

Mg₂MTaO₆ (*M* = Nd or La): a group of new pyrochlore oxides

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Abstract

Preparation of two novel mixed metal oxide ceramic materials, namely magnesium neodymium tantalum oxide (Mg₂NdTaO₆) and magnesium lanthanum tantalum oxide (Mg₂LaTaO₆) by conventional solid-state reaction method is reported in this paper. The crystal structure of these new compounds, were studied by indexing the X-ray diffraction patterns, powder pattern calculation and profile fitting. They were found to have a defective cubic pyrochlore structure, with the *A* site being randomly occupied by Mg and La/Nd, while, Ta and Mg are randomly distributed at the *B* site. The formula assigned were (MgNd)(MgTa)O₆ and (MgLa)(MgTa)O₆. The variation of dielectric constant, dielectric loss and conductivity of sintered pellets of these materials with applied frequencies in the range of 30 Hz–1 MHz were studied at room temperature. These room temperature studies at 1 MHz gave dielectric constant values of 24.8 and 25.35; conductivity values of 7.75×10^{-6} and 8.27×10^{-6} S/m as well as dielectric loss values of 0.0055 and 0.006 for Mg₂NdTaO₆ and Mg₂LaTaO₆, respectively. These new pyrochlore compounds were found to have dielectric constant, dielectric loss and conductivity values in the range suitable for possible electronic ceramic applications.

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Keywords: Pyrochlores; Mg₂NdTaO₆; Mg₂LaTaO₆; Crystal structure; Dielectric properties

1. Introduction

During the last decades there has been an increasing interest in the preparation of new functional ceramic oxides whose basic properties can be altered for specific applications like solid oxide fuel cells, sensors, etc. In contrast to materials for ambient temperature devices, these functional ceramics should have well defined electrical transport properties. Several such complex ceramic oxides with the general formula Ba₂MM'O_{6+x}, where *M* = Y, La or any of the rare-earth metals; *M'* = Sb, Sn, Nb, Zr, Hf and Ta and $-0.5 < x < 0.5$ were synthesized and characterized recently. Some compounds with the formula Sr₂MM'O_{6+x} are also reported [1–5]. These compounds crystallize in the perovskite structure. However in case of Ca₂MM'O_{6+x} and

Pb₂MnReO₆ compounds, apart from the perovskite structure, a few cases of metastable pyrochlore structures were also reported. These metastable pyrochlores transformed into perovskite structures on further heating [6–8]. Most of the magnesium-bearing ceramic oxides for possible electronic ceramic applications, reported in the literature had perovskite structure [1,9,10], while some Magnesium bearing compounds like Bi₂M'_{2/3}M''_{4/3}O₇, where *M'* = Zn, Mg, Ni, Sc, In and Cu and *M''* = Nb and Ta had pyrochlore structure [11].

However the compounds magnesium neodymium tantalum oxide (Mg₂NdTaO₆) and magnesium lanthanum tantalum oxide (Mg₂LaTaO₆) have not been reported. In this paper, which is a part of a series devoted to the preparation and characterization of a new class of complex ceramic oxides with the general formula Mg₂MTaO_{7-x}; the preparation of two new compounds, viz Mg₂NdTaO₆ and Mg₂LaTaO₆ as well as their properties including crystal structure, dielectric properties and conductivity are presented.

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2. Experimental

The novel mixed metal oxide compounds in the present study were prepared by the conventional solid-state reaction method. The chemicals used in the present work are magnesium carbonate (MgCO_3) of 99% Purity, neodymium oxide (Nd_2O_3) of 99.9% purity; lanthanum oxide (La_2O_3) of 99.9% purity and tantalum oxide (Ta_2O_5) of 99.9% purity. MgCO_3 was obtained from M/s Merck, Mumbai, India and the remaining three oxides were obtained from M/s Aldrich Chemicals, USA.

