

Dielectric and magnetic properties of holmium and ytterbium titanates

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Ytterbium and holmium titanates have been synthesized and their dielectric and magnetic properties have been investigated. The frequency dependences of the permittivity at $T = 77$ and 300 K, and measured magnetization curves and temperature dependences of the magnetic susceptibility in fields up to 30 kOe and at temperatures from 2 K to 50 K have been obtained. The properties of the doped and undoped titanates have been compared. Based on the temperature dependences of the magnetic susceptibility, the magnetic dipole and exchange couplings in the titanates have been analyzed.

Keywords: rare-earth titanates, pyrochlore structure, magnetic susceptibility, permittivity.

1. Introduction

Rare-earth titanates attract attention with their refractivity, oxygen-ion, and mixed conductivity, the possibility of using them as electrolytes and electrodes in solid oxide fuel cells, oxygen partial pressure sensors, catalysts, *etc.* Pyrochlore-like compounds are characterized by the existence of non-stoichiometric phases and nanostructured materials. The composition of these titanates is described by the formula $R_2^{3+}Ti_2^{4+}O_7$, where R_2^{3+} is a trivalent rare-earth ion. Some R^{3+} ions have a great magnetic moment, for example, holmium ions. In the crystal lattice, ions occupy the sites in the vertices of tetrahedra, which allows for the existence of frustrated magnetic moments.

The magnetic interaction between the rare-earth moment in $R_2^{3+}Ti_2^{4+}O_7$ is either ferromagnetic or antiferromagnetic, depending on the species of the rare earth element and the distances between neighboring rare earth ions. When the rare earth element is Dy or Ho, the magnetic interaction at low temperatures is ferromagnetic [1–3], originating from dipole interaction, with a strong Ising anisotropy along the local axis $\langle 111 \rangle$. In this case, “two-in–two-out” spin scheme, where two spins out of four corners of a tetrahedron are directed inside and the remaining two are directed outside, has locally the lowest energy. This local constraint, however, is not enough to decide the global spin structure uniquely, but allows many degenerate ground states is one of the possible ground states, and accordingly,

there is no magnetic ordering down to the lowest temperature. This situation is similar to the issue of the proton arrangement in ice, and thus, this spin state is often called “spin ice” [4].

The state of spin ice specifically leads to the appearance of a plateau on the magnetization curves, also to the instability in the magnetization process [5–8]. The magnetic properties of material in the spin ice state can be described by the concept of existence and motion of “magnetic monopoles” [9]. These unusual magnetic states are realized at ultralow temperatures, usually, less than 1 K. However, even at higher temperatures the magnetic properties of pyrochlore titanates deserve attentive study.

The $Yb_2Ti_2O_7$ titanate was previously considered to be a possible material with the quantum spin liquid properties [10–12]. In recent years, however, a different opinion prevails and this titanate is considered to be a ferromagnet with a noncollinear arrangement of magnetic moments [13].

Recently, observation of ferroelectricity in $Ho_2Ti_2O_7$ systems has renewed interests in their theoretical and experimental studies of dielectric properties [14–16]. Experimental finding suggests that $Ho_2Ti_2O_7$ has multiple ferroelectric transitions of different origin. In polycrystalline $Ho_2Ti_2O_7$ two ferroelectric transitions are observed at 60 and 23 K [14]. However, in single crystal $Ho_2Ti_2O_7$ only one transition at 28 K has been observed [15]. It has been suggested that ferroelectric transitions at 60 K (polycrystalline $Ho_2Ti_2O_7$), 28 K (single crystal $Ho_2Ti_2O_7$) have

structural origin [16], and ferroelectric transitions at 23 K (polycrystalline $\text{Ho}_2\text{Ti}_2\text{O}_7$) are related to the magnetism of these system [14, 17].

The temperature-dependent dielectric measurement shows two distinct relaxations around 90 and 36 K in polycrystalline $\text{Ho}_2\text{Ti}_2\text{O}_7$ [17], however, the authors conclude, that there are no ferroelectric phase transitions but observed dielectric transitions are thermally activated dielectric relaxations. The diffuse phase transitions at 90 and 36 K are generated by the crystal structure and related to the lattice distortions at O1 and O2 oxygen sites. Magnetic susceptibility and spin relaxation behavior confirms that crystal electric field controlled strong single ion anisotropy behavior is responsible for these structural distortions [17].

