Characterization and densification of defect pyrochlore oxide powders \( \text{ABi}_2\text{Ta}_5\text{O}_{16} \) (A=Na, Ti)

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1. Introduction

Among metallic oxides, compounds with general formula, \( \text{A}_2\text{B}_2\text{O}_6\text{O}' \), where A and B are different cation species with different oxidation states (e.g. \( A^{2+} \), \( B^{4+} \) or \( A^{2+} \), \( B^{5+} \)) and O and \( \text{O}' \) are anions, represent a family of phases isoostructural to the mineral pyrochlore (NaCa) (NbTa)O6F/(OH). The pyrochlore structure possesses cubic symmetry with space group \( \text{Fd}3\text{m}, \text{Oh}7 \), no. 227 and number of formula units (\( Z = 8 \)). Four crystallographically nonequivalent kinds of atoms: A, B, O and \( \text{O}' \) atoms occupy the 16d, 16c, 8f and 8b sites, respectively. The smaller B cations (16c) are six coordinated and located in a distorted octahedron formed by six oxygen ions \((4\text{f})\). The larger A cations (16d) are eight-coordinated, located within a distorted cubic polyhedron formed by six \( O(4\text{f}) \) and 2 \( O'(8b) \). The structural formula is often written as \( \text{B}_2\text{O}_6\text{O}' \), which emphasizes that the arrangement consists of two interpenetrating networks of vertex-linked octahedra (\( \text{B}_2\text{O}_6 \)) sharing corners, and a cuprite-like \( \text{A}_2\text{O}' \) tetrahedron [1]. This latter network is not essential for the stability of the structure and hence pyrochlore structure tolerates vacancies at A and \( \text{O}' \) sites giving rise to different stoichiometries from \( \text{A}_2\text{B}_2\text{O}_6\text{O}' \) to \( \text{A}_2\text{B}_2\text{O}_6 \). It is known that \( \text{AB}_2\text{O}_6 \) type defect pyrochlore are formed in the case where the A cation is a large monovalent metal such as Cs\textsuperscript{+}, Rb\textsuperscript{+}, Ti\textsuperscript{4+} or K\textsuperscript{+} [2]. The site occupancy of the A cations in defect pyrochlore is insertion because the structural considerations reveal that in addition to the 16d and 8b sites there in another possible site (32e) depending on the size, charge and polarizability of the A cation either full or fractional occupation of any of the three sites is possible. Studies showed that the A ions in \( \text{RbTa}_2\text{O}_6\text{F} \) occupy the 8b positions whereas in \( \text{TiNb}_2\text{O}_5\text{F} \) the Ti cations are delocalized from the ideal 16d position to occupy the 32e positions statistically [2]. Pyrochlore mixed oxides have many technological applications thanks to theirs wide spectrum of properties (electrical, dielectric, magnetic, magneto-resistive, optical, electro-catalytic etc.) and can also be used as electrolytes or anode materials for solid electrolyte fuel cells (SOFC) and fixatives for radioactive waste due to theirs oxygen nonstoichiometry and to the distribution of cations in the structure [1]. Recently, Bi-based pyrochlores in the Bi\textsubscript{2}O\textsubscript{3}-M\textsubscript{2}O\textsubscript{5} (X = Sb, Ta and Nb) ternary systems have triggered great research interests owing to their relatively low sintering temperatures and excellent dielectric properties [3, 4, 5]. Some pyrochlore compounds occurring in the \( \text{A}_2\text{O}-\text{Bi}_2\text{O}_3-\text{M}_2\text{O}_5 \) system (A = Ag, Na, K, Ti and M = Nb, Ta) are attractive candidates for temperature-stable, low-loss, high-permittivity dielectric applications [6].

