50 °C at 1 kHz) while the second is near the ferromagnetic Curie temperature of $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ phase (~ 300 °C at 1 kHz). The shift in the transition temperatures of the constituent phases are observed and reported earlier for different composites.[20,21] At higher temperature the maxima decreased and shifted to higher temperatures as the frequency rose. The position and shape of the maxima at higher temperature imply that the peaks tend to overlap, which is the result of the dielectric relaxation of the relaxor and the ferrite phases. In laminated sample, alternate ferrite and relaxor layers form capacitors connected in series. Thus, the dielectric permittivity of the laminated sample is lower than that of the particulate one since it is determined by a low permittivity of the ferrite layer. However, it can be seen from Fig. 1a and b, that the values of dielectric permittivity are decreased continuously with increasing frequency. The decrease in dielectric permittivity with increase in frequency is a normal dielectric behavior of materials.

Fig. 2 shows a comparison of the *M*(*T*) profiles measured at 50 Oe and 85 kOe for both, bulk composite (a) and laminated sample (b). The latter profiles, i.e. temperature variations of magnetization at saturating fields, show a dependence typical of such composite materials that consists of a dominating signal from ferrimagnetic (ferrite) and a weak signal from paramagnetic (relaxor) phase, namely a linear decrease of magnetization in a wide temperature range.[22] The difference in the absolute values of the bulk magnetization is proportional to the mass content of the ferrite phase in the samples. The ZFC and FC profiles diverge at the relatively high temperatures of 350 K for both samples, indicating that coercivity varies considerably with temperature. Going to the low temperatures, ZFC and FC magnetizations increase and reach their maxima between 60 K and 80 K. However, the temperature dependence is monotonous for bulk ZFC and both FC profiles, while the dependence of the ZFC profile of the laminated sample shows a wide plateau between 200 K and 300 K. At the lowest temperatures – below ~ 60 K – the ZFC and FC magnetizations of both samples are strongly reduced due to a significant increase of the coercive field at low temperatures, which reaches the value of the order of the applied field, i.e. 50 Oe.

Comparison of the hysteresis loops *M*(*H*) taken up to the 85 kOe fields for both samples is shown in Fig. 3 (bulk composite (a), laminated composite (b)). They do not reveal considerable differences between the two samples. The shape of the curves measured at higher temperatures is typical of a mixture of soft ferro(ferri)magnet (ferrite) with a significant amount of paramagnet (relaxor) – there is an abrupt increase up to the saturation field of ferrite and a further quasi linear increase. While the profiles measured at lower temperatures, especially at $T = 10$ K, show a slightly distinct shape due to the evolution of the magnetic properties of the relaxor phase, the mixture becomes antiferromagnetic below $T_N \sim 140$–160 K and may reveal additional spin-glass behavior below 20 K.[23] Thus, the appearance of frustration and/or antiparallel coupling of magnetic moments, which gradually compensates the ferromagnetic components, may affect the low field magnetization profiles. This could explain the low temperature decrease of magnetization and results in a maximum at the FC curves.

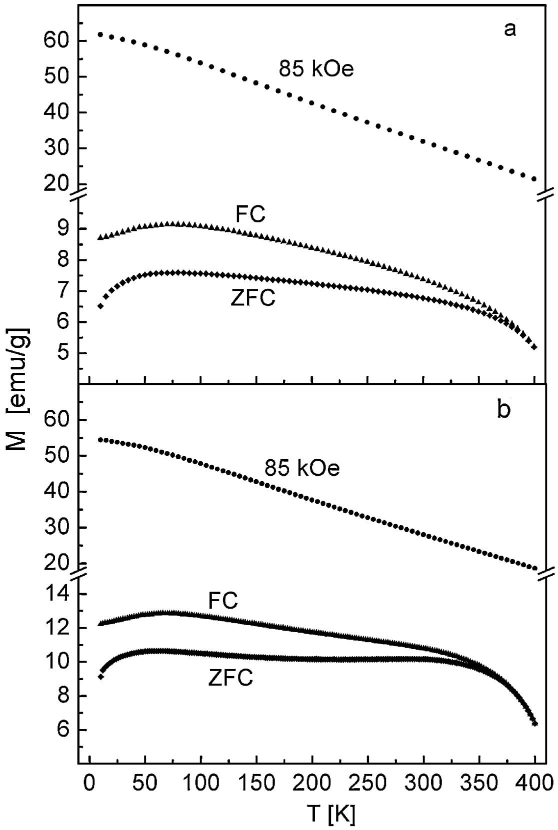

Fig. 2. *M*(*T*) profiles measured at 50 Oe and 85 kOe for bulk (a) and laminated (b) composite.