The aim of this paper is to investigate and compare the dielectric and magnetic properties of holmium and ytterbium titanates. Holmium and ytterbium titanates were chosen because of their extraordinary magnetic properties. The magnetic interactions in holmium titanate are described within the Ising model and, in ytterbium titanate, within the so-called easy-plane X - Y model [18].

2. Materials and methods

The $\text{Yb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, compounds with a pyrochlore structure were obtained by the solid-state synthesis from the initial Ho_2O_3 (chemically pure), Yb_2O_3 (chemically pure), TiO_2 (chemically pure, anatase modification) oxides. The oxide sample weights taken in the stoichiometric ratio were carefully grinded in a jasper mortar for 30 min T_0 accelerate the interaction between the initial oxides, the powder was tableted using a plexiglass mold. The tablets with a diameter of $d = 15$ mm and a height of $h = 1.0$ mm were placed in corundum crucibles and subjected to high-temperature annealing in a muffle furnace. After each intermediate annealing stage, the samples were grinded and pressed again to ensure the completeness of the solid-state reaction [19].

The x-ray phase analysis of powder samples has been carried out by using a Shimadzu XRD-6000 diffractometer with $\text{CuK}\alpha$ radiation with wavelength $\lambda = 1.54056$ nm at the 2θ angle ranging from 10° to 80° (with the step of 0.05°) and exposure time of 2 s. The x-ray diffraction patterns of the samples after the last calcination are shown in Fig. 1. All reflections in the x-ray diffraction patterns are described by the $Fd\bar{3}m$, which confirms the formation of a pyrochlore phase. The unit cell parameters a and density ρ calculated from the x-ray diffraction patterns are given in Table 1.

Table 1. Unit cell parameters and pyrochlore density at 25°C

Compound	a , Å	$R(\text{Bi}) - R$ distance for positions with a coordination number of 6, Å	$R(\text{Bi}) - R$ distance for positions with a coordination number of 12, Å	ρ , g/cm^3
$\text{Yb}_2\text{Ti}_2\text{O}_7$	10.025	3.5446	6.1394	7.30
$\text{Ho}_2\text{Ti}_2\text{O}_7$	10.092	3.5701	6.1813	6.95

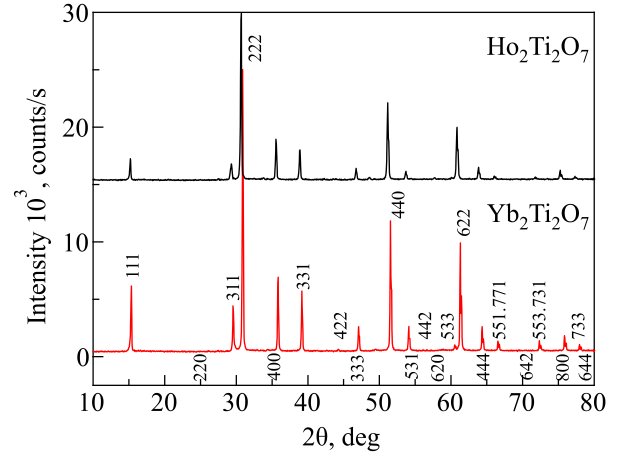


Fig. 1. X-ray diffraction patterns of the $\text{Yb}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ compounds with a pyrochlore structure at 25°C .

The x-ray diffraction data for the titanates are similar to those reported in [20, 21].

Scanning electron microscopy was used to study the microstructure of the samples. Electron microscopic images of holmium and ytterbium titanates obtained with a Quanta 200 microscope are shown in Figs. 2 and 3, respectively. The average size of structural elements is ~ 2 μm .

The measurements of the dielectric properties were made at frequencies up to 3000 Hz and different temperatures on MFLI, Zurich Instruments. The equipment allows to measure the impedance from which it can get the sample capacity, and then the real part of the permittivity. A thin layer of tantalum was sprayed onto two parallel surfaces of the sample. Thus, a capacitor with two parallel plates was obtained; the frequency and temperature dependence of its capacitance was measured, and then the permittivity was determined from the formula [22]:

$$C = \frac{\varepsilon ab}{d} \left[1 + \frac{d}{\pi b} + \frac{d}{\pi b} \ln \left(\frac{2\pi b}{d} \right) + \frac{d}{\pi a} + \frac{d}{\pi a} \ln \left(\frac{2\pi a}{d} \right) \right], \quad (1)$$

where C is capacitance of the sample, ε is the real part of the permittivity of the sample, a , b and d — length, width and thickness of the sample, respectively.