The magnesium carbonate and oxides of metal M (Neodymium or Lanthanum) and tantalum were mixed in the molar ratio $\text{Mg}:M:\text{Ta} = 2:1:1$ required for the formation of the compounds of the type $\text{Mg}_2\text{MTaO}_{7-x}$. This mixture was then ball milled for 24 h using acetone as the wetting medium. The resultant homogeneous mixture was dried and heated at high temperature in the range of 1300–1450 °C for 8–10 h. The calcined powders were mixed with PVA binder and uniaxially pressed into circular discs of about 13 mm diameter and 1–1.5 mm thickness. These samples were sintered by heating, for different durations at different temperatures between 1550 and 1600 °C.

The progress of the reaction and the structure of the compounds formed were examined by the X-ray diffraction technique using a computerized X-ray Diffractometer (Rigaku D/max, Japan) with Nickel filtered $\text{CuK}\alpha$ radiation. The X-ray powder diffraction patterns are indexed using software 'TREOR' from 'CRYSFIRE'. PowderCell2.3 provided by the CCP14 was used for powder pattern calculation and profile fitting.

The variation of dielectric property of these samples with applied frequency was studied using the sintered pellets. Both the surfaces of the pellets were polished and were then cleaned with acetone. Room temperature curing silver paint was applied to both the surfaces of the pellets and copper leads were fixed to the silver electrode surfaces. These samples were dried at about 200 °C for 2 h in an air oven. The dielectric properties of the novel ceramic compounds ($\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$) were measured using a complex impedance analyzer (Hewlett Packard model 4192A) in the frequency range from 30 Hz to 1 MHz at room temperature. The capacitance and dissipation factor were directly obtained from impedance analyzer as a function of frequency. The dielectric constant ϵ_r values were obtained from the capacitance values (C) using the relation; $C = \epsilon_0 \epsilon_r A/d$; where ϵ_r is the dielectric constant, ϵ_0 the permittivity of free space, ($\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$) A the area of the disc and d the thickness.

The conductivity (σ) values of the sintered samples were calculated from the value of conductance, which is directly measured from the impedance analyzer

(HP4192) as a function of frequency using the relation: $\sigma = \text{conductance} \times d/A$.

3. Results and discussion

The X-ray diffraction patterns from 20 to 60° 2θ of the reaction mixture for the preparation of magnesium neodymium tantalum oxide (MNTO) heated at two different temperatures are shown in Fig. 1. The pattern of the sample heated at 1350 °C (Fig. 1a) shows the presence of non-reacted oxides in addition to the peaks corresponding to MNTO. Therefore, this reaction mixture was further ground and heated at 1400 °C for 10 h and the XRD pattern of this sample is shown in Fig. 1b. This pattern shows a systematic regular set of reflections. This indicates the formation of a crystalline compound. The reaction mixture used for the preparation of magnesium lanthanum tantalum oxide (MLTO) also showed similar patterns and hence it can be concluded that the reaction mixtures of both MNTO and MLTO followed similar reaction sequence to form similar structures. However, in the case of MLTO temperature required to get phase pure compound was 1450 °C with a heating duration of 8 h at that temperature. Thus it is clear that crystalline phase pure compounds of MNTO and MLTO can be prepared by heating the mixture of the corresponding oxides and carbonates of the constituent metals at 1400 and 1450 °C for durations of 10 and 8 h respectively, with one intermediate grinding. Both these compounds have similar structure as can be judged by the similarity of their XRD patterns in terms of both peak position and intensities. The diffraction patterns of both these compounds are similar to the patterns reported for compounds like $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Eu}_2\text{Zr}_2\text{O}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$, $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5-x/3}\text{Sn}_x\text{Nb}_{1.5-2x/3})\text{O}_7$ ($x = 0-1.5$) [12,13].