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2. Experimental

The compounds ABi$_2$Ta$_5$O$_{16}$ (A = Na, Tl) were prepared by usual solid state reaction from starting reagents Bi$_2$O$_3$ (Sigma-Aldrich, 99.9%), Ta$_2$O$_5$ (Sigma-Aldrich, 99%) Na$_2$CO$_3$ and Tl$_2$CO$_3$ (Sigma-Aldrich, 99.9%). Weighted quantities of the reactants were intimately mixed and ground in an agate mortar. In order to avoid a possible oxidization of Tl$^+$ to Tl$^{3+}$, all compounds were treated under nitrogen atmosphere. Three thermal processings with intermittent regrinding at 300 °C (6 hours) (to provoke the departure of CO$_2$ and in the same time to avoid volatilization of Tl$_2$CO$_3$ [7]), 800 °C (12 hours) and 950–1000 °C (12 hours) were necessary to obtain the final compounds. X-ray powder diffractograms were obtained using Cu Kα line of a D5000 Siemens diffractometer equipped with a back monochromator. The data were recorded between 10 and 120 (2θ) in steps of 0.04° with a count time of 72 s. Temperature programmed X-ray diffraction was performed on a Siemens D5000 diffractometer fitted out with an ANTON PARR furnace (CHTK10) and a linear detector (Elphyse 14°). The powder of each prepared compound was ground and mixed with 5% of polyvinyl alcohol and polyethylene glycol and pressed using a uniaxial pressure 200 MPa into pellets with a diameter of 10 mm and thickness of about 2 mm. The sintering behavior of the powders was investigated by dilatometric method. The powders were uniaxially pressed at 200 MPa and the compacts were sintered in the vertical dilatometer (SETARAM TMA92) up to 1400 °C under air sweeping with heating rates of 3 °C/min. The relative densities were also calculated from comparisons of densities which are determined geometrically and theoretically. The surface morphologies of the samples were examined by scanning electron microscopy (SEM). The IR spectra for NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$, are represented in Table 1. We note at first that these spectra are similar to those of other pyrochlores prepared in [10].

3. Results and discussion

3.1. Structural analyses

3.1.1. XRD diffraction

The phase structures of the ABi$_2$Ta$_5$O$_{16}$ (A = Na, Tl) samples were determined by XRD patterns, as shown in Fig. 1. All characteristic peaks belong to a cubic pyrochlore and are fully indexed based on space group, Fd3m [8]. No impurity phases were detected in the XRD pattern of the three compounds NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$ indicating that the sample was phase-pure pyrochlore. These results are shown in Table 1. The lattice parameter of the ABi$_2$Ta$_5$O$_{16}$ (A = Na, Tl) compounds determined from the Rietveld refined XRD pattern are $a = 10.5013$ (1) Å and 10.5144 (1) Å, respectively, for NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$.

3.1.2. Infrared spectroscopy

The group theoretical analysis of the normal vibration of the ideal pyrochlore structure predicts 26 normal modes [9]: $A_g^7E_g^12F_g^4A_u^3E_u^3$. Only $A_{1g}$, $E_{2g}$, $4F_{2g}$ and $8F_{1u}$ (one of eight $F_{1u}$ modes refers to acoustic vibrations) are Raman active and infrared active respectively. The IR spectra for NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$ are represented in Fig. 2. We note at first that these spectra are similar to those of other pyrochlores prepared in [10].