The magnetic measurements were carried out on an MPMS-5XL setup in the temperature range from 2 K to 300 K and magnetic fields of up to 30 kOe. The magnetization curves at several temperatures and the temperature dependence of the magnetic susceptibility were measured.

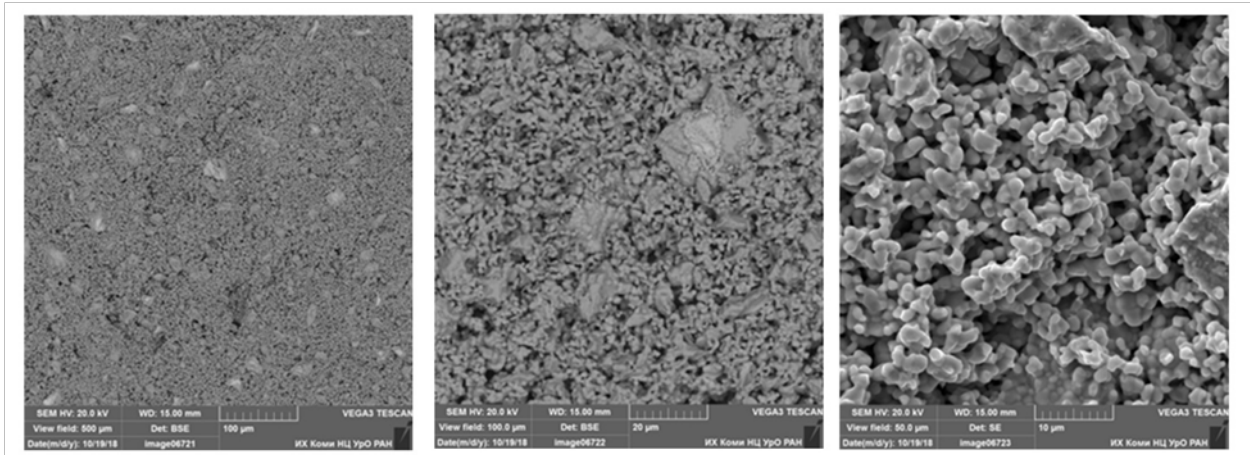


Fig. 2. The structure image of $\text{Ho}_2\text{Ti}_2\text{O}_7$ titanate, obtained by using Quanta-200 scanning electron microscope.

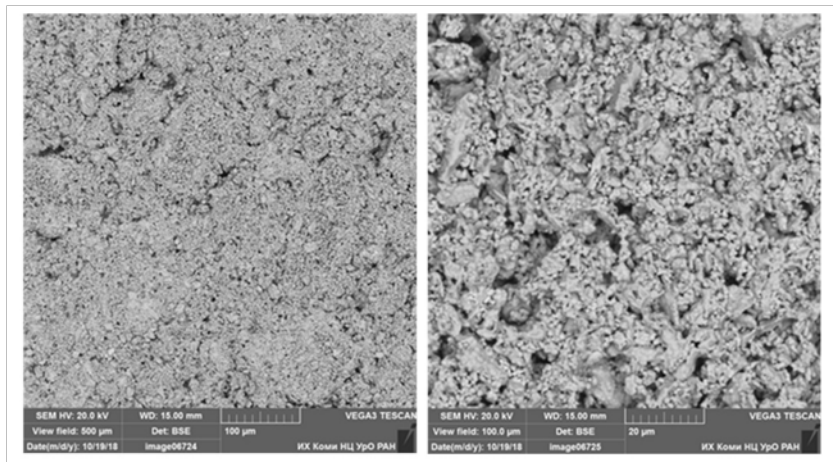


Fig. 3. The structure image of $\text{Yb}_2\text{Ti}_2\text{O}_7$ titanate, obtained by using Quanta-200 scanning electron microscope.

3. Results and discussion

3.1. Permittivity

Figure 4 shows the permittivity real part frequency dependence of the studied titanates at temperatures 77 and 300 K.