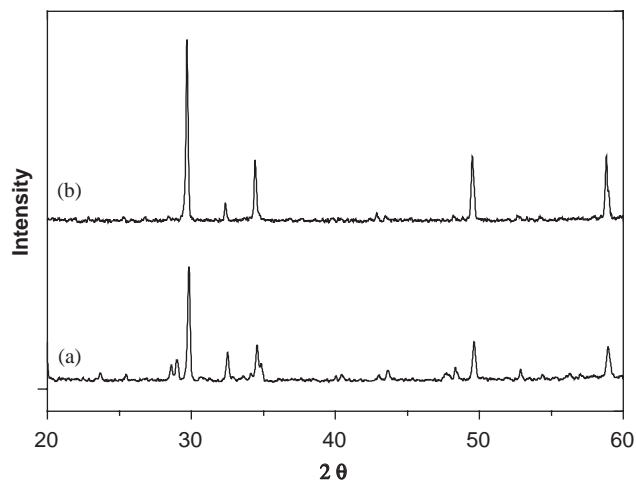


Fig. 1. XRD of the reaction mixture of $\text{Mg}_2\text{NdTaO}_6$ heated at (a) 1350 °C for 5 h and (b) 1400 °C for 10 h.

Hence the present compounds MNTO and MLTO can be considered to be isostructural with these compounds. All these compounds are reported to have a pyrochlore structure and therefore the structure of both MNTO and MLTO can be considered as pyrochlore structure.

In the case of the present compounds under investigation, taking the highest oxidation states of the metal ions involved ($Mg = +2$, $Ta = +5$, $Nd = +3$ and $La = +3$) the chemical formula of MNTO and MLTO works out to be Mg_2NdTaO_6 and Mg_2LaTaO_6 , respectively.

The structure of these compounds are identified and indexed as defective cubic pyrochlores with lattice constant 'a' values of 10.5050 and 10.5946 Å for Mg_2NdTaO_6 and Mg_2LaTaO_6 , respectively. XRD patterns of both these compounds Mg_2NdTaO_6 and Mg_2LaTaO_6 from 2θ values 10° – 90° are shown in Fig. 2. These XRD patterns were well indexed and data including hkl values are shown in Tables 1 and 2. The calcination conditions of these compounds, the lattice constants, sintering temperature, dielectric constant, dielectric loss, conductivity, etc are shown in Table 3. It may be noted that the samples could be sintered well at a temperature of 1600 °C in 6 h.

These pyrochlore oxides are having the same stoichiometry as that of double perovskites. The pyrochlore structure, usually have a formula $A_2B_2O_7$, which is derived by removing 1/8 of the oxygen from the regular fluorite structure. So the pyrochlore as such is a defective structure with only seven oxygen atoms per cell. But the structure in the present set of materials has only six oxygen atoms per cell and are therefore much more defective. We have prepared a set of two such magnesium-based tantalate pyrochlores viz., Mg_2NdTaO_6 and Mg_2LaTaO_6 by solid-state reaction route.

A calculation of the X-ray intensities for the stoichiometry Mg_2LaTaO_6 with the unit cell parameter = 10.5946 Å and standard position for a defective

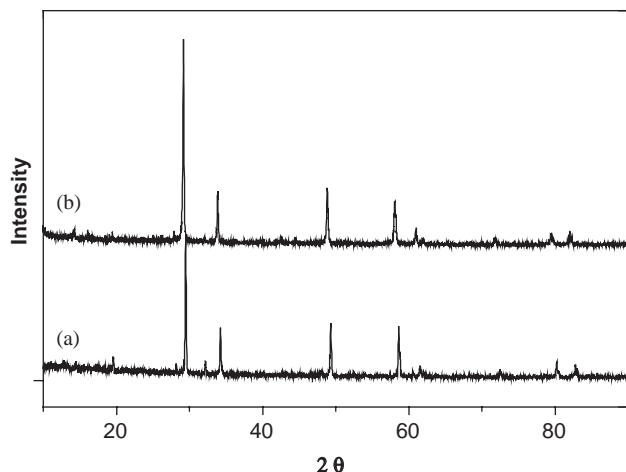


Fig. 2. XRD pattern of (a) Mg_2NdTaO_6 (b) Mg_2LaTaO_6 .

