

Phase formation and dielectric properties of $\text{Ln}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (Ln = rare earth element)

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Abstract

Weberites and pyrochlores ($\text{A}_2\text{B}_2\text{O}_7$), both fluorite-related superstructures, are attractive dielectric ceramics due to their ability to accommodate diverse cations, thus allowing their properties to be tailored. This study focuses on the fundamental understanding of the structure–dielectric property relationships in fluorite-related oxides. Specifically, Ln_3NbO_7 and $\text{Ln}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (where the ionic radius of Ln' is smaller than that of Ln) compounds are investigated. It has been previously shown that weberite-type Ln_3NbO_7 exhibits a composition dependent dielectric relaxation above room temperature. It is here shown that a dielectric relaxation also occurs in $\text{La}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ ($\text{Ln}' = \text{Yb}^{3+}$, Er^{3+} , and Dy^{3+}) compounds near or below -158°C . The temperature, at which the maximum permittivity occurs, is different for different compositions (-132°C for $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, -197°C for $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, and -187°C for $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ at 1 MHz) and is correlated with the distortion of the NbO_6 octahedra. The room temperature dielectric permittivity of all three compounds was measured to be between 40 and 50 at 1 MHz.

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1. Introduction

The weberite and the pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$) are both anion-deficiency fluorite (AO_2 or A_4O_8) superstructures. These two structures have a similar cationic sublattice, which is comprised by the stacking of cubic close-packed cation layers, the same as $\{1\ 1\ 1\}$ planes in the fluorite. These layers alternate between the compositions A_3B and AB_3 and are parallel to $\{1\ 1\ 1\}$ planes in the pyrochlore and $\{0\ 1\ 1\}$ planes in the weberite. The crystallographic relationship between the orthorhombic weberite and the cubic pyrochlore is further clarified by the fact that the space group of weberite (*Imma*) is a subgroup of *Fd-3m*, the space group of pyrochlore. These two structures can be described as a network of corner-shared BO_6 octahedra. However, a significant difference between the two is that all of the oxygen ions in weberites participate in the formation of BO_6 octahedra, but only 6 out of 7 oxygen ions participate in pyrochlore structures (see Fig. 1).¹

The field existence and stability of pyrochlores can typically be predicted based on the ratio of cation ionic radii R_A/R_B . For $\text{A}_2^{3+}\text{B}_2^{4+}\text{O}_7$ pyrochlores, the field existence and

stability is in the range of $1.46 < R_A/R_B < 1.80$, where R is the ionic radius of the cation.² $\text{Ln}_2(\text{Ln}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (Ln_3NbO_7 , $\text{Ln} = \text{La}^{3+}$, Nd^{3+} or Gd^{3+}) compounds, which have been reported as weberite-type structures, are not within the pyrochlore stability field.^{3–6} By contrast, $\text{Ln}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ compounds, where the ionic radius of Ln' is smaller than that of Ln , lie in or close to the stability area, and thus, as suggested by Isupov,⁷ $\text{Ln}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ are expected to crystallize in the pyrochlore structure. Therefore, to test this prediction and further understand fluorite-related superstructures, the structure of the three compounds, $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, were studied here.

In terms of dielectric properties, it has been reported that weberite-type Ln_3NbO_7 exhibits a composition dependent dielectric relaxation above room temperature.^{8–10} The relaxation temperatures are different, 47°C , 97°C , and 197°C for Gd_3NbO_7 , La_3NbO_7 and Nd_3NbO_7 , respectively. It has been proposed that different relaxation temperatures may be correlated with polyhedral distortion in the crystal structure of weberite-type Ln_3NbO_7 . To explore more on the origin of this dielectric relaxation, the dielectric properties of $\text{La}_2(\text{Ln}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ ($\text{Ln} = \text{Dy}^{3+}$, Er^{3+} , and Yb^{3+}) are here investigated. This study points to the possibility of tailoring the relaxation in the fluorite-related structures via distortion of the NbO_6 octahedra.