Closer inspection of the low field parts of the hysteresis loops shows significant differences between the samples (see Fig. 4a and b) as well as the temperature dependence of H_C and M_r (Fig. 5a and b). The main difference, which can be attributed to additional, magnetically hard phase, is an order of magnitude higher magnetic field of the irreversibility point (marked by arrows in Fig. 4a and b) of the hysteresis of laminate than that of the bulk composite. It also influences the coercive field that it is lower in a wide temperature range, except for the lowest and the highest temperature of measurements and does not show a significant reduction at high temperatures (close to the magnetic ordering temperature of ferrite) for the laminated sample.

The magnetoelectric effect was evaluated at room temperature by means of dynamic lock - in method, which has been

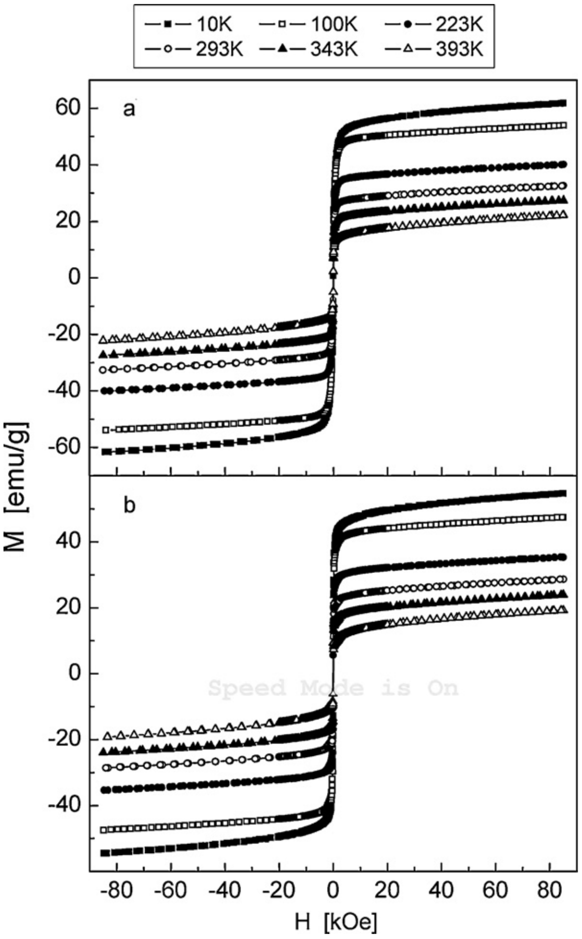

Fig. 3. $M(H)$ profiles measured up to 85 kOe in the temperature range 10–393 K for bulk (a) and laminated (b) composite.

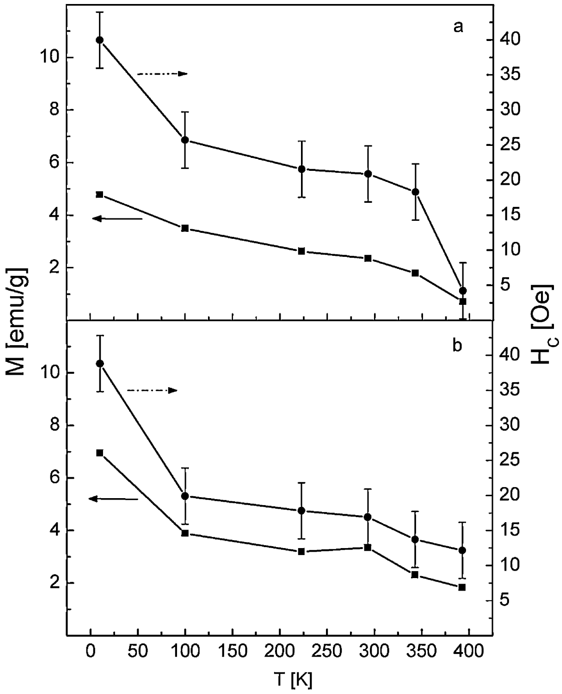

Fig. 5. Temperature dependence of H_C and M_r, as derived from $M(H)$ profiles, for bulk (a) and laminated (b) composite.

described elsewhere in the literature.[16] The ME effect was measured by applying a sinusoidal magnetic field H_{AC} produced by Helmholtz-type coils, superimposed on a bias magnetic field H_{DC} produced by the electromagnet. The magnetic fields were applied perpendicularly to the polished surfaces of the pellets onto which conductive electrodes had been applied. Magnetoelectric coefficient α_{ME} measurements were performed by measuring voltage output (V) as a function of bias magnetic field H_{DC} with sinusoidal magnetic field ($H_{AC} = 10$ Oe, $f = 1$ kHz). The α_{ME} coefficient was calculated from the voltage output following the relation (1).