Table 1
Indexed XRD data Mg_2NdTaO_6

S.No	d (Å)	I/I_0	hkl
1	6.0651	3	1 1 1
2	4.5210	3	*
3	3.1674	6	3 1 1
4	3.0325	100	2 2 2
5	2.8076	9	*
6	2.6263	37	4 0 0
7	1.8570	38	4 4 0
8	1.5837	30	6 2 2
9	1.5163	10	4 4 4
10	1.4710	2	7 1 1
11	1.3676	2	7 3 1
12	1.3131	5	8 0 0
13	1.2050	9	6 6 2
14	1.1745	6	8 4 0

$$a = b = c = 10.5050 \text{ \AA}; \alpha = \beta = \gamma = 90^\circ$$

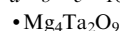


Table 2
Indexed XRD data of Mg_2LaTaO_6

S.No	d (Å)	I/I_0	hkl
1	6.1168	1	1 1 1
2	3.0584	100	2 2 2
3	2.8315	1	*
4	2.6487	28	4 0 0
5	1.8729	29	4 4 0
6	1.5972	23	6 2 2
7	1.5292	3	4 4 4
8	1.4835	5	7 1 1
9	1.3793	2	7 3 1
10	1.3243	2	8 0 0
11	1.2943	4	7 3 3
12	1.2153	5	6 6 2
13	1.1845	5	8 4 0

$$a = b = c = 10.5946 \text{ \AA}; \alpha = \beta = \gamma = 90^\circ$$

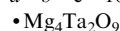


Table 3
Characteristics of Mg_2NdTaO_6 and Mg_2LaTaO_6

S.No		Mg_2NdTaO_6	Mg_2LaTaO_6
1	Lattice constant (Å)	10.5050 Å	10.5946 Å
2	Calcination conditions	1400 °C/10 h	1450 °C/8 h
3	Sintering conditions	1600 °C/6 h	1600 °C/6 h
4	Dielectric constant at 1 MHz	24.8	25.35
5	Dielectric loss at 1 MHz	0.0055	0.006
6	Conductivity at 1 MHz (S/m)	7.75×10^{-6}	8.27×10^{-6}
7	Color	Light blue	Milky white

pyrochlore, space group $FD3M$ (#227) with both the Mg atoms at $16c$ (000) positions, La and Ta distributed at random at $16d$ ($1/2, 1/2, 1/2$) positions and oxygen at $48f$ ($x, 1/8, 1/8$) positions, gives a profile totally different from the experimentally obtained profile shown in

Fig. 2. A theoretical profile obtained using the same space group and unit cell dimensions, with one Mg atom and La atom randomly distributed at $16c$ positions and one Mg atom and Ta atom randomly distributed at $16d$ positions and oxygen atoms at $48f$ with $x = 0.29334$ matches with experimentally obtained XRD profile of $\text{Mg}_2\text{LaTaO}_6$. The experimental profile, theoretical profile and the difference profile generated using 'PowderCell' are given in Fig. 3. The R -values obtained for the refinement were $R_p = 18.78$, $Rw_p = 24.44$ and $R_{exp} = 0.25$.

The calculated XRD profile of $\text{La}_2(\text{MgTa})\text{O}_{6.5}$ also matches with the experimental XRD profile obtained in case of $\text{Mg}_2\text{LaTaO}_6$. However the system contains Mg, La and Ta in the ratio 2:1:1. If the $\text{La}_2(\text{MgTa})\text{O}_{6.5}$ composition is accepted, there should be at least another phase containing the remaining 1.5 Mg and 0.5 Ta formed at the high temperatures used in the experiments. Since this is not observed in the experimental XRD pattern obtained, this phase can be ruled out in case of $\text{Mg}_2\text{LaTaO}_6$. The structure here is proposed as cubic pyrochlore with the A sites being randomly occupied by Mg and La, while Ta and Mg are randomly distributed at B site. The formulae may be given as $(\text{MgLa})(\text{MgTa})\text{O}_6$.