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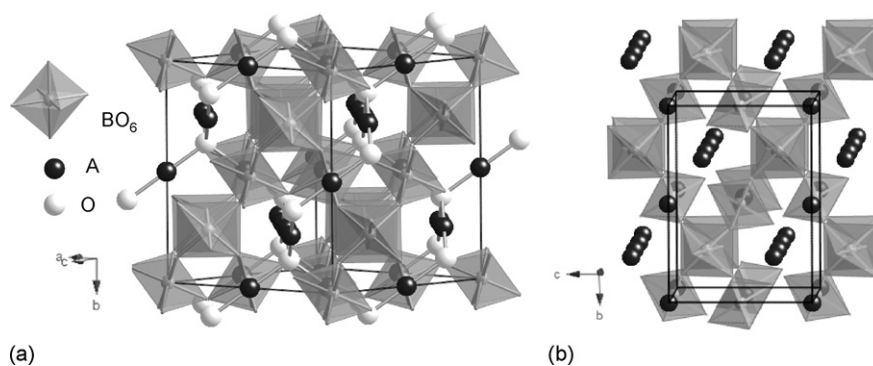


Fig. 1. BO_6 polyhedral view of (a) the pyrochlore and (b) the weberite. The line is the unit cell.

2. Experimental procedure

Polycrystalline specimens were prepared by solid state processing. The starting materials were Dy_2O_3 (Alfa, 99.99%), Er_2O_3 (Alfa, 99.99%), La_2O_3 (Alfa, 99.99%), Yb_2O_3 (Alfa, 99.9%) and Nb_2O_5 (Alfa, 99.9985%). A stoichiometric mixture of 20 g Ln_2O_3 and Nb_2O_5 was combined with 70 ml deionized water and 2 ml ammonium polyacrylate dispersant (Darvan 821 A). The slurry was ball-milled for 24 h, subsequently dried in the oven at 120°C for 16 h, then ground and sieved through a $212\text{ }\mu\text{m}$ mesh. The powder was then placed in an alumina crucible and calcined at $1400\text{--}1500^\circ\text{C}$. X-ray diffraction (XRD) was performed to verify phase formation using $\text{CuK}\alpha$ radiation at room temperature. The resulting XRD patterns were compared with the XRD profiles of stoichiometric mixture of unreacted precursors and the JCPDS PDF of all other possible compositions of rare earth niobates such as LaNbO_4 . Multiple calcinations were performed to ensure phase purity. Between each calcination stages, the powders were finely reground with mortar and pestle.

After calcination, 1–3 wt.% of PVA binder (Celvol 103) was added to assist in pellet formation. Pellets were uniaxially pressed at 150 MPa into cylindrical pellets, 3 mm in diameter and approximately 1.5 mm thick. Pellets were sintered at 1600°C for 8 h following a binder burnout at 450°C for 2 h. For dielectric measurements, parallel plate capacitors were made by sputtering Au/Pd electrodes on both sides of the pellets followed by a hand-painted coat of Ag-paste that was dried in air. Dielectric properties were measured using an Agilent 4284A LCR meter over the frequency range of 10 kHz–1 MHz. The measurements were performed in the temperature range of -253°C to 22°C with samples in a closed cycle cryogenic workstation (CTI - Cryogenics, Model 22). The measurements were conducted both on cooling and heating.

3. Results and discussion

3.1. Crystal structure

The XRD profiles of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ at different calcination temperatures and the stoichiometric mixture of the La_2O_3 , Yb_2O_3 and Nb_2O_5 are shown in Fig. 2(a). After initial calcina-

tion at 1400°C for 8 h, the resulting pattern showed a mixture phase of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, Yb_3NbO_7 , and La_2O_3 . After the subsequent calcination at 1500°C for 24 h, there was no obvious La_2O_3 phase, and the Yb_3NbO_7 phase was greatly depressed, which relative intensity of the strongest peak decreased from 42% to 7%. After the third calcination at 1500°C for 24 h, it was clearly shown that there are no unreacted La_2O_3 , Yb_2O_3 , Nb_2O_5 or Yb_3NbO_7 in the $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ pattern. The XRD profile remained the same after additional calcination at 1500°C for 12 h. Therefore, equilibrium was presumed after the third calcination. Initial inspection of the XRD pattern showed the five characteristic cubic fluorite reflections with 2θ ranging from 10° to 70° . However, upon further analysis, it was observed that several of the five peaks were in fact split into two reflections. The pattern also contained several weak peaks with intensities below 5% relative intensity (Fig. 2(b) and (c)).