Table 1

| hkl | d$_{calc}$ (Å) | d$_{obs}$ (Å) | I (%) | d$_{calc}$ (Å) | d$_{obs}$ (Å) | I (%) |
|-----|---------------|---------------|-------|---------------|---------------|-------|
| 111 | 6.06          | 6.06          | 16    | 6.07          | 6.07          | 9     |
| 220 | 3.713         | 3.712         | <1    | 3.718         | 3.717         | 1     |
| 311 | 3.166         | 3.166         | 11    | 3.170         | 3.170         | 21    |
| 222 | 3.0315        | 3.0314        | 100   | 3.0353        | 3.0352        | 100   |
| 400 | 2.6253        | 2.6253        | 35    | 2.6286        | 2.6286        | 29    |
| 331 | 2.4092        | 2.4091        | 1     | 2.4122        | 2.4121        | 1     |
| 422 | 2.1435        | 2.1436        | <1    | 2.1463        | 2.1462        | <1    |
| 511 | 2.0209        | 2.0210        | 2     | 2.0235        | 2.0235        | 3     |
| 440 | 1.8563        | 1.8564        | 41    | 1.8587        | 1.8587        | 38    |
| 531 | 1.7750        | 1.7750        | 4     | 1.7773        | 1.7772        | 6     |
| 442 | 1.7502        | -             | -     | 1.7524        | 1.7524        | <1    |
| 620 | 1.6604        | 1.6604        | <1    | 1.6625        | 1.6624        | <1    |
| 533 | 1.6014        | 1.6014        | 1     | 1.6034        | 1.6034        | 4     |
| 622 | 1.5831        | 1.5831        | 36    | 1.5851        | 1.5851        | 33    |
| 444 | 1.5157        | 1.5157        | 10    | 1.5176        | 1.5176        | 9     |
| 551 | 1.4704        | 1.4705        | 2     | 1.4723        | 1.4723        | 3     |
| 731 | 1.3671        | 1.3671        | 3     | 1.3689        | 1.3688        | 4     |
| 800 | 1.3127        | 1.3127        | 5     | 1.3143        | 1.3143        | 4     |
| 733 | 1.2829        | 1.2829        | <1    | 1.2845        | 1.2845        | 1     |
| 644 | -             | 1.2735        | -     | 1.2751        | 1.2751        | <1    |

Fig. 2. Infrared transmission spectra of NaBi$_2$Ta$_5$O$_{16}$ (a) and TlBi$_2$Ta$_5$O$_{16}$ (b).
The Infrared vibrational frequencies observed at around 840 and 490 cm$^{-1}$ attributed to the Bi–O$^\cdot$ stretching can be assigned on the one hand to the shorter bond distance (2.40 Å) bond distance Bi–O$^\cdot$ and on the other hand to longer (2.20 Å) bond distance Bi–O$^\cdot$. The static disorder of Bi and O$^\cdot$ is associated with tendency of lone pair electron of Bi (6s$^2$) to be ascribed to distortions in the TaO$\_6$ octahedra as seen in anticristobalite Cu$_2$O type structure and B$_2$O$_3$ (3D-network of corner shared BO$_6$ octahedra). The variations occurred in A atoms environment and in A–O$^\cdot$ bond length can be the consequence of A and O$^\cdot$ atoms displacement from their ideal positions in the O’A$^2$ network. The observed peak at about 237 cm$^{-1}$ is attributed to F$_{2g}$ mode, corresponding to the stretching vibration of O–B–O bond. The frequency at around of 343 cm$^{-1}$ is assigned to the stretching vibration of A–O bond, which is assigned to the (E$_g$ and F$_{2g}$) mode. The A$_{1g}$ mode observed at 477 cm$^{-1}$ is assigned to the breathing mode of the O octahedra [19, 20]. All the observed Raman modes can be attributed to the relaxation of the selection rules and they show a reduction in symmetry of these samples due to the displacement of the bismuth ions in Bi-based pyrochlore.

3.2. Densification

3.2.1. Raw powder

The morphology of the raw powder of NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$ obtained by solid state reaction is illustrated in Fig. 4 (a) and (b). It consists of grain sizes of around 1 μm. We note also in the raw powder the presence of agglomerates, large grains surrounded by smaller ones. This phenomenon seems to be related to a pre-sintering generated by the method of preparation.

3.2.2. Binder influence

Different samples from the powder have been cold-pressed without adding organic binder did not make good pellets of good mechanical strength. In order to improve the raw quality of the pellets, an addition of binder consisting of a mixture of ultrapure water, polyvinyl alcohol (PVA 4/125) and polyethylene glycol (PEG 1500) has been added to the powder.