The permittivity of the studied titanates decreases with increasing frequency, which is a common feature of dielectric materials. The frequency dispersion of the permittivity is weak. For both samples, the permittivity decreases with increasing temperature in the range $T = 77\text{--}300$ K, which is confirmed by the temperature dependence of the capacitance $\text{Yb}_2\text{Ti}_2\text{O}_7$ at fixed frequencies, shown in the inset of Fig. 4. Higher dielectric permittivities at low frequencies are observed for ytterbium titanate, which can be associated with a higher density and lower unit cell parameter calculated from x-ray diffraction patterns (Table 1) compared with holmium titanate.

There is no features associated with ferroelectric phase transitions in the studied frequency and temperature range.

The permittivity at room temperature for $\text{Yb}_2\text{Ti}_2\text{O}_7$ is $\epsilon = 9.5$ and 8.9 for $\text{Ho}_2\text{Ti}_2\text{O}_7$.

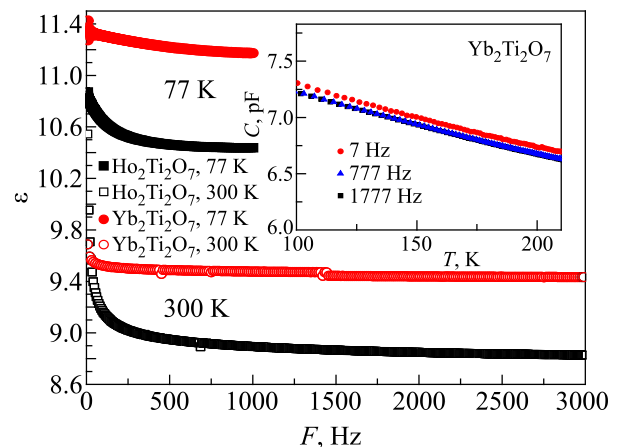


Fig. 4. The frequency dependence of holmium and ytterbium titanates permittivity at $T = 77$ K and $T = 300$ K. The inset shows the temperature dependence of ytterbium titanate capacitance at fixed frequencies $F = 7, 77, 1777$ Hz.

3.2. Magnetic susceptibility

The magnetization curves of titanates were measured at several temperatures from the interval $T = 2\text{--}50$ K in an external magnetic field up to 30 kOe in order to obtain the magnetic field dependences of the susceptibility of pyrochlore. The field dependences of the magnetic susceptibility do not have hysteresis [Figs. 5(a) and 5(c)].

There are the saturation signs in the magnetization curves of $\text{Ho}_2\text{Ti}_2\text{O}_7$ at $T = 2$ K. The magnetization value at 30 kOe is equal 92 emu/g, which is in good agreement with the data [14] where the magnetization value is equal 95 emu/g.

The magnetic susceptibility of the titanates decreases with increasing magnetic field, becoming almost independent of temperature at $H = 30$ kOe for $\text{Ho}_2\text{Ti}_2\text{O}_7$. A particularly sharp decrease in the magnetic susceptibility with increasing field is observed for $\text{Ho}_2\text{Ti}_2\text{O}_7$ at $T = 2$ K [Fig. 5(b)].

The temperature dependences of magnetic susceptibility have been measured in the range from 2 K to 300 K in the fields $H = 0.1$ and 0.3 kOe. These dependences are monotonous and reversible, i.e., there is no significant difference under the heating and cooling.

The magnetic susceptibility decreases monotonously with increasing temperature without any abnormal feature associated with magnetic phase transitions. The reason underlies in the fact that the ground states of $\text{Ho}_2\text{Ti}_2\text{O}_7$ can be ice-like, ordered, or partially ordered [23]. It can be argued that the absence of magnetic phase transition in the low temperature range is due to the fact that the change in the direction of the spins closer to their parallel orientation with decreasing temperature occurs a gradual, without sharp transitions, apparently due to the state of spin ice at the lowest temperatures $T < 2$ K. Therefore, we conclude that the magnetic ordering in studied titanates with decreasing temperature is a gradual process [14].