Pseudo-Voigt functions were used to fit the diffraction peaks and extract the peak positions using Xfit program.¹¹ It was observed that the peak splitting did not increase with increasing 2θ , which ruled out the possibility of the formation of two fluorite phases. The peak positions were input into Crysfire using Treor program (an indexing program that searches for solutions by varying Miller indices in a trial-and-error manner).¹² The best solution obtained by Treor was an orthorhombic unit cell. The lattice parameters were further refined using Checkcell program.¹³ The initial lattice parameters corresponded to an orthorhombic fluorite-related lattice ($\sqrt{2}a$, $2a$ and $\sqrt{2}a$, where $a \sim 5\text{ }\text{\AA}$)^{14,15} and therefore, the XRD profile of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ was then compared with the XRD of fluorite-related structures including orthorhombic pyrochlore, weberite, weberite-type, orthorhombic fluorite, and zirconolite. The XRD pattern of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ was consistent with that of an orthorhombic pyrochlore structure (e.g. $\text{Cd}_2\text{Nb}_2\text{O}_7$, space group $\text{Ima}2$). Therefore, the structural parameters of orthorhombic $\text{Cd}_2\text{Nb}_2\text{O}_7$ ¹⁶ were used as initial guess for the Rietveld refinement of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ using Maud program¹⁷; the lattice parameters were refined to be $7.5623(13)\text{ }\text{\AA}$, $10.766(2)\text{ }\text{\AA}$, $7.6619(3)\text{ }\text{\AA}$. While all experimental peaks can be assigned to the phase, the peaks with relative intensities larger than 4% are indexed and the others below 4% are indicated by diamond symbols in Fig. 2(b).

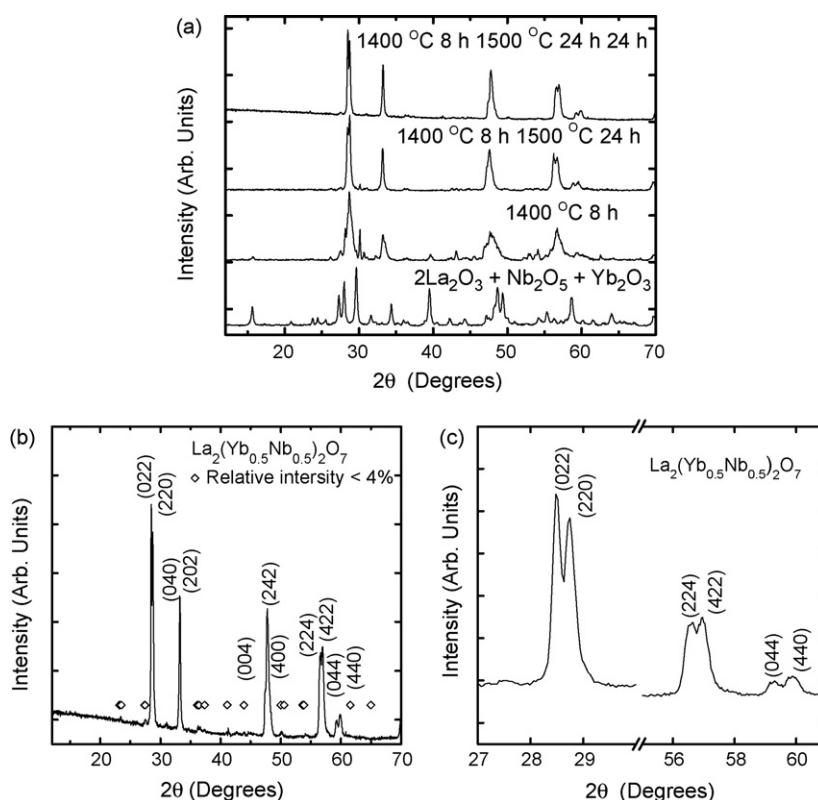


Fig. 2. (a) XRD patterns $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ at different calcination temperatures and time and the mixture of La_2O_3 , Nb_2O_5 and Yb_2O_3 . (b) Indexed XRD profile of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ after calcinations at 1400°C for 8 h and 1500°C for 24 h and 24 h. (c) Details of the peak splitting in $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