Similarly the 2θ –intensity profile for $\text{Mg}_2\text{NdTaO}_6$ was also generated using the PowderCell, assuming random distribution of one atom of Mg and the Nd atom at $16c$ positions and random distribution of one atom of Mg and the Ta atom at $16d$ positions and oxygen at $48f$ positions with $x = 0.28911$. This profile matched with the experimental profile shown in Fig. 2. The theoretical profile, experimental profile and difference between the experimental and calculated profiles for this $(\text{MgNd})(\text{MgTa})\text{O}_6$ is given in Fig. 4. The R -values obtained for the refinement were $R_p = 17.53$, $Rw_p = 23.94$ and $R_{exp} = 0.16$. The structure here is proposed as cubic pyrochlore with the A sites being

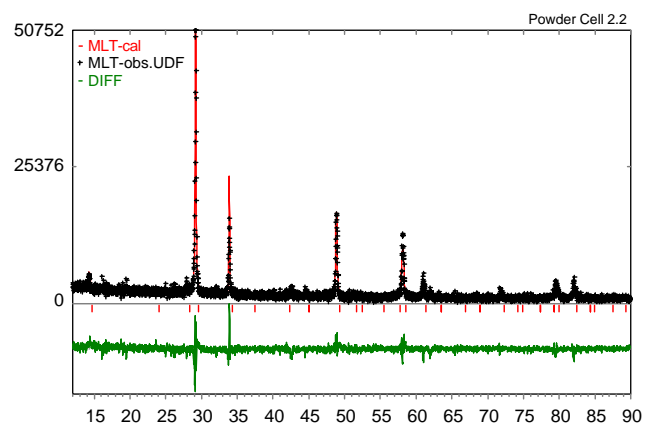


Fig. 3. Experimental, theoretical and difference XRD profile of $\text{Mg}_2\text{LaTaO}_6$.

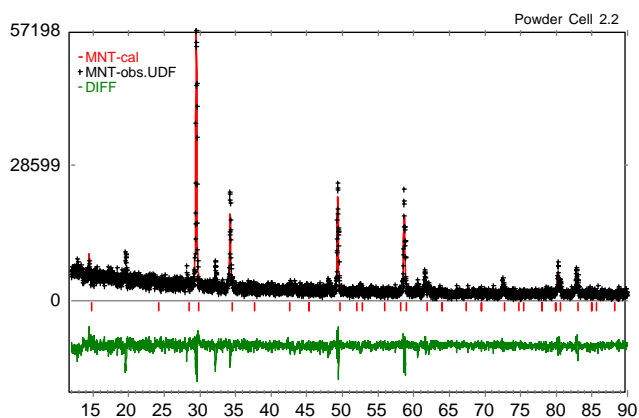


Fig. 4. Experimental, theoretical and difference XRD profile of $\text{Mg}_2\text{NdTaO}_6$.

randomly occupied by Mg and Nd, while Ta and Mg are randomly distributed at B site. The formulae may be given as $(\text{MgNd})(\text{MgTa})\text{O}_6$.

It may be noted from Fig. 3 that all the experimentally obtained reflections of $\text{Mg}_2\text{LaTaO}_6$ are matching with the theoretical profile both in intensity and positions. In case of $\text{Mg}_2\text{NdTaO}_6$, two peaks at 20° and 32° are not found in the calculated profile as can be seen from Fig. 4. The calculated XRD profile of $\text{Nd}_2(\text{MgTa})\text{O}_{6.5}$ also matches with the experimental XRD profile obtained in case of $\text{Mg}_2\text{NdTaO}_6$ except the peaks at about 20° and 32° 2θ . The system contains Mg, Nd and Ta in the ratio 2:1:1 and if the presence $\text{Nd}_2(\text{MgTa})\text{O}_{6.5}$ pyrochlore phase is accepted, there should be another phase containing the remaining 1.5 Mg and 0.5 Ta. The two additional peaks at about 20° and 32° found in the experimental XRD profile, correspond to the two intense peaks of $\text{Mg}_4\text{Ta}_2\text{O}_9$. Therefore it is possible that $\text{Nd}_2(\text{MgTa})\text{O}_{6.5}$ is also present in the system. The percentage of the $\text{Mg}_4\text{Ta}_2\text{O}_9$ phase is very low as can be seen from Figs. 2 and 4. This percentage is much less than that expected if the observed major phase was $\text{Nd}_2(\text{MgTa})\text{O}_{6.5}$ alone. Here, it is possible that the observed XRD pattern could be due to the similar patterns of mostly $(\text{MgNd})(\text{MgTa})\text{O}_6$ and some $\text{Nd}_2(\text{MgTa})\text{O}_{6.5}$ as well as that due to $\text{Mg}_4\text{Ta}_2\text{O}_9$. The presence of this $\text{Mg}_4\text{Ta}_2\text{O}_9$ phase in the Nd-bearing system and not in the La-bearing system could possibly indicate the influence of the size of the rare-earth metal on the stability of the structure.