When holding the Curie–Weiss law, the product χT should remain constant. However it has a maximum at the temperature 9.3 K for $\text{Ho}_2\text{Ti}_2\text{O}_7$ at applied external magnetic field 0.1 and 0.3 kOe (Fig. 6, insert). For $\text{Yb}_2\text{Ti}_2\text{O}_7$ titanate the maximum of the product χT is not observed, but the Curie–Weiss law in the temperature range from 2 K to 300 K is only approximately fulfilled. The deviation from the linearity of χT is associated with a violation of the applicability of the Ising model. According to our experimental data, the Curie–Weiss temperature θ_{CW} is -0.8 K, and from

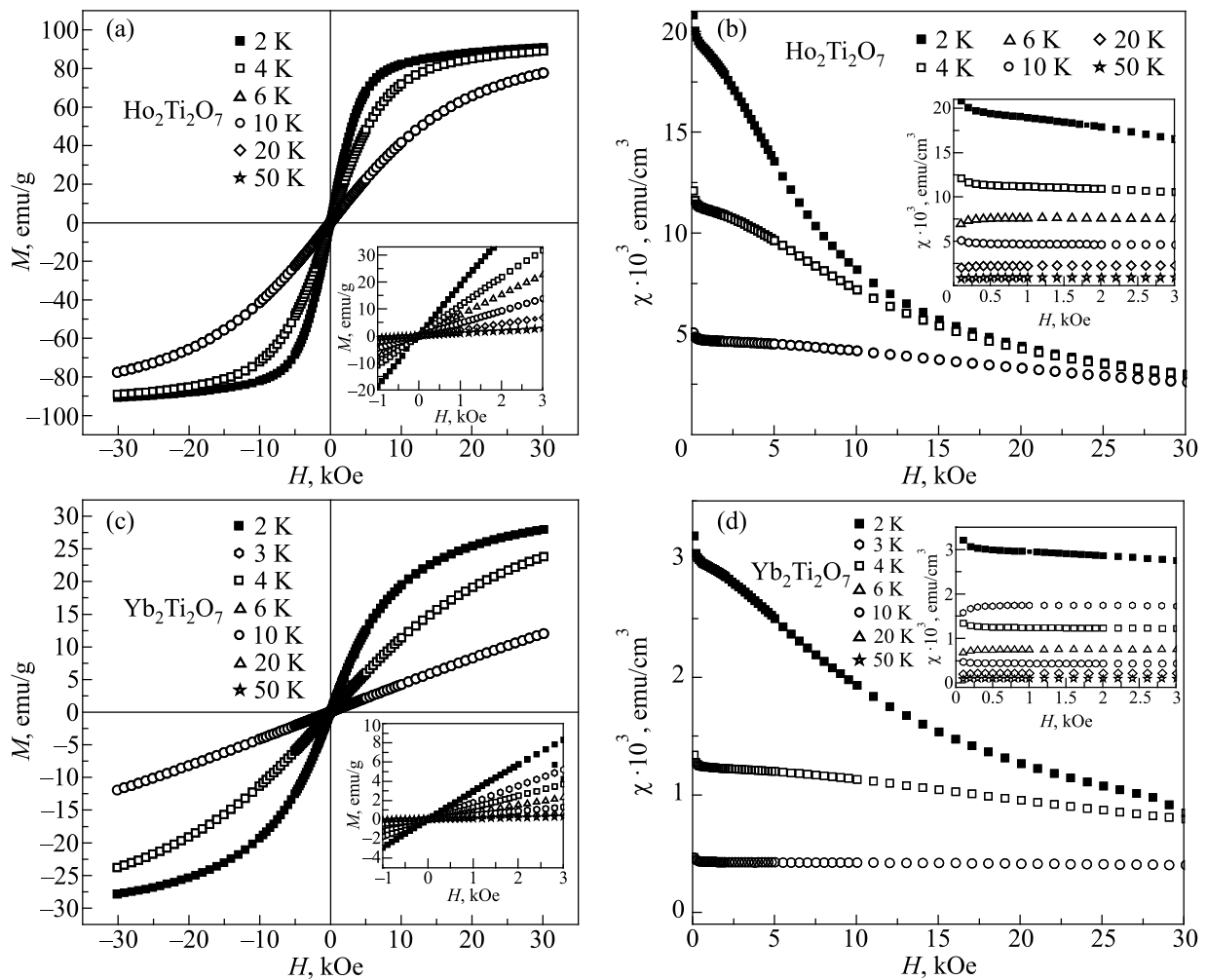


Fig. 5. Magnetization curves (a), (c); magnetic susceptibility (b), (d) of $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$ titanates at different temperatures. Inserts: the same dependences for $H < 3$ kOe.