The XRD profiles of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ are shown in Fig. 3. The 5 characteristic fluorite peaks were all split into two or more peak reflections. The patterns contained more weak peaks than in the case of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$. Similar XRD analysis as described above was performed on the XRD profiles of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$. In both cases, the minor peaks at $2\theta \sim 26^\circ$, 29.5° and 31° could not be indexed based on an orthorhombic pyrochlore. However, the XRD patterns were found to be consistent with the weberite-type

structure (e.g. Nd_3NbO_7 , space group Cmcm).³ Rietveld refinement of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ was thus based on the structure of Nd_3NbO_7 . The lattice parameters of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ are $10.921(2)\text{Å}$, $7.5646(12)\text{Å}$ and $7.7060(13)\text{Å}$. The lattice parameters of $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ are $10.9220(8)\text{Å}$, $7.5915(12)\text{Å}$ and $7.7189(5)\text{Å}$. While all observed peaks can be assigned to the phases, the peaks with relative intensities larger than 8% are indexed and the other less intense peaks are indicated by diamond symbols in Fig. 3. The summary of lattice parameters is listed in Table 1.

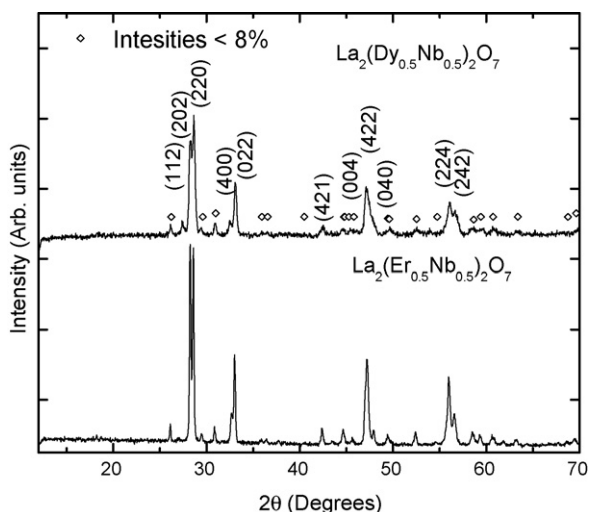


Fig. 3. XRD patterns of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

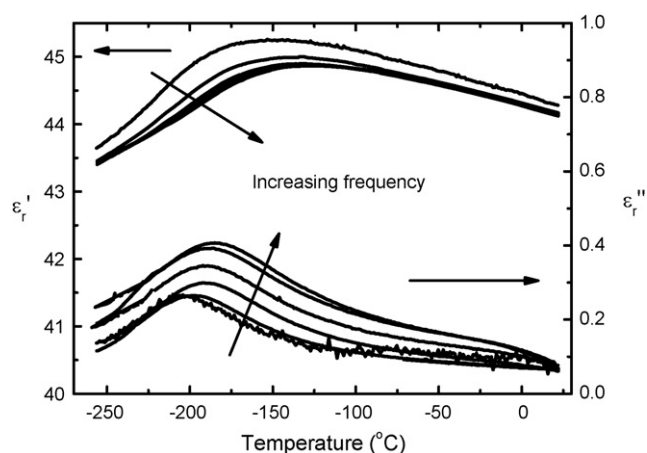
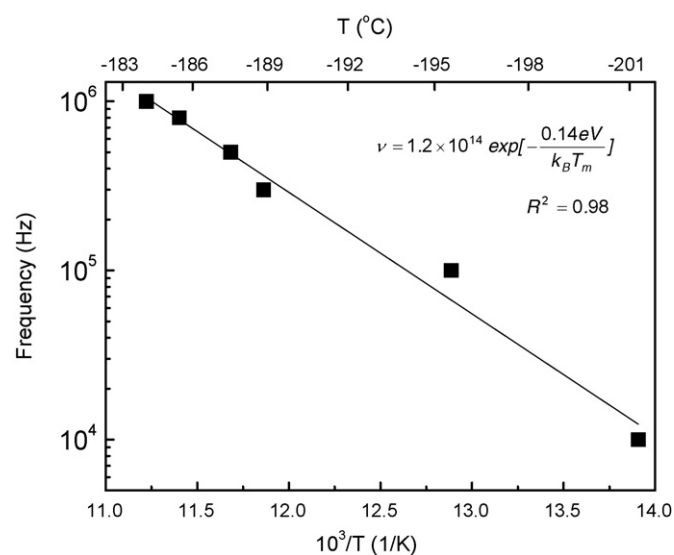
3.2. Dielectric properties