The defective pyrochlore structure of $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$ has large concentration of missing oxygen atoms. It is not certain if the missing oxygens relative to the ideal pyrochlore structures are an ordered part of the structure. If they are an ordered part of the structure they may not be mobile oxygen ion carriers, although they might affect mobility. Further studies would be required to establish the ionic contribution to the measured conductivity.

The dielectric properties of these compounds were studied in the frequency range of 30 Hz–1 MHz. Fig. 5 shows the variation of dielectric constant values with Log (frequency in Hz) for both $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$. Two trends can be seen from the figure; (i) the dielectric constant values decrease with increase in frequency, (ii) the dielectric constant values for the Neodymium containing compound is always less than the corresponding values for Lanthanum bearing compound. These variations can be explained by considering the factors contributing to dielectric constant. In the experimental range of frequencies, the dielectric constant (ϵ) of these defect pyrochlore materials are likely to be determined predominantly by the contribution of ionic polarization. The dielectric constant is inversely proportional to the frequency of the optical phonons, which in turn is determined by both the concentration of the oscillators in unit volume and the magnitude of the elastic co-efficient [14].

The decrease in dielectric constant with increasing frequency in case of both $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$, seen in Fig. 5 may be understood by the well known fact that polarization requires time to respond to applied field. In high-frequency field, there may not be sufficient time for this response to the electric field. However, at low frequencies polarization is affected as there is enough time for realignment with the frequency cycle [15].

By changing M in Mg_2MTaO_6 compounds, the dielectric constant also gets changed. The dielectric constant value of $\text{Mg}_2\text{LaTaO}_6$ was always higher than that of $\text{Mg}_2\text{NdTaO}_6$ at all frequencies. The dielectric constant values at 1 MHz for $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$ are 24.8 and 25.35, respectively. While substituting smaller Nd ions in place of larger La ions, the concentration of dipoles

(oscillators) in unit volume increases due to the decrease in unit-cell volume, which could allow an increase in ϵ , assuming that the magnitude of the elastic co-efficient of the dipoles remain constant. However, the experimental data indicate that by changing M from La to Nd, the permittivity decreases, which may be related to an increase in the elastic coefficient. It should be noted that the possible increase in elastic coefficient influences the permittivity more noticeably than an increase in concentration of dipoles [14].

The variation of room temperature conductivity with log (Frequency) is shown in Fig. 6. It is evident from the figure that electrical conductivity increases with frequency for both $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$. Of the two compounds the Lanthanum-bearing compound ($\text{Mg}_2\text{LaTaO}_6$) always showed higher conductivity than the corresponding Neodymium-bearing compound ($\text{Mg}_2\text{NdTaO}_6$) at all frequencies. At 1 MHz the conductivity values for $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$ are 7.75×10^{-6} and 8.27×10^{-6} S/m, respectively. This lower conductivity of $\text{Mg}_2\text{NdTaO}_6$ may be attributed to the increased lattice distortions, due to the smaller ionic size of Nd [16]. The range of conductivity values at room temperature, found in these compounds indicate the possibility of their classification as ionic conductors.