3.2.3. Pressure influence

Various powder samples of NaBi$_2$NbTa$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$ compounds were pressed into pellets between 50 and 400 MPa giving density...
before sintering between 60% and 70%. By using the same thermal cycle, pellets were sintered and give density between 70% and 92%. Fig. 5 (a) and (b) shows the typical evolution of density versus pressure before and after sintering (a) for NaBi₂NbTa₅O₁₆ and (b) for TlBi₂NbTa₅O₁₆. We can notice that on the one hand the density in raw pellets increases regularly with pressure and on the other hand the density of the sintered materials showed the highest density located around 200 MPa. Density of sintered materials did not increase any further at higher pressing, above 200 MPa. This latter was retained as optimal pressure, so all powders were uni-axially pressed at 200 MPa.

3.2.4. Elimination of binder

Before sintering, it is necessary to begin with the first step of elimination of binder. According to commercial data on the thermal characteristics of PVA and PEG, we started the sintering process at 500 °C with low heating rate to burn organic matter without cracking pellets [21, 22]. For this reason, the choice of the heating rate is set at 5 °C/min with holding at 500 °C for 1 hour to ensure complete elimination of binder.

The density percentage D (%) after sintering was carried out using the following formula:

\[ D = \frac{\rho_{\text{exp}}}{\rho_{\text{th}}} \]

The theoretical density (\( \rho_{\text{th}} \)) was calculated from the diffraction patterns applying the formula:

\[ \rho_{\text{th}} = \frac{Z \times M}{N \times V} \]

Where:
- M: Molar mass of sample
- Z: Number of formula units
- N: Avogadro number
- V: Volume of the cell

The experimental density (\( \rho_{\text{exp}} \)) was determined from diameter and thickness of pellets applying the formula:

\[ \rho_{\text{exp}} = \frac{m_p}{\pi \times \left( \frac{\phi}{2} \right)^2 \times e} \]

Where:
- \( m_p \): Mass of pellet
- \( \phi \): Diameter of pellet
- \( e \): Thickness of pellet

Fig. 5. Pressure versus density before and after sintering for NaBi₂NbTa₅O₁₆ (a) and TlBi₂Ta₅O₁₆ (b).
Fig. 6. Dilatometry curves of NaBi$_2$Nb$_3$O$_{16}$ (a) and TlBi$_2$Ta$_5$O$_{16}$ (b).

Fig. 7. Sintering thermal cycle.
3.2.5. Sintering temperature influence

After using heating rate at (5 °C/min), different attempt to determine sintering temperatures were applied to the pellets corresponding to NaBi₂Ta₅O₁₆ and TlBi₂Ta₅O₁₆. We note that between 1000 and 1400 °C, the density rises with temperatures and passes for both samples from 70% to 90% for NaBi₂Ta₅O₁₆ and from 73% to 92% for TlBi₂Ta₅O₁₆ but in parallel with this increase in density; we noted a slight loss of mass.

Table 2  
Characteristics of the thermal sintering adopted for ABi₂MT₅O₁₆ (A = Na, Tl) compounds.

| Compounds       | Temperature (°C) | Holding time (h) | Densification (%) |
|-----------------|------------------|------------------|------------------|
| NaBi₂Ta₅O₁₆     | 1330             | 1                | 90               |
| TlBi₂Ta₅O₁₆     | 1380             | 1                | 92               |

Fig. 8. SEM images of NaBi₂Ta₅O₁₆ (a) and TlBi₂Ta₅O₁₆ (b) sintered at about 1350 °C.

Fig. 9. Frequency dependence of dielectric constant vs. temperature of NaBi₂Ta₅O₁₆ (a) and TlBi₂Ta₅O₁₆ (b).
observed and became significant at 1400 °C. So, we have to find exactly optimal sintering temperatures. We have used dilatometry curves which consist to measure the evolution of $\Delta L/Lo$ as a function of temperature Fig. 6 (a) and (b).

Analysis of these curves leads to distinguish two regions:

- The first region, between room temperature and 1000 °C, characterized by a weak variation of $\Delta L/Lo$ (no shrinkage).
- The second region, between 1000 and 1400 °C for the two compounds indicate notable variations of $\Delta L/Lo$ characterized by the beginning and ending of shrinkage process.