The dielectric measurements have been performed both on cooling and on heating in the temperature range of -253°C – 22°C . It is important to note that dielectric data measured on cooling matches well with that on heating for all the compounds. The dielectric behavior of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ as a function of temperature at the frequencies from 10 kHz to 1 MHz is shown in Fig. 4. The real part of permittivity is between 43.5 and 44.5 from -253°C to 22°C , and the imaginary part of permittivity is on the order of 10^{-1} at 1 MHz. It is observed that the dielectric behavior undergoes a frequency and temperature dependent dielectric relaxation. The permittivity increases slightly with increasing temperature from -253°C to about -133°C where a maximum is reached (~ 44.5 at 1 MHz). The temperature, where the maximum permittivity occurs, and consequently the temperature

Table 1

Summary of lattice parameters and the temperature where the maximum of the permittivity occurs ($T(\epsilon_m)$).

Compound	a (Å)	b (Å)	c (Å)	Unit cell volume (Å ³)	$T(\epsilon_m)$
Nd ₃ NbO ₇	10.8606(17)	7.5122(10)	7.5973(9)	619.8409	204 °C
La ₃ NbO ₇	11.1798(19)	7.6562(11)	7.7757(11)	665.5594	90 °C
Gd ₃ NbO ₇	10.6114(5)	7.5202(4)	7.5393(3)	601.6350	48 °C
La ₂ (Yb _{0.5} Nb _{0.5}) ₂ O ₇	7.5623(13)	10.766(2)	7.6619(13)	623.8339	−132 °C
La ₂ (Er _{0.5} Nb _{0.5}) ₂ O ₇	10.9220(8)	7.5915(5)	7.7189(5)	640.0076	−197 °C
La ₂ (Dy _{0.5} Nb _{0.5}) ₂ O ₇	10.921(2)	7.5646(12)	7.7060(13)	636.6158	−187 °C

Fig. 4. Dielectric properties of La₂(Yb_{0.5}Nb_{0.5})₂O₇ at 10 kHz, 100 kHz, 300 kHz, 500 kHz, 800 kHz and 1 MHz.Fig. 5. Arrhenius plot of temperature at which the maximum of imaginary parts of permittivity occurs for La₂(Yb_{0.5}Nb_{0.5})₂O₇.

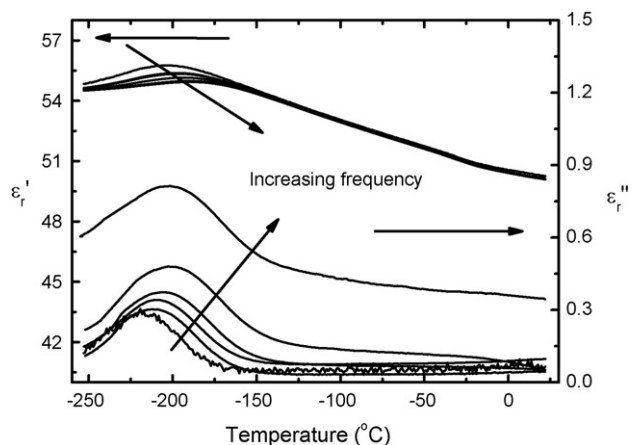
(T_m), where the peak of the imaginary part of permittivity is located, both increase with increasing frequency. However, the dielectric relaxation behavior of La₂(Yb_{0.5}Nb_{0.5})₂O₇ is different from that observed in weberite-type Gd₃NbO₇.⁹ In Gd₃NbO₇, there is no clear shift in the maxima of the dielectric permittivity and a larger variation of T_m as a function of frequency.