The variation of dielectric loss values with log (frequency) of both $\text{Mg}_2\text{NdTaO}_6$ and $\text{Mg}_2\text{LaTaO}_6$ are shown in Fig. 7. It can be seen that the dielectric loss value of $\text{Mg}_2\text{NdTaO}_6$ is 0.0055 at 1 MHz, while the corresponding value for $\text{Mg}_2\text{LaTaO}_6$ is 0.006. From the figure it is clear that $\text{Mg}_2\text{LaTaO}_6$ is having relatively higher loss throughout the range of frequencies. This is corroborated by the conductivity data in Fig. 6, where, $\text{Mg}_2\text{LaTaO}_6$ always showed a higher conductivity. It can be seen that for both the compounds, the dielectric

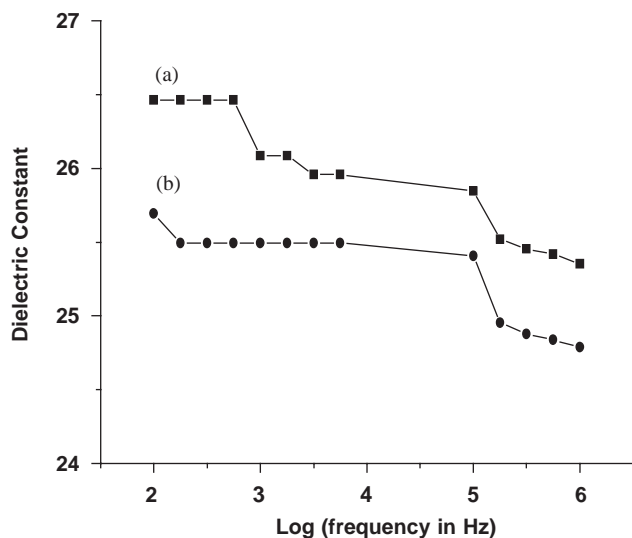


Fig. 5. Variation of dielectric constant with log(frequency) of (a) $\text{Mg}_2\text{LaTaO}_6$ and (b) $\text{Mg}_2\text{NdTaO}_6$.

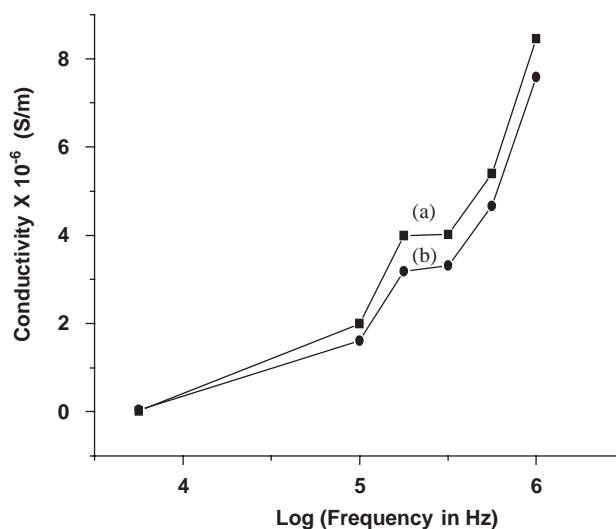


Fig. 6. Variation of conductivity with log(frequency) of (a) $\text{Mg}_2\text{LaTaO}_6$ and (b) $\text{Mg}_2\text{NdTaO}_6$.

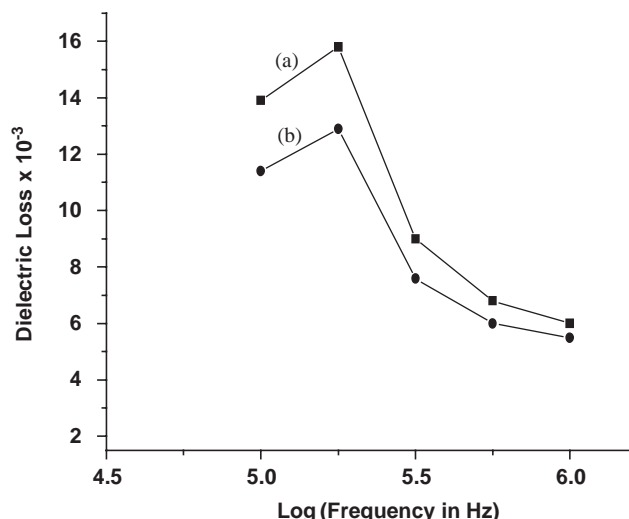


Fig. 7. Variation of dielectric loss with log(frequency) of (a) Mg₂LaTaO₆ and (b) Mg₂NdTaO₆.

loss value decreases with the frequency. This decrease in dielectric loss with applied frequency indicates that ion migration is the dominant mechanism of conduction in both the tantalates.