During the sintering process we have found that at optimal sintering temperature, sintering reaches its maximum. Treatments carried above 1400 °C do not affect density but only contribute to increase mass losses of pellets. So, the optimal sintering temperature chosen for both pressed samples to increase densification and to decrease losses of mass, was 1330 °C and 1380 °C respectively for NaBi$_2$Ta$_5$O$_{16}$ and TlBi$_2$Ta$_5$O$_{16}$.

3.2.6. Influence of the holding time

The effects of holding time (HT) between 1330 and 1380 °C for both compounds was investigated and for one hour at optimal temperatures leads to a reasonable densification (90–92%). Longer heating times do not improve the density, but promote the sublimation of the material elements.

3.2.7. Thermal cycle

Given the influence of the parameters studied above sintering heating, heating rate and heating time, we performed the thermal cycle shown in Fig. 7.

A first step for one hour at 500 °C allowing the total elimination of the binder used and a second step also for one hour at sintering temperature to reach good density of pellets. The characteristics of the thermal sintering cycles used are summarized in Table 2.

The morphological examination under the scanning electron microscope (SEM) of the sintered pellets, reveals the presence of relatively large grains (~5 μm) showing angles of 60–120°, indicating a good densification of the materials (Fig. 8 (a) and (b)).

3.3. Dielectric properties

Fig. 9 and Fig. 10 show frequency and temperature dependence of dielectric properties (dielectric constant and dielectric loss tanδ) for
energies were determined due to experimental measurement of the dielectric loss peaks as a function of temperature. From this plot we can calculate the activation energy corresponding to the relaxation phenomenon: \( E_a = (0.16 \pm 0.01) \text{ eV} \).

There are several other important parameters which can be also obtained from dielectric data. \( \tau_o \), relaxation time can be calculated from the data such as shown in Fig. 13. Values of \( 10^{-12} \) to \( 10^{-14} \) s are indicative that the relaxation process is ionic in origin. However, very low values of \( \tau_o \) are suggestive that the relaxation process is electronic space charge polarization [25, 26, 27]. In our case, \( \tau_o \) = 0.6 \times 10^{-12} s (\tau_o = 10^{-12} s for the pyrochlore phase \( \text{Pb}_1.35\text{Na}_{1.72}\text{Mg}_{0.29}\text{O}_{6.39} \)).

### 4. Conclusions

Defect pyrochlore oxide powders \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) (A = Na, Ti) have been prepared by the solid state method and characterized by powder XRD and infrared and Raman spectroscopies. Both materials crystallize in the cubic crystal lattice with \( \text{Fd}3m \) space group. The infrared and Raman bands observed for these compositions are consistent with the Raman spectra expected for defect pyrochlores, ABB\( \text{O}_7\text{X} \). The morphology of sintering ceramics indicates a good densification of the materials. The dielectric constants of the samples are in the range of 107–110 together with a negative temperature coefficient of permittivity. Dielectric losses (tg\( \delta \)) of the compound \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) presented maximum versus temperature and frequency, this phenomenon is related to dielectric relaxations. The activation energy \( E_a \) and relaxation time \( \tau_o \) corresponding to this phenomenon were found to be 0.16 eV and 0.6 \times 10^{-12} \text{ s} respectively. Such dielectric and electrical properties make the compound \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) attractive in the applications of ceramic capacitor and resonators.

### Declarations

**Author contribution statement**

Omar Ait Sidi Ahmed: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Abdeslam Chagraoui, Abdennajib Moussaoui, Sylvie Villain, Abdelmjid Tairi, Lamia Bourja, Hajar Ait Oulahyane: Analyzed and interpreted the data.

Bouchaib Manoun: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

**Funding statement**

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

### References

[1] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Oxide pyrochlores - A review, Prog. Solid State Chem. 15 (1983) 55-143.

[2] S. Yonezawa, Y. Muraoka, Y. Matsushita, Hiroi, Superconductivity in a pyrochlore-related oxide \( \text{K}_2\text{O}_7\text{O}_8 \). J. Phys. Condens. Matter 16 (2004) 9-12.