To better understand the phenomena, as customarily, the Arrhenius function is used to model the relaxation behavior of La₂(Yb_{0.5}Nb_{0.5})₂O₇:

$$\nu = \nu_0 \exp \left[-\frac{E_a}{k_B T_m} \right] \quad (1)$$

where ν is the frequency, the pre-exponential ν_0 is the attempt jump frequency, E_a is the activation energy, and k_B is Boltzmann's constant. The resulting Arrhenius plot is presented in Fig. 5. From the linear fit, $\nu_0 = 1.2 \times 10^{14}$ Hz, and the activation energy E_a is 0.14 eV. The attempt frequency is lower than cubic pyrochlore CaO-TiO₂-Nb₂O₅ (4.6×10^{14} Hz), but higher than pyrochlore Bi_{1.5}ZnNb_{1.5}O₇ (3×10^{12} Hz).^{18,19} It is proposed that lighter A site cations result in a higher attempt frequency because the attempt frequency is related to that of O'-A-O' bending phonon mode.^{18,20} The calculated attempt frequency of La₂(Yb_{0.5}Nb_{0.5})₂O₇ is also acceptable as the mass of A cations (La³⁺) is intermediate among these three compounds. The observed activation energy is smaller than that of weberite-type Gd₃NbO₇, 0.45 eV and close to Bi_{1.5}ZnNb_{1.5}O₇, 0.136 eV.^{9,19}

The dielectric properties of La₂(Dy_{0.5}Nb_{0.5})₂O₇ are shown in Fig. 6. The permittivity slightly increases from 54.9 to 55.2 from −248 °C to −187 °C, and then decreases to 51 at room temperature at 1 MHz. The imaginary part of permittivity is on the order of 10^{-1} at 1 MHz, the same as the other two compounds. This compound also exhibits a dielectric relaxation. The maximum of the permittivity shifts to a higher temperature with increasing frequency. The Arrhenius function is also used

Fig. 6. Dielectric properties of La₂(Dy_{0.5}Nb_{0.5})₂O₇ at 10 kHz, 100 kHz, 300 kHz, 500 kHz, 800 kHz and 1 MHz.

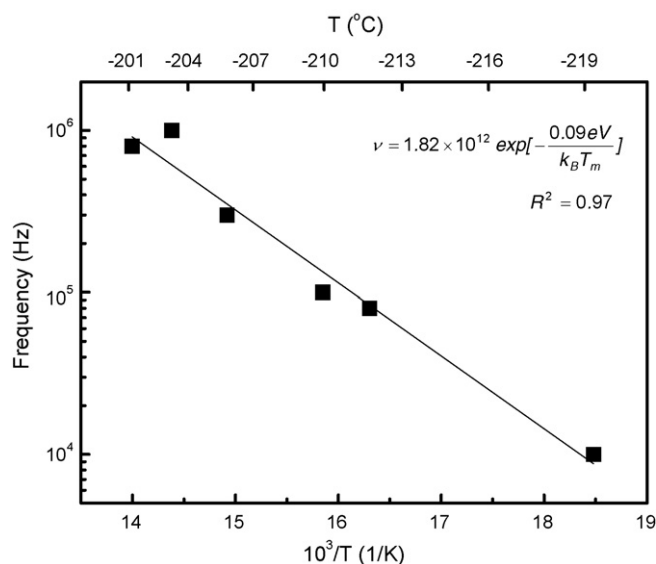


Fig. 7. Arrhenius plot of temperature at which the maximum of imaginary parts of permittivity occurs for $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

to model the relaxation behavior of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$. The resulting Arrhenius plot is presented in Fig. 7. From the linear fit, $\nu_0 = 1.82 \times 10^{12}$ Hz, and the activation energy E_a is 0.09 eV. The attempt frequency of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ is on the same order of that of cubic pyrochlore $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ (3×10^{12} Hz).¹⁹ The activation energy is below those of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$, $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_7$ and Gd_3NbO_7 .^{9,19} While this compound is neither, a dipolar glass or relaxor ferroelectric, it is important to note that similar activation energies have been observed or calculated for those type of materials, and thus the measured activation energy value (0.09 eV) is not unheard of.^{21–23}