The observed variation in conductivity and dielectric loss with applied frequency can be explained as follows. Since the opposite charge of the nearest neighbours tries to hold any ion in equilibrium position and provide the energy barrier, more energy must be supplied before that ion can be moved. At low frequencies (below 10⁴ Hz) the conductivity is negligible and this shows that there is practically no ion migration at these frequencies. So the loss values are also negligible (beyond the precision of the instrument) at these low frequencies. As the conductivity starts increasing from intermediate (10⁵ Hz) frequency range, the samples show maximum loss values. But once the ions move away from their equilibrium positions, the energy required for the further migration will be less and hence the loss values decrease with increasing frequency [15].

4. Conclusion

Two new compounds viz., Mg₂NdTaO₆ and Mg₂LaTaO₆ were prepared by solid-state reaction route and

their structure was established. The XRD patterns of these compounds are well indexed and they are found to have a defective cubic pyrochlore structure. The calcination and sintering condition of these compounds were also established. In addition to that the dielectric properties and conductivity of these compounds were also studied and the scope for using them as ionic conductors is explored.

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References

- [1] C.D. Bradle, V.J. Fratello, *J. Mater. Res.* 5 (10) (1990) 2160–2164.
- [2] J. Koshy, J. Kurian, R. Jose, A.M. John, P.K. Sajith, J. James, S.P. Pai, R. Pinto, *Bull. Mater. Sci.* 22 (3) (1999) 243–249.
- [3] J. James, O.B.S. Kumar, S. Senthil Kumar, P. Prabhakar Rao, K.V.O. Nair, *Mater. Lett.* 57 (2003) 3641–3647.
- [4] J. James, M. Sankar, S. Senthil Kumar, K.V.O. Nair, *Mater. Chem. Phys.* 83 (2004) 328–333.
- [5] T.G.N. Babu, J. Koshy, *J. Solid State Chem.* 133 (1997) 522–528.
- [6] S. Ya Istomin, O.G. D'yachenko, E.V. Antipov, *Mater. Res. Bull.* 32 (4) (1997) 421–430.
- [7] K. Ramesha, L. Sebastian, B. Eichhron, J. Gopalakrishnan, *Chem. Mater.* 15 (2003) 668–674.
- [8] Y.Z. Chen, J. Ma, L.B. Kong, R.F. Zhang, *Mater. Chem. Phys.* 75 (2002) 225–228.
- [9] M. Thirumal, A.K. Ganguli, *Mater. Res. Bull.* 36 (2001) 2421–2427.
- [10] Yee-Shin Chang, Yen-Hwei Chang, In-Gann Chen, Guo-Ju Chen, *Solid State Commun.* 128 (2003) 203–208.
- [11] M. Valant, P.K. Davis, *J. Mater. Sci.* 34 (22) (1999) 5437–5442.
- [12] J.M. Sohn, M.R. Kim, S.I. Woo, *Catalysis Today* 83 (2003) 289–297.
- [13] H. Du, X. Yao, L. Zang, *Ceram. Int.* 23 (2002) 231–234.
- [14] A. Belous, O. Ovchar, M. Valant, D. Suvorov, *J. Appl. Phys.* 92 (7) (2002) 3917–3922.
- [15] D.W. Richerson, *Modern Ceramic Engineering*, 2nd ed, Marcel Dekkar, Inc, New York, 1992, p. 214.
- [16] A. Fondado, J. Mira, J. Rivas, *J. Appl. Phys.* 87 (9) (2000) 5612–5614.