[3] K. Sudheendran, K.C.J. Raju, M.V. Jacob, Microwave Dielectric Properties of Ti-Substituted \( \text{Bi}_2\text{(Zn}_{2/3}\text{Nb}_{4/3})\text{O}_7 \). Microwave dielectric properties at Cryogenic Temperatures, J. Am. Ceram. Soc. 92 (6) (2009) 1268-1271.

[4] H.J. Youn, T. Sagabe, C.A. Randall, T.R. Shront, M. T. Phase Relations and Dielectric Properties in the \( \text{Bi}_2\text{O}_3\text{-ZnO-TeO}_2 \) System, J. Am. Ceram. Soc. 84 (2001) 2557-2562.

[5] C.C. Khaw, K.B. Tan, C.K. Lee, High temperature dielectric properties of cubic bismuth zinc tantalate, Ceram. Int. 35 (2009) 1473–1480.

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**Table 3**

| Compound                | Relative density | \( \varepsilon \) | \( \text{tg}\delta \) | \( \tau_o = \Delta \varepsilon /\varepsilon \Delta T \times 10^6 \) (K\(^{-1}\)) | Reference |
|------------------------|-----------------|-----------------|-----------------|---------------------------------|-----------|
| \( \text{Bi}_2\text{Nb}_{1.2}\text{Zn}_{0.8}\text{O}_{6.2} \) | 94              | 178             | -               | \(-647\)                         | [23]      |
| \( \text{Bi}_2\text{Mg}_{2.2}\text{Ta}_{5.8} \) | 84              | 0.003           | \(-328\)        | \(-28\)                         | [9]       |
| \( \text{RbBi}_2\text{Ta}_5\text{O}_{16} \) | 70              | 0.266           | -               | \(-28\)                         | [24]      |
| \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) | 90              | 0.284           | \(-1327\)       | \(-28\)                         |           |
| \( \text{TlBi}_2\text{Ta}_5\text{O}_{16} \) | 92              | 0.045           | \(-953\)        | \(-28\)                         |           |

**Table 4**

| Compound                | Frequency \( 10^{-4} \) (Hz) | Temperature \( T_{\text{max}} \) (K) |
|------------------------|-------------------------------|------------------------------------|
| \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) | 1                             | 294                                 |
|                        | 5                             | 338                                 |
|                        | 10                            | 358                                 |
|                        | 50                            | 414                                 |
|                        | 100                           | 442                                 |
|                        | 200                           | 470                                 |
|                        | 500                           | 506                                 |
|                        | 1000                          | 546                                 |

**Fig. 11.** Frequency Logarithmic temperature dependence of the frequency location at the dielectric losses peak for compound \( \text{NaBi}_2\text{Ta}_5\text{O}_{16} \) heated from 25 °C to 500 °C.
[6] O. Ait Sidi Ahmed, A. Tairi, A. Chagraoui, S. Khairoun, J.C. Champamaud, B. Frit, Nouveaux matériaux ABi2B5O16 (A = Na, Ag, K, Rb, Tl et B = Nb, Ta) de type purochlore déficitaire, Ann. Chim. Sci. Mat. 25 (2000) 201–209.

[7] M. Bouchama, M. Tournoux, Revue de Chimie Minérale, t12, 1969, p. 80.

[8] O. Ait Sidi Ahmed, A. Tairi, A. Chagraoui, S. Khairoun, J.C. Champamaud, B. Frit, Dielectric properties of new defect pyrochlore compounds AB2 M5O16 (A = Na, K, Rb, Tl et B = Ta, Nb, and A = K, Tl FROM M = Nb), Ann. Chim. Sci. Mat. 25 (suppl. 1) (2000) 181–186.

[9] P.Y. Tan, K.B. Tan, C.C. Khaw, Z. Zainal, S.K. Chen, M.P. Chon, Structural and electrical properties of bismuth magnesium tantalate pyrochlores, Ceram. Int. 38 (2012) 5401–5409.

[10] M. Chen, D.B. Tanner, J.C. Nino, Infrared study of the phonon modes in bismuth pyrochlores, Phys. Rev. B 72 (2005) 054303.