Fig. 8 shows the dielectric properties for $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ as a function of temperature at different frequencies from 10 kHz to 1 MHz. The permittivity is between 48 and 50.4 from -253°C to 22°C , and the imaginary part of permittivity is also on the order of 10^{-1} at 1 MHz. This compound also exhibits a frequency and temperature dependent dielectric relaxation. The real part of permittivity of $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ at different frequencies becomes more dispersive near the relaxation

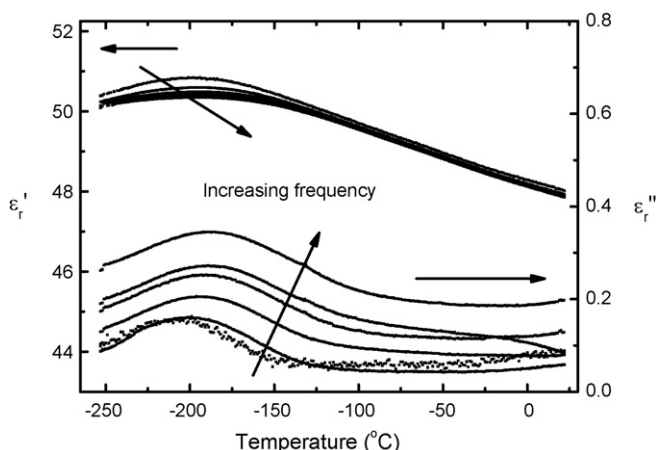


Fig. 8. Dielectric properties of $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ from 10 kHz to 1 MHz.

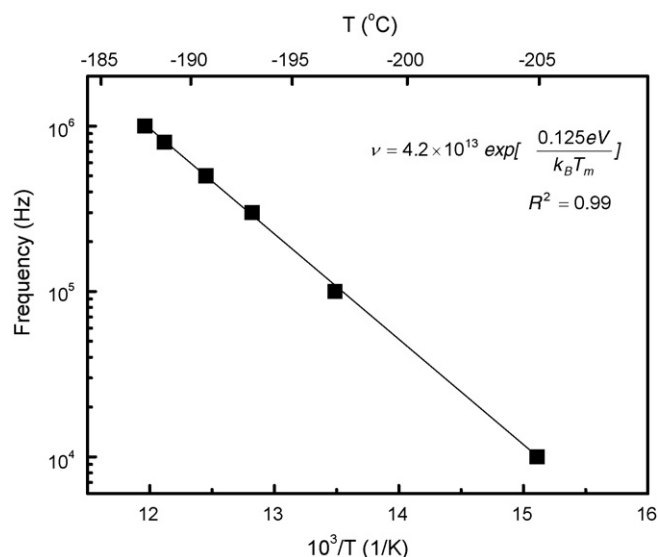


Fig. 9. Arrhenius plot of temperature at which the maximum of imaginary parts of permittivity occurs for $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

temperature while above -123°C , the variation of permittivity as a function of frequency is negligible. At the same time, the variation of the real part of permittivity as a function of temperature near the relaxation temperature is smaller than that from room temperature to -173°C . There is no clear shift in the maxima of the dielectric permittivity with respect to frequency in $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, which is similar to Gd_3NbO_7 .⁹ T_m increases with increasing frequency from 10 kHz to 1 MHz. The Arrhenius function is also used to model the relaxation behavior of $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ as shown in Fig. 9. The calculated ν_0 is 4.2×10^{13} Hz, and the activation energy E_a is 0.125 eV. These two values are close to those of $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

3.3. Structure–property relationship

It has been shown in the past that different degrees of polyhedral distortion in LnO_8 and NbO_6 correlate well with the

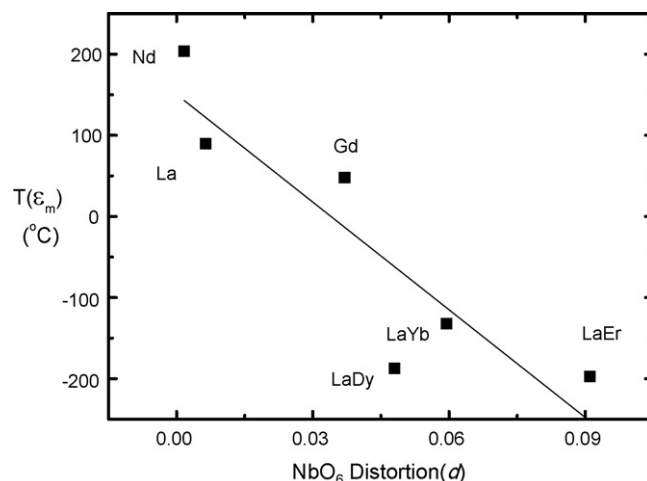


Fig. 10. NbO_6 octahedra distortion (d) vs. $T(\epsilon_m)$.