In Fig. 6, the magnetoelectric coefficient determined for bulk and laminated composite is plotted versus the bias magnetic field. The AC ($H_{AC} = 10$ Oe, $f = 1$ kHz) and DC magnetic fields were applied perpendicular to the sample surfaces. At lower magnetic field, the α_{ME} coefficient increases slightly before reaching a maximum at $H_{DC} = 600$ Oe and then decreasing. The comparison of the results presented in Fig. 6 leads us to conclude, that the magnetoelectric coefficient of multilayer composite is markedly higher than that of bulk ceramic composite. The magnetoelectric effect depends on magnetostriction of magnetic phase and polarization of ferroelectric phase. Magnetostriction

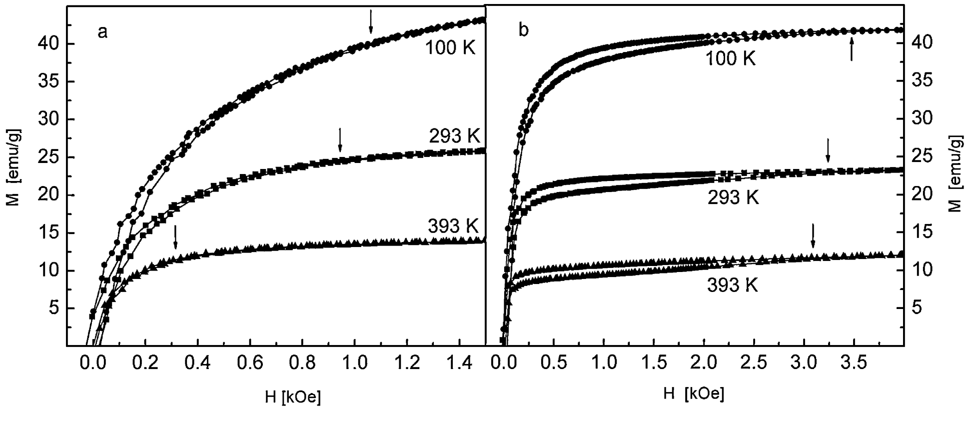

Fig. 4. Low field part of the $M(H)$ profiles measured at $T = 100$ K, 293 K, and 393 K, showing evolution of the irreversibility point of the hysteresis (marked by arrows) of bulk (a) and laminated (b) composite. Note the difference in magnetic field scale of both panels.

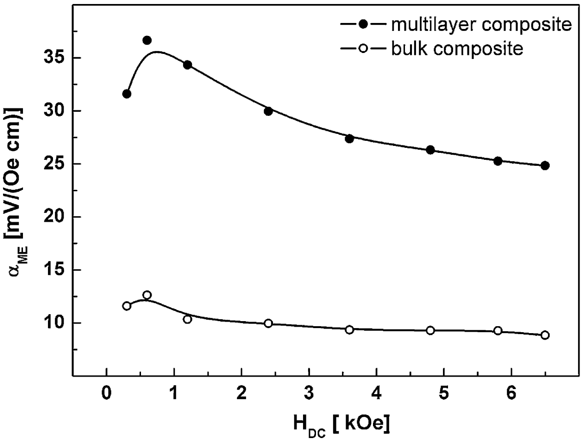

Fig. 6. The magnetoelectric coefficient determined for bulk and laminated composite is plotted versus the bias magnetic field H_{DC}.

and polarization are partly associated with the movement of the magnetic and electric domain walls. When the magnetic field is applied to a material, the magnetic domain walls will bend in a direction, in which increases the volume of the domains that are closer to being parallel to the applied field. In bulk composite, the grains of relaxor have magnetic poles induced on its surface, which will repel an approaching domain wall, thus impeding its progress. Analogously, the progress of electric domain walls is restrained by the ferrite grains. Since in the pure layers, stacked alternately with the relaxor layers in a laminated composite, the progress of magnetic and electric domain walls is not restrained, the magnetoelectric effect of the bulk composite is lower than that of the layered one.

4. Summary and conclusions

The magnetoelectric composites consisting of a solid solution containing ferrimagnetic ferrite $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ and ferroelectric relaxor $Pb(Fe_{0.5}Nb_{0.5})O_3$ were prepared as bulk ceramics and multilayer tape cast laminates. The ceramic samples show high dielectric permittivity. At moderate and high magnetic fields both the samples reveal properties typical of a mixture of ferrimagnetic and para/antiferromagnetic phase, while at a low magnetic field significant differences are observed. Here the properties are affected by a small amount of additional phase of the higher magnetocrystalline anisotropy observed in the laminated sample. The additional phase is likely of a carbide type (e.g. cementite-like) which could be created at the ferrite/relaxor interface from the carbon included in the organic additives. The magnetoelectric effect exhibited by both types of composites was larger in the case of the laminates.

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