[11] M.T. Vendenborre, E. Husson, Comparison of the force field in various pyrochlore families. I. The A2B2O7 oxides, J. Solid State Chem. 50 (1983) 362.

[12] H.C. Gupta, S. Brown, N. Rani, V.B. Gohel, Lattice dynamic investigation of the zone center wavenumbers of the cubic A2Mn2O7 pyrochlores, J. Raman Spectrosc. 34 (2003) 240–243.

[13] A. Garbout, S. Bouattour, A.W. Kolsi, Sol-gel synthesis, structure characterization and Raman spectroscopy of Gd2₋ₓBi2ₓMgO17₋ₓ solid solutions, J. Alloy. Comp. 469 (2009) 229–236.

[14] L.B. Gao, S.W. Jiang, R.G. Li, Y.R. Li, Structure and dielectric properties of rf sputtered Bi2₋ₓMgO₋ₓNb2₋ₓO9 pyrochlore thin films, Ceram. Int. 40 (2014) 4225–4229.

[15] W. Xia, et al., Dielectric properties and atomic-scale microstructural characteristics of cubic-pyrochlored ceramics in the system of Bi2₋ₓMgO₋ₓNb2₋ₓO9, J. Alloy. Comp. 701 (2017) 682–688.

[16] Yangyang Li, Xinhua Zhu, T.A. Kasab, Atomic-scale microstructures, Raman spectra and dielectric properties of cubic pyrochlore-type Bi1₋ₓMgNb1₋ₓO7 dielectric ceramics, Ceramics Int. 40 (6) (2014) 8125–8134.

[17] S. Brown, H.C. Gupta, J.A. Alonso, M.J. Martinez-Lope, Vibrational spectra and force field calculation of A2Mn2O7 (A = Y, Dy, Er, Tb) pyrochlores, J. Raman Spectrosc. 34 (2003) 240–243.

[18] M.T. Vandenborre, E. Husson, H. Brunset, Analyse en coordonnées normales des composés A2B2O7 (A = La, Nd; B = Zr, Hf) de structure pyrochlore, Spectrochim. Acta Part A 37 (1980) 113–118.

[19] S. Kamba, H. Hughes, D. Noujni, S. Surendran, R.C. Pullar, P. Samoukhina, J. Petzlés, R. Freer, N.M. Alford, D.M. Iddles, Relationship between microwave and lattice vibration properties in Ba(Zn1₋ₓNb2₋ₓ)O3-based microwave dielectric ceramics, J. Phys. D Appl. Phys. 37 (2004) 1980–1986.

[20] F. Shi, H. Dong, Correlation of crystal structure, dielectric properties and lattice vibration spectra of (Ba1₋ₓSrₓ)(Zn1₋ₓNb2₋ₓ)O3 solid solutions, Dalton Trans. 40 (2011) 6659–6667.

[21] D. Bernache-Assollant, Chimie Physique de Frittage FORCERAM, Editions Hermès Paris, 1993.

[22] R.A. Dimilia, J.S. Reed, Dependence of compaction on the glass transition temperature of the binder phase, Am. Ceram. Soc. Bull. 62 (4) (1983) 484.

[23] A.F. Qasrawi, Bayan H. Kmail, A. Mergen, Synthesis and characterization of Bi1.5Zn0.92Nb1.5₋ₓO6.92₋ₓ/2 pyrochlore ceramics, J. Phys. D Appl. Phys. 37 (2004) 1980–1986.

[24] M.K. Ehlers, J.E. Greedan, M.A. Subramanian, Novel defect pyrochlores ABi2B5O16 (A = Cs, Rb; B = Ta, Nb), J. Solid State Chem. 75 (1988) 188.

[25] B. Dominique, These, Université de Rennes, 1976.

[26] L.L. Hench, J.K. West, Principles of Electronic Ceramic, Wily-Interscience, 1988, p. 205.

[27] T.R. Shrout, S.L. Swartz, Dielectric properties of pyrochlore lead magnesium niobate, Mater. Res. Bull. 18 (1983) 663.