different relaxation temperatures ($T(\epsilon_m)$), the temperature where maximum real parts of permittivity occurs) in weberite-type Ln_3NbO_7 .^{1,8} Here, it may be possible that the polyhedral distortion can also explain the origin of different dielectric relaxation temperatures in $\text{Ln}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (the summary of $T(\epsilon_m)$ is listed in Table 1). The distortion index by Baur²⁴ were used to characterize the polyhedral distortion:

$$\text{Distortion } (d) = \frac{1}{n} \sum_{i=1}^n \frac{|d_i - d_{\text{ave}}|}{d_{\text{ave}}} \quad (2)$$

where in MO_n polyhedra, d_i is the polyhedral edge length (O–O) and d_{ave} is the average polyhedral edge length. The polyhedral characterization is focused on NbO_6 octahedra since weberite-type Ln_3NbO_7 and $\text{La}_2(\text{Ln}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ have common Nb sublattice (or NbO_6 octahedra). It is found out the distortion of NbO_6 may closely relate to the dielectric properties. As shown in Fig. 10, $T(\epsilon_m)$ at 1 MHz decreases with increasing distortion (d) of NbO_6 with exception of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (the line is for visual aid). The NbO_6 distortion may be attributed to the “openness” of the structure which causes an easier polarization of the material and thus lower $T(\epsilon_m)$.^{8,10} The attributed “openness” can be easily observed by comparing $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$. $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a larger unit cell volume than $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ though the ionic radius of Er^{3+} (0.890 Å) is smaller than that of Dy^{3+} (0.912 Å).²⁵ The larger unit cell volume of $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ is probably contributed by the greater NbO_6 distortion. Therefore, $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a slightly lower $T(\epsilon_m)$ (−197 °C) than that of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (−187 °C). However, $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a greater NbO_6 distortion than that of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, but $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a higher $T(\epsilon_m)$. If considered from normalized unit cell volume ($V_{\text{unit cell}}/(2 \times R_{\text{La}^{3+}} + R_{\text{Ln}^{3+}}) \text{ Å}^2$), $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a smaller value (195.68 Å²) than that of $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ (196.97 Å²). Therefore, $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has a more open structure, which may result in a lower $T(\epsilon_m)$. Thus, NbO_6 distortion appears to be an important factor to determine the $T(\epsilon_m)$, nonetheless, it is clear that other factors such as normalized unit cell volume, dipole interactions and polarization may also play a role.

In summary, $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has the highest dielectric permittivity among the three compounds at all measured temperatures, $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ intermediate, and $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ has the lowest value, which can be expected by the polarizability of Ln^{3+} ions. The temperature at which the maximum permittivity occurs are different, −132 °C for $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, −197 °C for $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and −187 °C for $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$.

4. Conclusion

The series of $\text{La}_2(\text{Ln}'_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ compounds were synthesized by solid state processing. These compounds have an orthorhombic fluorite-related structure. $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ is orthorhombic pyrochlore, and $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ are weberite-type. Their dielectric properties were also investigated. The three compounds show

temperature and frequency dependent dielectric relaxation. Arrhenius function was used to model the dielectric relaxation. The calculated attempt frequency is 1.2×10^{14} Hz, 4.2×10^{13} Hz and 1.82×10^{12} Hz for $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, respectively. The activation energy is 0.14 eV, 0.125 eV and 0.09 eV for $\text{La}_2(\text{Yb}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, $\text{La}_2(\text{Er}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$ and $\text{La}_2(\text{Dy}_{0.5}\text{Nb}_{0.5})_2\text{O}_7$, respectively. It is also found out that the NbO_6 distortion correlates with $T(\epsilon_m)$.

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