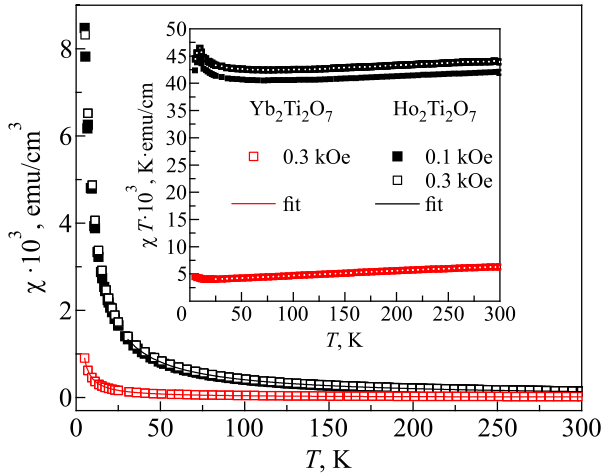


Fig. 6. (Color online) The temperature dependences of the magnetic susceptibility of the studied titanates approximated by the Curie–Weiss law. Inset: temperature dependences of the product χT of the rare-earth titanates $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$.

the data obtained in [24], the Curie–Weiss temperature is $\theta_{CW} = -0.75$ K.

Magnetic susceptibility for $\text{Ho}_2\text{Ti}_2\text{O}_7$ titanate has been computed within Ising model based on the calculation of the magnetic moment of system of spins located in the vertices of tetrahedron of pyrochlore crystalline structure [25]. The magnetic susceptibility temperature dependence:

$$\chi(T) = \frac{N(g\mu_B)^2 S^2}{k_B T} \left[1 - \frac{3S^2}{2k_B T} (2.8J_D + 2.67J_S) \right], \quad (2)$$

where $S = 2$ is the spin of Ho^{3+} ion, g is the Lande factor, N is the number of magnetic ions inside 1 cm^3 [26].

Magnetic dipolar interaction between the nearest ions and superexchange interaction are taken into account with the constants J_D and J_S , respectively. The second term in the square brackets describes deviation from the Curie–Weiss law. The magnetic dipolar interaction with positive constant J_D tends to a parallel ordering of spins and the superexchange interaction with negative constant J_S promotes to frustration. The analysis performed according to (2), has shown that for $\text{Ho}_2\text{Ti}_2\text{O}_7$ the magnetic dipolar interaction dominates at the temperatures below 8 K. For $\text{Yb}_2\text{Ti}_2\text{O}_7$ the sign of the slope of the low temperature dependency of the product χT is opposite, probably, due to the domination of superexchange.

4. Conclusion

Ytterbium and holmium titanates have been synthesized and their dielectric and magnetic properties have been investigated. The frequency dispersion of the permittivity is weak. The permittivity decreases with increasing temperature in the range $T = 77\text{--}300$ K for both samples. There is no features associated with ferroelectric phase transitions in the studied frequency and temperature range.

The magnetic susceptibility decreases monotonously with increasing temperature without any anomalous features associated with magnetic phase transitions. Apparently, the absence of magnetic phase transition in the low temperature range is due to the fact that the rotation of the spins to their parallel orientation with decreasing temperature occurs gradually, without abrupt transitions. Therefore, we conclude that the magnetic ordering in studied titanates with decreasing temperature is a gradual process.

The Curie–Weiss law is approximately satisfied for holmium titanate in the temperature range from 30 K to 300 K, and there are deviations from this law for ytterbium titanate. For $\text{Ho}_2\text{Ti}_2\text{O}_7$ the magnetic dipolar interaction dominates at the temperatures below 8 K, for $\text{Yb}_2\text{Ti}_2\text{O}_7$ the sign of slope of the low temperature dependency of the product χT is opposite, probably, due to the domination of superexchange.

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Діелектричні й магнітні властивості титанатів гольмію та ітербію

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Синтезовано титанати ітербію та гольмію, досліджено їх діелектричні й магнітні властивості. Отримано частотні залежності діелектричної проникності при $T = 77$ та 300 К, криві намагнічування та температурні залежності сприйнятливості в полях до 30 кЕ при температурах від 2 К до 50 К. Проведено порівняння властивостей титанатів. Завдяки використанню температурних залежностей сприйнятливості проведено аналіз магнітної, дипольної та обмінної взаємодій титанатів.

Ключові слова: рідкісноземельні титанати, структура пірохлору, магнітна сприйнятливість, діелектрична проникність.